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Oily wastewater treatment: removal of dissolved organic components by forward osmosis

Rajab M. Abousnina

University of Wollongong

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Oily Wastewater Treatment: Removal of Dissolved Organic Components by Forward Osmosis

Rajab M. Abousnina

This thesis is presented as part of the requirements for the award of the Degree of Master of Engineering Research

University of Wollongong

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Produced water is water brought to the surface with crude oil or natural gas; it is the largest waste stream by volume associated with the production of oil and gas. Some crude oil and traces of organic compounds, particularly organic acids, are known to occur in produced water. Although the current international standard limits the amount of dissolved oil in produced water to less than 30 mg/L prior to environmental discharge, no regulations exist for other dissolved organic constituents. This is mostly because of the lack of low cost, high efficiency technologies capable of removing dissolved organic constituents from produced water. This work investigated the removal of dissolved organics from produced water by the forward osmosis (FO) process, with a particular focus on Libya. In an off-shore platform, seawater can be utilised as the draw solution for the FO process as it allows for a significant reduction in the cost of treatment before discharging produced water into the sea. Two membranes specifically designed for the FO process (namely HTI-Cartridge and HTI-Pouch) provided by Hydration Technology Innovation and two typical NF membranes (namely NF270 and NF90) provided by Dow Chemical were used in this study. Acetic acid was selected as a model organic acid and a synthetic oil-in-water emulsion was prepared using motor cycle oil (Fork w2.5) in Milli-Q. The water flux, reverse salt flux, the rejection of acetic acid, and the effects of concentrated oil in produced water were systematically evaluated. This investigation appears to be the first attempt to study the removal of dissolved components from produced water using an FO membrane. Water flux and reverse salt flux were investigated at different pH values (un-adjusted pH, pH4, and pH6), and the results showed that the HTI-Cartridge membrane
produced a higher permeate flux than the HTI-Pouch membrane when the same draw solution concentration was used in the FO mode (e.g. active layer facing the feed solution). On the other hand, there were no significant differences in the water flux and reverse salt flux at different pH values for each individual membrane. The transport phenomena of the HTI-Cartridge were also investigated since it performed better as a permeate flux than the HTI-Pouch membrane. An HTI-Cartridge membrane was evaluated in the FO and pressure retarded osmosis (PRO) modes (in the PRO mode, the active layer of the membrane is in contact with the draw solution). Higher water flux and reverse salt flux were observed under the PRO mode rather than the FO mode because the internal concentration polarisation (ICP) phenomenon which is considered to be unique in the FO process.

The performance of the FO membranes (HTI-Cartridge and HTI-Pouch) and NF membranes (NF-90 and NF-270) were also investigated under reverse osmosis (RO) mode and the results were compared with the FO mode. The rejection of acetate by the FO and NF membranes was strongly pH-dependent. At near neutral pH (6.7-7.3), acetate rejection by either the HTI-Cartridge or HTI-Pouch membranes was almost 100%. The rejection of acetate decreased dramatically as the feed solution pH decreased to pH 4, although both of them rejected acetate more efficiently under FO mode where the active layer faced the feed solution and the backing layer faced the draw solution. Acetate rejection by the NF-270 and NF-90 membrane was considerably lower than the FO membranes. The rejection of acetate increased from 55% to 92% with the NF-90 membrane, as the feed pH increased from 4 to 9. Similarly, the rejection of acetate by the NF-270 membrane (which has a larger pore size than the NF-90 membrane), increased from as low as 2% to 89% as the feed pH increased from pH 4 to pH 9. In the FO mode, acetate rejection was also strongly pH
dependent. More importantly, acetate rejection in the FO mode was at least 10% higher than in the RO mode. In addition, the allowable oil content (30 mg/L) did not affect acetate rejection in either the FO or RO modes. Furthermore, the allowable oil content of 30 mg/L did not cause any discernible membrane fouling in either the FO or RO modes. The reported results indicate that a highly efficient removal of acetate from produced water can be achieved using the FO process without pH adjustment, because the pH range of the produced water produced from light crude oil is usually from pH 6 to pH 7.7.
Firstly, I am very grateful to my supervisor A/Prof. Long Duc Nghiem, who has encouraged, supported, and guided me from the beginning to the end of my thesis. His encouragement has enabled me to develop a good understanding of the subject.

I would also like to thank the Ministry of Higher Education in Libya for providing me with a postgraduate scholarship.

I offer my blessing and regards to my parents, sisters and brothers for their moral support during the difficult times.

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Rajab Abousnina
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## Acronyms

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AL/DS</td>
<td>Active layer to the draw solution</td>
</tr>
<tr>
<td>AL/FS</td>
<td>Active layer to the feed solution</td>
</tr>
<tr>
<td>BTEX</td>
<td>Benzene, toluene, ethylbenzene and Xylene</td>
</tr>
<tr>
<td>CTA</td>
<td>Cellulose triacetate</td>
</tr>
<tr>
<td>CFMF</td>
<td>Cross-flow membrane microfiltration</td>
</tr>
<tr>
<td>CFUF</td>
<td>Cross-flow membrane ultrafiltration</td>
</tr>
<tr>
<td>CP</td>
<td>Concentration polarisation</td>
</tr>
<tr>
<td>DS</td>
<td>Draw solution</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental protection agency</td>
</tr>
<tr>
<td>FO</td>
<td>Forward osmosis</td>
</tr>
<tr>
<td>GC</td>
<td>Gas chromatography</td>
</tr>
<tr>
<td>GC-MS</td>
<td>Gas chromatography with Mass spectrometry</td>
</tr>
<tr>
<td>GC/PID</td>
<td>Gas chromatography/Photoionisation detector</td>
</tr>
<tr>
<td>GC/FID</td>
<td>Gas chromatography with flame ionisation detector</td>
</tr>
<tr>
<td>HTI</td>
<td>Hydration technology innovation</td>
</tr>
<tr>
<td>IC</td>
<td>Ion chromatography</td>
</tr>
<tr>
<td>ICP</td>
<td>Internal concentration polarisation</td>
</tr>
<tr>
<td>LC-MS</td>
<td>Liquid chromatography with mass spectroscopy</td>
</tr>
<tr>
<td>MF</td>
<td>Microfiltration</td>
</tr>
<tr>
<td>MW</td>
<td>Molecular weight</td>
</tr>
<tr>
<td>NPDES</td>
<td>National Pollutant Discharge Elimination System</td>
</tr>
<tr>
<td>NF</td>
<td>Nanofiltration</td>
</tr>
<tr>
<td>OG</td>
<td>Oil and grease</td>
</tr>
<tr>
<td>OGP</td>
<td>International association of oil &amp; gas producers</td>
</tr>
<tr>
<td>OSPAR</td>
<td>Protection of the marine environment of the north-east atlantics</td>
</tr>
<tr>
<td>PRO</td>
<td>Pressure retarded osmosis</td>
</tr>
<tr>
<td>RO</td>
<td>Reverse osmosis</td>
</tr>
<tr>
<td>SS</td>
<td>Suspended solid</td>
</tr>
<tr>
<td>TSS</td>
<td>Total suspended solid</td>
</tr>
<tr>
<td>UF</td>
<td>Ultrafiltration</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
</tbody>
</table>
US-EPA  US Environmental protection agency
VOC       Volatile organic compound
CHAPTER 1

Background

1.1 Introduction

Produced water is water extracted from underground formations and brought to the surface during the production of either oil or gas. Produced water is a major source of many pollutants and can pose a considerable threat to the environment. Produced water can have different potential impacts, depending on where it is disposed. For instance, disposal into small streams are more likely to have a larger impact on the environment than into the open sea due to the natural process of dilution. The US Environmental Protection Agency (US-EPA) has recognised the potential impact that the disposal of produced can have on the environment, and have stipulated set regulations for controlling the amount of mineral oil and other associated contaminants [1]. It has been proven that produced water contaminates the soils and can cause the outright death of plants and aquatic life [2-4]. In addition, contaminated soil can lead to wide spread contamination of surface water and shallow aquifers.

The volume of produced water does not remain constant over time because the ratio of water-to-oil increases over the life of the oil or gas well. Whereas water makes up a small percentage of fluids when a well is new, over time the percentage of water increases as the percentage of product declines. The estimated worldwide average of produced water is 210 million barrels (bbl) per day, resulting in an annual estimation of 77 billion bbl per year [1]. The volume of produced water has increased dramatically over the last few decades as more oil and gas reservoirs are being exploited in areas where extraction is difficult. Produced water contains a high amount of dissolved components such as hydrocarbons, carboxylic, phenols and BTEX (benzene, toluene, ethylbenzene and xylene). Some of these components
are toxic to the environment, so there are obvious concerns with substances such as these because they involve toxicity and the process of removing them before they are discharged into the sea is complex. These components in produced water signify the importance of research in terms of eliminating them from those sources.

Several studies have been conducted to develop suitable technologies for the treatment of produced water [5-12]. Treatment processes such as oxidation, extraction, stripping, sorption, biological treatment, and membrane technologies have been widely investigated. Membrane processes such as micro-filtration (MF), ultra-filtration (UF), nano-filtration (NF), and reverse osmosis (RO) are increasingly being used to treat oily wastewater [13-15]. In contrast, forward osmosis (FO) is an emerging treatment that can be used to remove organic contaminants from the aqueous phase [16]. Due to the very low hydraulic pressure required, FO delivers many potential advantages such as less energy input [17], lower fouling tendency, easier fouling removal [18-20], and higher water recovery [21] over pressure driven processes like reverse osmosis (RO), nano-filtration (NF) and ultra-filtration (UF). The FO process offers high rejection of a wide range of contaminants, and if the draw solution is readily available, energy consumption can be very low [22]. Therefore, this research will investigate the effects of discharging produced water into the environment, the available removal technologies, and the capability of FO to remove dissolved components and oil droplets from produced water.

1.2 Statement of the problem

The volume of produced water discharged worldwide is significant and is expected to increase in the future [11]. An estimated 107 million bbl/day of produced water is sourced from offshore platforms worldwide. More than 44 million bbl/day of produced water is
discharged into the marine environment. The monthly average oil droplets standard is set at 30 mg/L, based on the Convention for the Protection of the Marine Environment of the North-East Atlantic [23]. No performance standards currently exist for the other components in produced water. These components can also adversely impact the environment, and on humans and animals [4]. Therefore, reducing the components being discharged with produced water, either inshore or offshore, are the main goals of this research, although there is also an emphasis on offshore production where sea water can be used as the draw solution.

1.3 Research objectives

The treatment of produced water requires the separation of suspended and dissolved components, as well as emulsified droplets of oil. Since membrane filtration technologies are playing a major role in separating these components, the main objective of this investigation is to evaluate the FO process for the removal of organic contaminants from produced water. The specific objectives are as follows:

- Analyse the factors affecting the performance of FO (such as the water flux, reverse salt flux and rejection) of dissolved organics and droplets of oil.

- Compare the efficiency of FO with pressure driven membrane filtration technologies such as nano-filtration (NF), because using FO in produced water is considered to be unprecedented.

- Investigate FO membrane fouling
1.4 Expected outcomes

This study will result in a comprehensive understanding of the removal of dissolved organic components by FO, and also fouling in FO. This thesis will enhance the attractiveness of using FO to efficiently and economically remove components such as acetic acid from produced water, and eliminate the negative impact of such components from discharged oily wastewater.

1.5 Thesis structure

The structure of this thesis is schematically described in Figure 1-1. It consists of five Chapters, beginning with the Introduction in Chapter 1. Chapter 2 will provide a comprehensive literature review on the current state of knowledge on discharging produced water into the environment and the treatment technologies available, with a particular focus on Libya. A detailed description of each technology, including the advantages and disadvantages, will be reviewed in this chapter. This chapter will also include the very latest findings from previous studies. The study approach, materials, and methods are presented in Chapter 3, while Chapter 4 will present both fouling in FO and the removal of dissolved organic compounds. The conclusion and recommendations will be presented in Chapter 5, including suggestions for future research to further enhance the potential of membrane technology to deal with dissolved organic compounds in the oil industry.
Figure 1-1: Schematic roadmap of the dissertation.
CHAPTER 2  

2.1 Introduction

Produced water is polluted water brought to the surface along with crude oil or natural gas. When hydrocarbons are produced they are extracted to the surface as a produced fluid mixture. Produced water is considered to be the largest by volume by-product associated with oil production operations [11,12, 24]. The composition of the fluid mixture depends on whether crude oil or natural gas is being produced, although it generally includes either liquid or gaseous hydrocarbons, dissolved or suspended solids, sediments such as sand or silt, and injected fluids and additives placed in the formation during the exploratory phase and subsequent production activities [1].

Produced water can have an adverse impact on the environment, depending on where it is discharged. In general, produced water contains a large range of organic and inorganic compounds, including emulsified oil, organic acids, dissolved organic molecules, and salts. The organic content of produced water also includes benzene, toluene, ethylbenzene, and xylenes (commonly referred to as BTEX), which are very toxic. The toxicity and solubility of these compounds are high, and therefore signify a significant environmental hazard for humans [25]. According to the U.S. Environmental Protection Agency (US EPA), there is evidence that benzene can cause cancer and other significant diseases in humans [26], which is why reducing exposure to these chemicals is essential to protecting human and marine life [27].

Several studies have been conducted to develop suitable technologies for the treatment of produced water [5-12]. Treatment processes such as oxidation, extraction, stripping,
membrane technologies, sorption, and biological treatment have been widely investigated. This chapter will review the effects of discharging produced water into the environment and the currently available treatment technologies. The chapter also provides a brief introduction to forward osmosis (FO) which can be used for removing dissolved components and oil droplets from produced water.

2.2 Volume of produced water

Produced water is a major volume waste stream in the oil production industry—roughly three barrels of water for every barrel of oil [28] (one barrel is approximately 159 L). It exists as a consequence of the production of oil and gas from underground reservoirs, which consist of formation water [29]. The global estimated average of produced water is 210 million bbl/day, resulting in an annual production of 77 billion bbl/year [30].

The estimate of produced water in offshore platforms worldwide is approximately 107 million bbl/day, while the estimation of total offshore oil production is 120 million bbl/day. Figure 2-1 shows the comparison between onshore and offshore produced water over a period of fifteen years. More than 44 million bbl/day of produced water is discharged into the ocean [23]. The quantity of produced water from the oil industry has increased dramatically and it does not remain constant during an oil well’s operation time. It has been shown that the amount of produced water increases as oil production deceases [11]. In some older oil fields, the water cut exceeds 95% [28, 30].
2.3 Produced water in Libya

2.3.1 General Overview

More than 95% of the Libyan economy depends on the production and export of oil and gas. Libya holds about 46.4 billion bbl of oil (one barrel is approximately 159 L), and is known to have the largest oil reserve in Africa (Figure 2-2). In addition, Libya also has 55 trillion cubic feet of natural gas reserves [31]. Libya has five major onshore sedimentary and one offshore basin, namely the Sirt basin, the Murzuq basin, the Kufra basin, the Ghadamis basin, the Cyrenaica platform, as well as the Tripolitanian offshore basin [32]. The main production basins in Libya are Sirt, Ghdamis, Murzuq, and the offshore Tripolitanian basin (Figure 2-3). The Tripolitanian basin was discovered in 1976 in the Mediterranean Sea, and is part of the El Bouri oil field. The proven oil reserves in this field is 2 billion barrels [33].
Figure 2-2: Proven African oil reserve holders as in 2011[31].

Figure 2-3: Location of major Sedimentary Basins Libya [33].

2.3.2 Oil classification

The quality of crude oil is measured in terms of its density and sulphur content (sweet or sour). The density is directly related to gravity, and is classified by the American Petroleum Institute (API). Crude with an API gravity of more than 38 degrees is considered light whereas crude oil with an API gravity of 22 degrees or less is considered heavy.
Libyan oil is generally light (with high API gravity) and sweet (sulphur content of less than 5%) [32]. Libyan crude contains a high percentage of hydrocarbons and is commercially called “Brent”. Libyan and North Sea crudes are similar; both are considered as light and sweet “Brent”. The majority of oil platforms in Libya, the North Sea, or any other countries that have offshore oil fields, discharge produced water directly into the sea. This study investigates the potential for using FO membranes to reduce pollution from these sources, as wastewater discharge has become a global issue. This thesis will focus on light crude oil which is produced in Libya and other countries, and to acquire further knowledge of how to achieve zero-harm discharge.

2.3.3 Total Oil Production in Libya

Libyan oil production peaked at more than 3 million bbl/day in the late 1960s, and has been in decline ever since (Figure 2-4). The National Oil Corporation (NOC) of Libya planned to raise oil production to 2.3 million bbl/day by 2013 [34]. This data was taken before the revolution and the impact of the regime change are not yet clear. In the Libyan Desert, all oil companies are committed to using alternative solutions to optimise the amount of water resources used and to eliminate the environmental impact of water disposal. One solution is to re-inject produced water into onshore oil fields [35].
**Figure: 2-4** Libyan oil production over the past 40 years (million bbl/day) [36].

Figure 2-5 shows the estimated reserves (remaining hydrocarbon potential of the sediments in Libya during 1999). This study shows the estimation of hydrocarbon in each basin as 107 billion barrels, and the relative proportion of reserves estimated in each basin. The offshore total includes prospective areas in the Mediterranean offshore Sabratha basin areas (Misrata Trough, Tripolitianan), Gulf of Sirt, and Cyrenaica (Gulf of Bomba and offshore Benghazi) areas [32].
2.3.4 Estimated Produced Water in Libya

A previous study estimated that the world average of produced water was three times that of oil production [30]. Table 2-1 shows the current total production of oil and the expected total production of produced water by 2014. Figure 2-6 shows the major oil pipelines, refineries and major oil fields in Libya.

Table 2-1: Estimated total oil and produced water production in Libya in million bbl/day 2010-2014 (one barrel is approximately 159 L)[37].

<table>
<thead>
<tr>
<th>Year</th>
<th>Total produced oil</th>
<th>Estimated produced water</th>
</tr>
</thead>
<tbody>
<tr>
<td>2010-2011</td>
<td>1.8</td>
<td>5.1</td>
</tr>
<tr>
<td>2013-2014</td>
<td>2.3</td>
<td>9.6</td>
</tr>
</tbody>
</table>
Figure 2-6: Libyan major oil pipelines, refineries and major oil fields (source: National Oil Corporation, Energy Intelligence, Petroleum Economists) [31].

2.4 Current situation of onshore and offshore produced water in Libya

2.4.1 Multi-media Filtration System

Multi-media filtration has been successfully used to remove solid particles and droplets of oil larger than 10 µm. A multi-media filter uses a variety of media types that are distinctly layered, with the coarsest medium at the top and the finest at the bottom. This layering structure of the media allows larger particles to be removed near the top of the bed while the
smaller particles are filtered out towards the bottom. It has been reported that the most efficient multi-media filters can efficiently remove large solid particles and oil droplets [38]. If they are not removed, these large solid particles can foul the injection well and cause formation damage due to the plug near the well bore. Nevertheless, multi-media filtration systems are not effective at removing small oil droplets (less than 10 µm) and dissolved contaminants [11].

2.4.2 Discharge of produced water

On offshore platforms, there is neither space nor time to allow a long retention time for produced water that must be treated prior to disposal. Processes that require significant treatment time, such as oil skimming and biological reactors, are therefore not suitable for offshore platforms. Figure 2-7 illustrates the final stage of produced water offshore and onshore and shows the affected area around the discharge disposal point. Produced water discharged offshore may be up to 10 times oilier than discharge from onshore facilities. In the US most produced water in an offshore operation is discharged into the sea. In Norway, the total volume of produced water discharged into the sea in 2007 was 162 million m³. Overall, around 40% of the total offshore produced water is discharged into the sea [1].

The amount of produced water has increased dramatically every year [23, 39]. In Libya, the Eni Oil Company estimated that an average of 5.6 million bbl of produced water from the Al-bouri platform will need to be treated between 2010-2014 [35]. Although the National Pollutant Discharge Elimination System NPDES and Environmental protection Agency EPA have issued a maximum monthly average of dispersed oil standard of 29 mg/L; presently there are no performance standards for other contaminants in produced water [23, 40].
2.5 Characteristics of Produced Water

The characteristics of produced water are a combination of physical and chemical properties that vary significantly, based on the location of the oil field, the geological formation with which the produced water has been in contact and the type of hydrocarbon product being produced. The properties and volume of produced water can even vary during the life span of a reservoir, while water injection plays a large role in changing the properties and volume of produced water [1]. Total dissolved solids (TDS), oil and grease (OG), inorganic, organic compounds, and naturally occurring radioactive materials (NORM) are the main concerns with produced water. Total production can be increased if the characteristics of produced water are understood, because understanding related parameters such as suspended solids (SS) and the constituents of produced water is an important part of determining applications such as scale inhibitors and chemical treatment, as well as helping to identify down-hole problems such as plugging [41].

Exploring and better understanding the constituents of produced water enhances the ability to select the proper options for managing produced water—for instance, its disposal and the recovery of oil. One of the most important constituents of onshore and offshore produced water...
water is oil and grease (OG), due to the presence of many organic chemicals, since the average OG content of produced water is between 40 to 2,000 mg/L [42]. At the same time, salinity is also considered to be an important constituent in onshore produced water because a high percentage of it is more saline than seawater [43]. The TDS concentration of produced water from the western USA varies from 1,000 mg/L to 400,000 mg/L [42].

Additional constituents are usually found in produced water due to several operational treatments, and oil production and recovery developments. Water injection is used to maintain the reservoir pressure to help increase oil production. This water, which is usually supplied by a different aquifer, may contain SS and micro-organisms [44], while additive chemicals such as coagulants, emulsion breakers, scale inhibitors, corrosion inhibitors, and solvents are usually used during the production operation stages. The aim of adding these chemicals is to improve the productive capacity of the oil well [41], but they may appear with the produced water and can affect its overall toxicity. Table 2-2 outlines the characteristics of produced water.

Table 2-2: Typical Produced Water Characteristics for Light crude Oil [45].

<table>
<thead>
<tr>
<th>Produced Water Characteristics</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil-in-Water</td>
<td>Normal average: 100-500 mg/L</td>
</tr>
<tr>
<td></td>
<td>Maximum rate: 3000 mg/L</td>
</tr>
<tr>
<td>Total Suspended Solid (TSS)</td>
<td>Normal average: 2 mg/L</td>
</tr>
<tr>
<td></td>
<td>Maximum rate: 3000 mg/L</td>
</tr>
<tr>
<td>pH</td>
<td>Average: 5.1-7.0</td>
</tr>
<tr>
<td>Specific Gravity at 15°C</td>
<td>Average: 1.03-1.15</td>
</tr>
<tr>
<td>Sulphide (H₂S)</td>
<td>Range: 0-1000 mg/L</td>
</tr>
<tr>
<td>Dissolved CO₂</td>
<td>Range: 50-2000 mg/L</td>
</tr>
<tr>
<td>Salinity</td>
<td>Range: 1-300,000 mg/L</td>
</tr>
</tbody>
</table>
Produced water usually varies from 3-80°C. Table 2-3 illustrates effluent from different fields in terms of pH, salinities, and temperature in North Sea and Libyan offshore oil fields.

Table 2-3: Produced water characteristics.

<table>
<thead>
<tr>
<th>Produced water parameters</th>
<th>pH</th>
<th>Chloride (g/L)</th>
<th>Temp. °C</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brent</td>
<td>6-7.7</td>
<td>12.4-14.8</td>
<td>3-80</td>
<td>[46]</td>
</tr>
<tr>
<td>Other northern</td>
<td>6-7.7</td>
<td>14.7-16.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Central North Se</td>
<td>6-7.7</td>
<td>81.0-100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Contract Area c (Bouri) D1</td>
<td>6.2-7</td>
<td>22.6</td>
<td>12-27</td>
<td>[47]</td>
</tr>
<tr>
<td>Contract Area c (Bouri) D2</td>
<td>6.2-7</td>
<td>22.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al-Jurf platform</td>
<td>6.2-7</td>
<td>-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.5.1 Inorganic constituents

The major inorganic constituents and concentration in produced water listed in table 2-4 are based on International Association of Oil and Gas Producers (OGP) [48].

Table 2-4: Major inorganic constituents and its average concentration in produced water (mg/L) [49].

<table>
<thead>
<tr>
<th>Component</th>
<th>Worldwide discharge</th>
<th>Seawater</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bicarbonate</td>
<td>771</td>
<td>28</td>
</tr>
<tr>
<td>Chloride</td>
<td>60874</td>
<td>19000</td>
</tr>
<tr>
<td>Sulphate</td>
<td>325</td>
<td>900</td>
</tr>
<tr>
<td>Sulphide</td>
<td>140</td>
<td>-</td>
</tr>
<tr>
<td>Nitrate</td>
<td>1</td>
<td>0.67</td>
</tr>
</tbody>
</table>

Dispersed oil consists of small oil droplets suspended in oily produced water. The concentration of dispersed oil can be affected by several factors such as its density, the efficiency of the separation stages, chemical treatment, shear history of the droplet, and interfacial tension between the water and oil [50]. Chemical treatment and soluble organics play a large role in decreasing the interfacial tension between oil and water in produced water.
The removal methods of OG depend on the end use of the produced water and the internal composition of oil. Table 2-5 illustrates the typical treatment and performance of oil removal expressed by the minimum size particle of oil removed.

Table 2-5: Oil and grease removal technologies based on the size of the particles removed [51].

<table>
<thead>
<tr>
<th>Oil Removal Technology</th>
<th>Minimum size of particles removed (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>API gravity separation</td>
<td>150</td>
</tr>
<tr>
<td>Corrugated plate separator</td>
<td>40</td>
</tr>
<tr>
<td>Induced gas flotation (no flocculants)</td>
<td>25</td>
</tr>
<tr>
<td>Induced gas flotation (with flocculants)</td>
<td>3-5</td>
</tr>
<tr>
<td>Hydroclone</td>
<td>10-15</td>
</tr>
<tr>
<td>Mesh coalesce</td>
<td>5</td>
</tr>
<tr>
<td>Media filter</td>
<td>5</td>
</tr>
<tr>
<td>Centrifuge</td>
<td>2</td>
</tr>
<tr>
<td>Membrane filter</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Produced water from the separators (which is an item of production equipment used to separate liquid components of the well stream from gaseous elements), contains typically 40-1200 mg/L oil droplets of less than 20 µm and 1-50 mg/L solid particles of less than 10 µm. Because the current systems cannot remove particles (oil droplets) less than 10 µm, small droplets of oil can interfere with oily produced water [52]. The target standard for droplets stated that the monthly average is 30 mg/L which is equal to the Australian offshore oil and grease limitation for the discharge of produced water [53]. Based on EPA regulations, the daily maximum limit for OG is 42 mg/L and the monthly average limit is 29 mg/L [11], while in China the monthly average limitation of OG discharge is 10 mg/L and in the Northeast Atlantic, the limitation on the discharge of dispersed oil in produced water is 40 mg/L [54]. Many countries have implemented more stringent regulations for discharges of produced
These regulations were implemented to reduce the effect of these components on the environment.

### 2.5.2 Dissolved components

Deep produced water has large polar constituents that enhance the amount of dissolved hydrocarbons in produced water. The solubility of the organic components can be affected by several parameters, including the pH and temperature [55]. The major dissolved compounds in produced water are BTEX, carboxylic acids, polycyclic aromatic hydrocarbons, and phenols. Some of these dissolved organic compounds can be very toxic, and thus their removal is of high priority in the treatment of produced water [55, 56]. Removing the dissolved compounds from produced water is a major challenge for the oil industry.

The concentration of dissolved components in produced water is based on the molecular weight of the compounds, so if the molecular weight decreases, the concentration of the dissolved compound increases [57]. Therefore, all organic components that have low molecular weights, such as carboxylic acids, and alcohols, and ketones, have high solubility in produced water, and the concentration of highly soluble organic components in some sites (oil fields) exceeds 5,000 mg/L [50]. While organic components that have a medium to high molecular weight from C6 to C15 in the hydrocarbon range are partially soluble in water, they also include aliphatic and aromatic carboxylic acids, aromatic hydrocarbons, phenols and aliphatic [58]. The concern with these components is that they involve toxicity and the complexity of removing them because they end up being discharged into the sea.

#### 2.5.2.1 Carboxylic Acids

Carboxylic acids (e.g. formic acid, acetic acid, propionic, butyric, pentanoic, and naphthenic acid) have the highest concentrations of organic components in produced water. According to the International Association of Oil and Gas Producers, the concentration averages between
40-349 mg/L [48], but the environmental effect depends on the concentration and duration of exposure to these acids, since at high concentrations, acetic acid can be harmful to plants, animals, and aquatic life [59]. Table 2-6 illustrates the concentration of carboxylic in Libyan and North Sea oil, where the presence of high concentrations of acetic acid either in Libyan or NS oil can be clearly seen.

**Table 2-6: Concentrations of carboxylic acids**

<table>
<thead>
<tr>
<th>Oil fields North sea</th>
<th>No</th>
<th>Chemical name</th>
<th>Concentration mg/L</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>Formic acid</td>
<td>1.2</td>
<td>[23]</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>Acetic acid</td>
<td>163</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>Propionic acid</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>Buthanoic acid</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>Valeric (Pentanoic)</td>
<td>1.8</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Oil fields Libya</th>
<th>No</th>
<th>Chemical name</th>
<th>Concentration mg/L</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>Formic acid</td>
<td>2.9</td>
<td>[60]</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>Acetic acid</td>
<td>175.1</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>Propionic acid</td>
<td>10.1</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>Buthanoic acid</td>
<td>5.6</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>Valeric (Pentanoic)</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

2.5.2.2 Benzene, toluene, ethylbenzene and xylene (BTEX)

BTEX are aromatic compounds that exist in high concentrations in produced water (Table 2-7). The main characteristics of BTEX are high volatility, high bio-degradation in water, medium solubility in seawater, and an increase in toxicity that corresponds to an increase in molecular weight [23]. The existing methods for removing BTEX from seawater are vaporisation, bio-degradation, photolysis, and adsorption. Vaporisation is considered the most essential method for removing BTEX from seawater.
Several methods have been applied and successfully implemented to determine BTEX in produced water. Methods such as Gas chromatography/Mass spectroscopy (GC/MS), Gas chromatograph/Photoionisation detector (GC/PID), and Gas chromatography with flame ionization detector (GC/FID) were recommended by several standards [61-63] to determine BTEX compounds in produced water. A variety of previous methods have also been developed to detect BTEX. Chromatography, either GC or LC, is usually combined with other techniques such as spectrometry [64]. Previous studies on the detection and determination of BTEX constituents in oily produced water through GC/MS show that highly accurate results can be obtained by extracting a sample in the preparation stage [65, 66].

**Table 2-7: Concentrations of BTEX [17]**

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>Concentration mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>4</td>
</tr>
<tr>
<td>Toluene</td>
<td>3.2</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>0.2</td>
</tr>
<tr>
<td>Xylenes</td>
<td>1.2</td>
</tr>
</tbody>
</table>

The fate of BTEX compounds in the environment can be predicted based on their physical and chemical properties, which are summarised in Table 2-8.
<table>
<thead>
<tr>
<th>Properties (Unit)</th>
<th>Benzene</th>
<th>Toluene</th>
<th>Ethylbenzene</th>
<th>m-Xylene</th>
<th>o-Xylene</th>
<th>p-Xylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical structure</td>
<td><img src="image1" alt="Chemical structure of Benzene" /></td>
<td><img src="image2" alt="Chemical structure of Toluene" /></td>
<td><img src="image3" alt="Chemical structure of Ethylbenzene" /></td>
<td><img src="image4" alt="Chemical structure of m-Xylene" /></td>
<td><img src="image5" alt="Chemical structure of o-Xylene" /></td>
<td><img src="image6" alt="Chemical structure of p-Xylene" /></td>
</tr>
<tr>
<td>Chemical formula</td>
<td>C₆H₆</td>
<td>C₇H₈</td>
<td>C₈H₁₀</td>
<td>C₈H₁₀</td>
<td>C₈H₁₀</td>
<td>C₈H₁₀</td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
<td>78.11</td>
<td>92.14</td>
<td>106.17</td>
<td>106.17</td>
<td>106.17</td>
<td>106.17</td>
</tr>
<tr>
<td>Trade names and synonyms</td>
<td>Benzol90</td>
<td>Pyrobenzol</td>
<td>Coalnaphtha</td>
<td>Phenylbenzene</td>
<td>Phenylethane</td>
<td>Ethylbenzene</td>
</tr>
<tr>
<td>Water solubility (mg/L) at 25°C</td>
<td>1785.5</td>
<td>532.6</td>
<td>161.5</td>
<td>161.5</td>
<td>171.5</td>
<td>181.6</td>
</tr>
<tr>
<td>Boiling point temp. (°C)</td>
<td>80.0</td>
<td>110.6</td>
<td>136.1</td>
<td>139.1</td>
<td>144.5</td>
<td>138.3</td>
</tr>
<tr>
<td>Vapour pressure (mmHg) at 20°C</td>
<td>95.19</td>
<td>28.4</td>
<td>4.53</td>
<td>8.3</td>
<td>6.6</td>
<td>3.15</td>
</tr>
<tr>
<td>Melting point temp.(°C)</td>
<td>5.50</td>
<td>-94.9</td>
<td>-94.9</td>
<td>-47.8</td>
<td>-25.2</td>
<td>13.2</td>
</tr>
<tr>
<td>Specific density °C</td>
<td>0.8765(20)</td>
<td>0.8669(20)</td>
<td>0.8670(20)</td>
<td>0.8642(20)</td>
<td>0.8802(10)</td>
<td>0.8611(20)</td>
</tr>
<tr>
<td>Octanol-water partition coefficient 25 °C</td>
<td>2.13</td>
<td>2.73</td>
<td>3.15</td>
<td>3.20</td>
<td>3.12</td>
<td>3.15</td>
</tr>
<tr>
<td>Henry law constant at 25°C (KPam³/mol)</td>
<td>0.557</td>
<td>0.660</td>
<td>0.843</td>
<td>0.730</td>
<td>0.551</td>
<td>0.690</td>
</tr>
</tbody>
</table>
2.5.3 Suspended Solids

Suspended solids (SS) such as sand, silt, clays, and other solids are usually carried out from the reservoir with the produced water. The size and quantity of the SS vary from one location to another. When the quantities of SS increase, the solids become solid slurry that significantly influences the fate of produced water. The efficiency of the oil separation stage can be affected if the crude oil contains a high quantity of SS [67].

2.5.4 Metals

The percentage of metals in produced water can vary significantly. There are several causes for this variation, including geology and the age of the reservoir [57]. The main produced metals are lead, iron, barium, magnesium, and zinc, and their percentage usually exceeds the percentage of these metals in seawater. The potential impact on marine organisms may be low because dilution reduces their concentration and because the form of the metals adsorbed onto sediments is less bio-available to marine animals than metal ions in solution [68]. In addition, metals affect production through chemical reactions with oxygen that produce solids. These solids cause a reduction in produced water because they plug the well bore downhole [52].

2.5.5 Bacteria

Produced water can contain bacteria that can cause effects that include clogged pipelines, equipment, and spillage which is usually caused by corrosion [1]. Bacteria are classified as either sessile, which means attached to surfaces associated with biofilm, or planktonic, which means free floating. This classification may be further refined by considering the main types of organisms likely to be encountered in a produced water injection system. The main types of bacteria are sulphate-reducing bacteria, iron bacteria, slime formers, sulphur oxidising bacteria, and hydrocarbon oxidising bacteria.
2.6 Summary

The quantity of produced water and the effects of discharging this wastewater into the environment are significant areas of environmental concern. Standards to protect the environment by limiting the amount of OG in produced water have been implemented. Other pollutant components that are found in high concentrations in produced water, such as acetic acid and BTEX, are not included in these regulations. The issue of acetic acid and BTEX contamination centres on its toxicity. Both acetic acid and BTEX have high toxicity and solubility, which signifies a significant environmental hazard. Meanwhile, the existence of these pollutants sets barriers to achieving the discharge of clean, produced water into seawater. In the following chapter the present techniques to treat produced water are described.

2.7 Produced Water Treatment Technologies

2.7.1 Oil-in-Water Emulsion & Separation Methods

A large amount of liquid waste in the form of either oil-in-water (o/w) or water-in-oil (w/o) emulsion is generated by petrochemical and other industries [69]. Demulsification has become a critical process associated with these industries. Thus, the separation of water from w/o emulsions is important in industries involved in the recovery of solvents desalination of oil [70]. Water-in-oil emulsions are also encountered in the petroleum industry, especially during the production of crude oil [71]. They are of interest for offshore crude oil producers for two reasons. First, as the production time of oil wells continues there is an increased co-production of oil and water from emulsions. Second, for the establishment of multi-phase transport systems, as large quantities of water are in an emulsified form during transportation
[72]. Hence, water-in-oil emulsions are also encountered in liquid membrane processes for metal extraction or wastewater treatment.

2.7.2 Chemical treatment

A standard method for the treatment of emulsions is chemical demulsification followed by gravity settling. This process requires a variety of chemicals and the water recovery phase needs secondary purification. Consequently, it requires additional energy, which results in higher costs [73]. Gravity settling, centrifuging, or heating can also break down some emulsions. Centrifuges are efficient for some emulsions, but are more expensive to run and maintain. Electric field methods are used to demulsify w/o emulsions and electrostatic coalesces are widely used in the petroleum industry but extremely high voltages (10-20 kV) are required to cause droplet coalescence.

2.7.2.1 Oxidation

Oxidation through the use of ozone and hydrogen peroxide is one of the main treatment options for dissolved organic compounds. The main advantage of this method is its relatively simple operation, while the main disadvantage is the high energy it requires and disposal of the toxic waste generated by this process [74]. A long contact time is required in this technique to achieve efficient degradation of the targeted soluble components [75]. Ultraviolet (UV) light and titanium dioxide are used as catalysts in the advanced oxidation method. The advantage of using UV and titanium dioxide is the avoidance of generating waste streams, while the main disadvantage is the fouling of UV lamps. In addition, heavy metals cannot be removed by any oxidation technique.
2.7.2.2 Chemical precipitation

Suspended solids can be removed using chemical precipitation (coagulation and flocculation), but this method is ineffective at removing dissolved components. In this method, lime softening is usually used. In a study on the treatment of produced water containing 2000 mg/L hardness, 500 mg/L sulphides, 10,000 mg/L TDS, and 200 mg/L oil droplets, a hot lime press was used to achieve a 50% reduction in the production of sludge and consumption of alkali [76, 77].

A mixture of metal (Fe, Mg, and Al) polynuclear polymers has shown good coagulation, scale inhabitation, and de-oiling qualities in produced water containing high SS up to 400 mg/L [78]. Additionally, other studies have used calcite, spillsorb, and lime to examine the efficiency of removing heavy metals from produced water [79]. Lime proved most efficient at removing heavy metals, as the removal was greater than 95%.

2.7.3 Biological treatment

Biological treatments, either aerobic or anaerobic, have successfully been used in the treatment of produced water, especially for the removal of aromatic compounds. Different reactors have been used for these treatments, the most common of which are fluidised bed reactors, moving bed biological reactors, submerged fixed film reactors, and fixed activated sludge [80-82]. Granular activated carbon is used in fluidised bed reactors, and it has resulted in a more rapid establishment of bio-film structures due to the adsorption of pollutants on carbon particles [83]. The main disadvantage of this method is the amount of sludge produced, approximately 1600-3200 Kg DS/day per 8000 m³/day of produced water. Handling this amount of sludge in offshore fields is a primary challenge in terms of disposal regulations, but it is a cost effective step for onshore fields. A high percentage of this sludge comes from the degradation of organic acids, which are usually not required to be removed.
because of their minimal impact on the environment. Bio-degradation of heavy metals is not achievable, which may cause the sludge to retain these pollutants. If pre-discharge treatment is needed it will increase the cost of this method.

2.7.4 Physical treatment

2.7.4.1 Adsorption

Adsorption is another method that has been used in the treatment of produced water to remove dissolved components. Adsorbents can either be regenerated or disposed of after the adsorption capacity is exhausted. One of the most efficient adsorbent materials is activated carbon, which has been widely used in the treatment of industrial wastewater. Used carbon can be regenerated onsite by wet air oxidation but it is mainly regenerated offsite [84]. Zeolite was successfully regenerated by aeration when it was modified to remove dissolved components such as BTEX, but this regeneration transfers pollutants from the liquid to the gaseous phase, which is a primary drawback [85]. As a consequence, further treatment is required before the gas is released into the atmosphere. Furthermore, this method is not efficient in terms of removing heavy metals.

2.7.4.2 Sand filter

This method (sand filtration) is highly effective at removing metals, with its efficiency exceeding 90% when proper pre-treatment steps are followed. The main components of this technique are an aeration unit, a solid separation unit, pH adjustment, and sand filtration.

2.7.4.3 Stripping

This technique is one of the most practical methods for treating produced water, especially for volatile components, as heavy compounds such as polycyclic aromatic hydrocarbons (PAHs) can be removed by increasing the temperature [74]. This method is considered to be a proven
technology in the oil and gas industry [23]. One major drawback however, is that it creates a new waste stream which means that further treatment, such as off-site gas treatment, is required for air stripping, and separating the hydrocarbons from condensed vapours is required for steam stripping [23]. In addition, it is costly and impractical for small areas such as platforms because a large stripping column is needed to comply with worldwide standards for produced water treatment projects. Additionally, inorganic scaling (which is usually caused by calcium and iron precipitates) and the inefficient rate of removing heavy metal are other disadvantages of this method.

2.7.4.4 Membrane treatment

The cost effectiveness and the space needed for installation were the main challenges in terms of implementing the previous conventional methods in offshore platforms. Therefore, finding alternative methods to treat produced water has been a primary goal over the last decade. Membrane technologies have been explored and are considered to be a promising technology [86].

Membranes are thin films made of artificial organic or inorganic materials with the ability to separate the fluid from its contaminated components. Membranes such as micro-filtration (MF), ultra-filtration (UF), nano-filtration (NF), and reverse Osmosis (RO) have the ability to remove different size components. For instance, MF membranes can be used to remove suspended particles, UF membranes can remove macromolecules, and RO membranes can remove dissolved components [87].

Heavy metals and dissolved organic compounds can be removed from produced water by using RO membranes. The drawback with using RO membranes is the energy needed to produce the high pressure necessary for their operation [23], whereas NF requires less energy.
but is less efficient than RO in terms of removing components with low molecular weight because the pores of NF membranes are larger [74]. Nonetheless, aromatic components such as BTEX and light phenols (C1-C3) can be removed with NF. The main disadvantage of both NF and RO is membrane fouling [74, 88, 89], while the short lifetime of the membrane material is considered to be another drawback.

UF is considered to be one of the most successful techniques for treating produced water because it is highly efficient at removing oil. In addition, UF does not need any chemical additives and only requires a small installation space and low energy [90]. A study compared MF and UF membranes in terms of their components’ removal efficiencies, and the results showed that UF membranes could meet removal standards for SS and dissolved components. The total removal of hydrocarbon was 96%, BTEX was reduced by 54%, while heavy metals such as Cu and Zn were reduced by 95% [91]. A combination of MF and UF membranes could be used to remove oil droplets from produced water [23].

As a contrast, electrodialysis (ED) is an industrial membrane separation process where the membranes are placed between two electrodes to allow cations or anions to pass through depending on the charge of the membrane [92]. This method is not recommended for produced water with a high concentration of TDS. Dallbauman and Sirivedhin [93] indicated in their results that ED is suitable for reclaiming produced water with a low TDS, but it is not considered to be cost effective for high concentrations of produced water. Hayes and Arthur [84] indicated that the major disadvantages of ED are its inefficient removal of dissolved compounds such as aromatic hydrocarbons, and the high energy that is required.
2.7.5 Membrane technology and produced water treatment

Membrane processes such as MF, UF, NF, and RO are strongly considered for treating produced water [69-71] because membrane technology can be an inexpensive and efficient alternative method for separating emulsions [69]. The development of membrane technologies has recently focused on applications that process emulsions. Several studies illustrated that crossflow membrane micro-filtration (CFMF) and crossflow membrane ultra-filtration (CFUF) are effective processes for concentrating o/w emulsion [73, 94].

The pros of using membrane processes rather than other processes are summarised as follows:

- low energy costs, especially with micro-filtration membranes that operate at low pressures;
- no degradation or extra safety considerations, as in high voltage demulsification [95].

2.7.6 Advantages and disadvantages of produced water treatment technologies

The existing methods for treating produced water in terms of its advantages and disadvantages are summarised in table 2-9. All the advantages and disadvantages are summarised in terms of providing a better understanding of the current treatment technologies.
Table 2-9: Shows a list of the methods for treating oily wastewater, including the advantages and disadvantages of each method.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Advantages</th>
<th>Drawback</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption</td>
<td>compact packed bed modules, cheaper, efficient</td>
<td>high retention time, less efficient at higher feed concentration</td>
<td>[45]</td>
</tr>
<tr>
<td>Chemical precipitation</td>
<td>High efficiency of heavy metal removal, cheaper, accessible, can be modified</td>
<td>chemical addition, post treatment necessary</td>
<td>[39, 79]</td>
</tr>
<tr>
<td>(Lime softening)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Microfiltration</td>
<td>higher recovery of fresh water, compact modules</td>
<td>High energy required, less efficiency for divalent, viruses etc.</td>
<td>[45]</td>
</tr>
<tr>
<td>Ultrafiltration</td>
<td>higher recovery of fresh water, compact modules, viruses and organics etc. removal</td>
<td>high energy, membrane fouling, low molecular-weight MW organics, salts etc</td>
<td>[45]</td>
</tr>
<tr>
<td>Nanofiltration</td>
<td>low molecular-weight MW organics removal, hardness removal, divalent salts removal, compact module</td>
<td>high energy required, less efficient for lower molecular-weight MW organics, membrane fouling</td>
<td>[45]</td>
</tr>
<tr>
<td>Reverse Osmosis</td>
<td>removes dissolved contaminants</td>
<td>high pressure requirements, even trace amounts of oil &amp; grease can cause membrane fouling</td>
<td>[45]</td>
</tr>
<tr>
<td>Electrodialysis</td>
<td>Clean technology, no chemical addition, mobile treatment possible, less pre-treatment</td>
<td>Inefficient with high concentration as well as removing dissolved compounds such as aromatic hydrocarbons and high energy is required.</td>
<td>[45, 88]</td>
</tr>
<tr>
<td>stripping</td>
<td>practical treatments for oily wastewater especially for volatile components, and it</td>
<td>highly cost and it impractical to be used in small area such as in platforms because a</td>
<td>[23]</td>
</tr>
</tbody>
</table>
Several studies have been conducted to develop suitable techniques for the removal of dissolved organic components; these include chemical treatment (e.g. chemical clarification and oxidation), physical treatment (e.g., membrane filtration, dissolved air floatation and sorption) and biological treatment. These treatment techniques were generally used to remove dissolved organic components from produced water, with a focus on removing BTEX. While only one study presented a high percentage of carboxylic acid (acetic acid) and used the sorption method in terms of removing the acetic acid and BTEX, a study by Tao et al [96] evaluated the chemical clarification, softening filtration and reverses osmosis methods and concluded that these methods are quite expensive and are thus not cost effective. Another study by Santos, S.M. and M.R. Wiesner evaluated the technical feasibility of using ultrafiltration to treat oily waste water but did not assess its economic effectiveness due to variations in the quality of influent water [97]. An investigation was conducted by Thoma et al [98] in terms of evaluating the dissolved air floatation separation and reported that 40% of dissolved components were removed, but they did not present the financial cost of the project. Oxidation using titanium oxide as the catalyst was also investigated. The results are promising but this technique is still being developed and could be expensive [99]. The sorption method using surfactant-modified Zeolite (SMZ) has been studied for its ability to sorb dissolved organic contaminants [100-102]. Scurtu C. T. (2009) investigated the sorption method using an organoclay to sorb acetic acid and BTEX. The outcome of their study demonstrated that cheaper in terms of the cost
large stripping column is usually required

<table>
<thead>
<tr>
<th>Method</th>
<th>Efficiency</th>
<th>Adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand filter</td>
<td>this efficiency exceeds 90% when proper pre-treatment steps are followed</td>
<td>cannot remove small oil droplets and dissolved elements</td>
</tr>
</tbody>
</table>

[11]
acetic acid and BTEX compete for sportive sites of the organoclay. Furthermore, Scurtu C. T. (2009) suggested that oil residues may affect the sorption capacity of sorbents, which may cause a reduction of the total removal capacity [23]. Membrane technologies are increasingly being applied for treating produced water [13, 15], but forward osmosis (FO) is considered to be an advanced technique for removing the organic contaminants from water [103]. If the draw solution is readily available and draw solute recovery is not required, the FO process is low energy and may offer the advantages of high rejection of a wide range of contaminants and low membrane fouling [104]. In addition, the FO process is compact and can be built in restricted areas such as off-shore oil platforms, where seawater can be utilised as the draw solution for the FO process.

2.7.7 Forward Osmosis FO

2.7.7.1 Forward Osmosis Applications

The forward osmosis (FO) process exploits the natural phenomenon of osmosis that occurs when two different solutions are placed on opposite sides of a semi-permeable membrane [22]. The differences in osmotic pressure drive the permeation of water across the membrane from the low concentration feed solution to the high concentration draw solution, while the selective property of the membrane keeps the solutes in their respective solutions (Figure 2-8). The unequal concentration of solute on both sides of the membrane provides the force required to pull the water from the feed solution to the draw solution. Issues such as the characteristics of the membrane, the draw solution, concentration polarisation, and membrane fouling are discussed in the following sub-sections.
Selected membrane and its characteristics

Osmotically driven membrane processes are designed to reject dissolved solutes, produce high-permeate water fluxes, be compatible with the draw solution, and withstand the chemical stresses generated by the operating conditions [105]. The first commercial FO membranes were produced by Hydration Technologies Inc (HTI) [http://www.hydrationtech.com/low/hydration_contact.html]. FO membranes are made of cellulose triacetate (CTA), which is supported by an embedded polyester screen mesh. These kinds of membranes are widely used in FO experiments, whereas, the Catalyx Inc. membranes are considered to be new products that require further investigation.

HTI FO membranes have been studied widely in an effort to better understand their properties. For instance, the morphology and structure of an HTI FO membrane has been calculated using scanning electron microscopy (SEM) and atomic force microscopy (AFM) [106]. Another study investigated the contact angle of the HTI FO membrane [107], and concluded that these membranes have a moderate degree of hydrophilicity. Table 2-10
illustrates the performance of the HTI FO membrane in terms of the water flux, its orientation, and test conditions.

**Table 2-10:** The performance of HTI FO membranes.

<table>
<thead>
<tr>
<th>Membrane type</th>
<th>Material</th>
<th>Testing conditions</th>
<th>FO performance</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTI FO</td>
<td>Cellulose acetate</td>
<td>Feed solution: DI water</td>
<td>Draw solution: 4 NaCl</td>
<td>Temp: 10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Feed solution: DI water</td>
<td>Draw solution: 4 NaCl</td>
<td>Temp: 20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Feed solution: 0.5 NaCl</td>
<td>Draw solution: 4 NH₄HCO₃</td>
<td>Temp: 55</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Feed solution: DI water</td>
<td>Draw solution: 0.5 NaCl</td>
<td>Temp: 22.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Feed solution: 0.05 NaCl</td>
<td>Draw solution: 6 NH₄HCO₃</td>
<td>Temp: 50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Feed solution: Active sludge</td>
<td>Draw solution: 4.5 NaCl</td>
<td>Temp: 25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Feed solution: DI water</td>
<td>Draw solution: 0.5 NaCl</td>
<td>Temp: 25</td>
</tr>
</tbody>
</table>

* Note: AL-FS Active layer facing feed solution, AL-DS active layer facing draw solution

### 2.7.7.3 Membrane skin layer thickness

The development of an anisotropic membrane has led to a major breakthrough in membrane technology. Anisotropic membranes consist of a very thin top layer called skin, and a supporting layer that is much thicker and more porous. The skin provides selective properties to the membrane [113]. The skin layer of most FO membranes ranges from 30-59 µm thick and are mechanically supported by orthogonally arranged polyester meshes. A cross sectional SEM image of the HTI FO membrane is shown in Figure 2-9.
Figure 2-9: A cross sectional SEM image of an HTI FO membrane. A polyester mesh is embedded within the polymer material for mechanical support. The membrane is less than 50µm thick [22].

2.7.7.4 Membrane morphology

AFM is considered to be an excellent tool for studying the topography of the membrane skin layer. An extremely sharp tip mounted on the end of a tiny cantilever spring is moved over the surface of the membrane by a mechanical scanner. Every variation in the height of the surface varies the force acting on the tip and the bending of the cantilever, and this bending is then measured and recorded. In the final stage the image is reconstructed by special software related to AFM [113]. AFM is used to characterise the surface properties of the FO membrane because the surface morphology of a membrane plays a large role in membrane fouling. The membrane has some bumpy areas on the surface that are primarily caused by the embedded polyester mesh (Figure 2-10a). Figure 2-10b shows a more localised surface morphology, and depicts a roughness of the order of several tens of nanometres. The surface roughness of an FO membrane does not differ much from typical RO and NF membranes [22,114,115]. While Figure 2-11 shows the SEM and AFM micrographs of the HTI FO membranes.
Figure 2-10: AFM images of the active layer of an FO membrane. The images were taken in 50 mM NaCl solution. The scanned area are: (left) 20 µm × 20 µm and (right) 2 µm × 2µm. Note also the difference in the vertical scales of the images.
Figure 2-11: SEM and AFM micrographs of the HTI Hydrowell FO membrane. (a) SEM image of the cross section of a membrane, (b) SEM image of the back (support) side of the membrane, (c) SEM image of the active surface, and (d) AFM image of the active surface [116].

SEM micrograph of the membrane active rejection layer (Figure 2-11 (c)) suggests that the surface of the active layer is relatively smooth, while the mean roughness of the HTI membrane surface was ~36 nm on the basis of AFM measurements (Figure 2-11 (d)), which is significantly smoother compared to typical aromatic polyamide RO membranes (~100 nm and due to the lack of the ridge-and-valley structure for the HTI membrane [116].

2.7.7.5 Draw solutions

When selecting a draw solution, the main criterion is that the solution has a higher osmotic pressure than the feed solution in terms of producing high water flux because the osmotic difference is the driving force in FO [22]. The second important criterion in some applications of FO is the selection of a suitable process for re-concentrating the draw solution after it has been diluted in the FO process. The third criterion is to consider the diffusion of the solute from the draw solution through the membrane. Based on these criteria, several inorganic compounds (salts) have been used as draw solutions in the FO process, including seawater [117], Dead Sea water [118], and salt lake water [119].

Several other chemicals such as sulphur dioxide [120], aliphatic alcohols [121], aluminium sulphate [122], glucose solution [123], glucose and fructose [124], and concentrated fructose [125], have also been used as a draw solution. On the other hand, McGinnis [126] suggested potassium nitrate (KNO₃) and sulphur dioxide (SO₂). This patent took advantage of these two solutes having a highly temperature dependent solubility, as well as a relatively temperature indifferent solubility of NaCl, the primary solute present in seawater. A combination of
ammonia and carbon dioxide gases is used as the draw solution to remove ammonium salts [127-129]. Among these chemicals a NaCl solution is often used because it has high solubility and is relatively simple to re-concentrate to a higher concentration with RO without the risk of scaling. So it can be concluded that an ideal draw solution would be inexpensive, easily available, economical, and completely recoverable after permeation. Figure 2-12 illustrates the osmotic pressure as a function of the solution concentration for various potential draw solutions. It can be seen that all the osmotic pressures of different solutions increases with increasing concentration of the solutions. Despite magnesium chloride MgCl$_2$ obtaining the highest osmotic pressure, NaCl is widely used due to it is high solubility and the risk of scaling is considered to be low.

![Figure 2-12: Osmotic pressure for various potential draw solutions [22].](image)

### 2.7.8 Concentration polarisation

In the FO process the water flux is described by Equation 1. This equation only expresses the water flux without concentration polarisation (CP). The osmotic pressure difference in FO
across the active layer is much lower than the bulk osmotic pressure difference, and that results in a much lower water flux than expected [22, 130-132]. Therefore, due to the reduction of water flux, two types of CP are used, internal CP and external CP.

\[ J_w = A (\sigma \Delta \pi - \Delta P) \]  

(1)

where \( J_w \) represents the water flux, \( \sigma \) is the reflection coefficient, \( A \) represents the membrane water permeability coefficient, and \( \Delta \pi \) represents the osmotic pressure difference across the active layer of the membrane.

2.7.8.1 External concentration polarisation

In pressure driven membrane processes the flow of convective permeate causes the solute at the surface of the membrane active layer to build up, while it hampers the flow of permeate due to an increased osmotic pressure at the surface of the membrane active layer [133]. This phenomenon occurs in FO during osmotic driven membrane processes on the feed and draw solution side of the membrane. When the feed solution flows onto the active layer of the membrane, solutes build up at the active layer. This phenomenon is called concentrative external CP and is similar to CP in pressure driven membrane processes. At the same time the draw solution in contact with the permeate side of the membrane is being diluted at the interface between the permeate and the membrane, by the permeating water. This is called dilutive external CP (Figure 2-13).
Figure 2-13: Illustration of osmotic driving force profiles for osmosis through several types and orientations, incorporating both ICP and ECP. (a) illustrates concentrative and dilutive ECP, (b) illustrates concentrative ICP and dilutive ECP, (c) illustrates dilutive ICP and concentrative ECP [134].

Concentrative and dilutive external CP phenomena decrease the effective osmotic driving force. The adverse effect of external CP on FO can be minimised by increasing the velocity of the flow and turbulence at the surface of the membrane, or by manipulating the water flux [135]. Due to the low hydraulic pressure used in FO, membrane fouling induced by external CP has milder effects on the water flux compared to the effects in pressure driven membrane processes. Several studies and models have proven that external CP plays a minor role in FO [134,136].

2.7.8.2 Internal concentration polarisation

Internal concentration polarisation (ICP) is a phenomenon unique to FO, and hence, when a composite or asymmetric membrane consisting of a dense active layer and porous supporting layer is used in FO, two ICP phenomena can occur, depending on the orientation of the membrane. If the porous support layer on the FO membrane faces the feed solution (Figure 2-14a), a polarised layer is established along the inside of the dense active layer and solute propagates to the porous layer. Referred to as concentrative internal CP [136], this
phenomenon is similar to the concentrative external CP, except that it takes place within the porous layer and cannot be minimised by crossflow.

When the feed solution is against the active layer and the draw solution is against the supporting layer (Figure 2-14b), the ICP phenomenon occurs on the permeate side. It is referred to as dilutive ICP because the draw solution is diluted by the permeate water within the porous support of the membrane.

**Figure: 2-14** (a) Concentrative internal CP and (b) dilutive internal CP across a composite or asymmetric membrane in FO.

### 2.7.9 Membrane Fouling

Membrane fouling has a significant impact on the operational sustainability and economics of FO. In real water matrices, the low fouling propensity of FO membranes means a reduction in both operational and capital costs, further enhancing the attractiveness of FO membranes for pilot and industrial applications. Organic fouling of FO membranes has been highlighted and investigated thoroughly. Algae, humic acid, and bovine serum albumin (BSA) are typical organic foulants in FO membranes. However, based on current studies FO membranes have a lower risk of irreversible fouling than a pressure driven membrane process because of the lack of applied hydraulic pressure.
The draw solution can have a significant impact on FO membrane fouling [137]. Comparing the fouling behaviours with the draw solutions of NaCl and dextrose, a study has shown that cake enhanced osmotic pressure (CEOP) was an important mechanism in FO fouling [138]. The reverse diffusion of salt from the draw solution to the fouling layer on the feed side accelerated CEOP and consequently reduced the net driving force for water permeation.

The initial concentration of the draw solution can also affect membrane fouling in FO [139]. Different fouling behaviours of BSA molecules were observed at both low and high initial draw solution concentrations [108]. The higher the concentration of draw solution is, the stronger the permeate drag. Thus, there is an obvious transition from a loose fouling layer to a more compact one. The foulant deposits on the surface of the FO membrane were measured at different initial concentrations of draw solution, and as expected, a greater amount of foulant deposition occurred at a higher concentration of draw solution [140].

Membrane orientation has a significant influence on FO membrane fouling. The active layer to the feed solution (FO mode) orientation was more resistant to fouling than the active layer to the draw solution (PRO mode) orientation [141]. In contrast to the relatively stable flux in FO mode, the flux in PRO mode can be drastically affected by the presence of foulant containing feed [140]. Other studies have reported better flux stability using the FO mode orientation. The main reasons are severe internal clogging and the compensating effect of ICP [108, 140]. When the support layer faces the feed, foulants enter the membrane’s porous layer, causing severe internal clogging as well as reducing the porosity of the support layer and thus, a reduced mass transfer coefficient $K_m$ [142]. Severe internal clogging in the PRO mode tends to significantly reduce the FO flux without significant mitigation from the compensating effect of ICP.
2.8 Summary and Research Needs

It can be summarised that the components of produced water have a different potential impact on the environment. Hence, reducing these components, especially the harmful ones, in order to reach the lowest level in terms of reducing the percentage discharged with produced water, is the primary goal of the oil industry. The literature review describes the techniques dealing with the treatment of produced water. Each method has been described and their advantages and disadvantages have been listed. Membrane technologies were highlighted as an alternative method in terms of efficiency and cost, and FO was selected as a notable approach to remove dissolved compounds in produced water. MF, UF, NF, and RO membranes have the ability to remove different size components. For instance, MF membranes can remove suspended particles, UF membranes can remove macro-molecules, and dissolved components such as BTEX and light phenols (C1-C3) can be removed with NF membranes and RO. The main disadvantages of NF and RO are the high driven pressure required and membrane fouling.

FO is a relatively new membrane technology in the treatment of wastewater. Currently it has been reported that applications include the treatment of industrial wastewater [143, 144], and desalination at bench scale [145, 146]. The main advantages of using FO are that it operates at low or no hydraulic pressures, it has a high rejection of a wide range of contaminants, and it may have a lower propensity for membrane fouling than pressure driven membrane processes. Furthermore, it can be installed in specific areas such as offshore platforms. From the literature review, the removal of produced water contaminants by FO is limited or it can be considered as unprecedented, although several studies have shown the efficiency of an FO membrane in terms of the high rejection of dissolved components and an energy efficiency compared with existing treatment technologies [147].
Despite the fact that other membrane technologies such as RO technology is widely used, the cost remains high due to its high consumption of energy [148]. The current FO membrane developed by HTI showed a better water permeability than RO membranes, although its performance is still not comparable to an RO membrane in an RO system, despite a much higher osmotic driving force [146]. Therefore, the goal of this current research was to develop a prototype treatment system that economically treats produced water from oil and/or natural gas operations for the benefit of industries located in offshore platforms where sea water can be used as a draw solution. In addition to that, higher water fluxes and recoveries are possible with a properly designed FO process, as large driving forces can be induced with a properly chosen membrane and draw solution.
3.1 Introduction

The literature presented in Chapter 2 shows that little is known about the removal of dissolved organic contaminants from produced by the FO process. In fact it can be considered as unprecedented, although several studies have shown the efficiency of the FO membrane in terms of a high rejection of dissolved components and energy efficiency compared to existing treatment technologies [147]. In addition to these advantages, the FO system can be built in restricted areas such as off-shore platforms. Therefore, the main goal beyond choosing this method was to validate the technical feasibility of the FO process for removing dissolved organic contaminants from produced water.

3.2 Experimental Systems

In order to study and fully understand the FO process, a laboratory-scale FO system was designed and constructed. Results obtained from the FO system were compared with high pressure driven processes, and hence, a laboratory-scale NF crossflow was also designed and constructed. The details of these experimental systems are described in the following sections.

3.2.1 FO System

To elucidate and fully understand the FO process, a laboratory scale FO system was designed, constructed, and used in this study. A schematic drawing of the system is illustrated in Figure 3-1 while the Forward Osmosis (FO) system layout is shown in Figure 3-2. To circulate the feed and draw solutions, two variable speed gear pumps (Micro-pump, Vancouver, WA) were used. The flow rates of the feed and draw solution flow were monitored using two rotameters. The tank for the draw solution was placed on a digital scale (Mettler Toledo Inc., Highstown,
NJ) and any changes in the weight were recorded by a personal computer to determine the permeate flux. The conductivity of the draw solution was measured continuously with a conductivity probe (Cole-Parmer, Vernon Hills, Illinois). A (peristaltic pump, USA) was controlled by a conductivity controller to occasionally pump a small volume of high concentration draw solution (6 M) of NaCl into the draw solution tank to maintain a constant concentration of draw solution. The tank of concentrated draw solution was attached to the draw solution on the same digital balance to avoid any interference when measuring the permeate flux between the two tanks during the experiment.

**Figure 3-1:** Schematic Diagram of FO System.

**Figure 3-2:** Forward Osmosis (FO) system layout.
A membrane cell was designed and constructed to produce the required volumes of water for analysis within a reasonable time (Figure 3-3). The membrane cell consisted of two identical semi-cells which were made of acrylic plastic (Figure 3-4). The channel of each cell was 0.2 cm high, and the total effective membrane area for mass transfer was 135.82 cm².

Figure 3-3: FO membrane cell.

Figure 3-4: Effective membrane area.

3.2.2 NF System

The cross flow NF filtration test unit was designed and built to compare the mass transfer properties (i.e. water flux and solute rejection) of the FO and pressure driven membrane filtration processes. A schematic diagram of the cross flow NF filtration system, a picture of the cross flow cell, and a picture of the system are shown in Figures 3-5, 3-6, and 3-7 respectively.
The effective membrane area of the membrane cell is $4 \text{ cm} \times 10 \text{ cm}$ and the height of the membrane channel was 2 mm. The system was equipped with a Hydra-Cll pump (Wanner Engineering Inc., Minneapolis, MN). The temperature of the feed reservoir was controlled using a chiller/heater (S SERIES WATER CHILLER 001-D081 ISS E, Aqua Cooler, Australia) the permeate flux was monitored by a digital scale (Mettler Toledo Inc., Highstown, NJ), and changes in weight are transmitted by a computer to determine the permeate flux. The feed reservoir was made from stainless steel.

**Figure 3-5:** Schematic diagram of NF test set-up.

**Figure 3-6:** Stainless steel cross flow cell NF filtration system.
3.3 Materials

3.3.1 Representative membranes

Four different flat sheet membranes were used in this study. Two membranes specially designed for FO applications were obtained from Hydration Technologies Inc. They are called HTI-Pouch and HTI-Cartridge, respectively. The HTI-Pouch is used in the HydroPack, LifePack, X-Pack, and SeaPack products that are currently available in the market from HTI. The HTI-Cartridge is used in the Expedition and HydroWell devices, which actually contains small spiral wound elements. Two NF membranes provided by Dow Chemical namely NF-90 and NF-270 were also used in this study.

The HTI-Cartridge membrane is cellulose triacetate with an embedded polyester screen mesh. The membrane was shipped as flat sheet samples and was preserved in vegetable based glycerin to avoid dehydration. Prior to any experiments or analysis, the HTI-Cartridge membrane was soaked in Milli-Q water for 30 minutes and rinsed with Milli-Q water to remove any residual glycerin.

Figure 3-7: NF filtration system set up.
The HTI-Pouch membrane is a cellulose triacetate that has been cast onto a non-woven backing that consists of polyester fibers individually coated with polyethylene. The backing can be heat welded or RF (radio-frequency) welded. The total thickness is 230 µm [149]. The rejection layer is the smooth side, to the inside of the roll. As with the HTI-Cartridge membrane, this membrane was also obtained as flat sheet samples and was preserved in vegetable based glycerin. Prior to any experiments or analysis, the glycerin was carefully removed, as described above.

![SEM image of HTI-pouch membrane](image)

**Figure 3-8:** An SEM image of the HTI-pouch membrane at 300x magnification [149].

Figure 3-9 shows HTI-Pouch and HTI-Cartridge membranes provided by Hydration Technologies Inc.
Figure 3-9: Photographs of the HTI-Pouch and HTI-Cartridge membranes.

The NF-90 and NF-270 membrane were obtained as flat sheet samples and were stored dry. Both membranes consist of a thin active skin layer made from aromatic polyamide for the NF90 or semi-aromatic piperazine-based polyamide for the NF270, on a more porous polysulphone supporting layer. It is these layers of active skin that determine the separating properties of the membrane. The NF-270 membrane can be classified as a loose nanofiltration membrane while the NF-90 is a tight nanofiltration membrane. Based on the contact angle measurement, the NF-90 is moderately hydrophobic while the NF270 is quite hydrophilic.
Figure 3-10: Photographs of the NF90 and NF270 membranes.

Table 3-1: Specifications of the NF membranes used [150].

<table>
<thead>
<tr>
<th>Membrane</th>
<th>NF90</th>
<th>NF270</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact angle (°)</td>
<td>-</td>
<td>26±2</td>
</tr>
<tr>
<td>Pure water permeability (m³/(m²sPa))</td>
<td>1.90×10⁻¹¹</td>
<td>3.20×10⁻¹¹</td>
</tr>
<tr>
<td>Maximum operating pressure (Pa)</td>
<td>41×10⁵</td>
<td>41×10⁵</td>
</tr>
<tr>
<td>Maximum operating temperature (°C)</td>
<td>45</td>
<td>45</td>
</tr>
<tr>
<td>pH range</td>
<td>3-10</td>
<td>3-10</td>
</tr>
</tbody>
</table>

3.3.2 Simulated produced water

Produced water often contains emulsifying agents such as sulphur, asphalt, salt, and clay. The emulsifiers absorb the oil droplets and spread in the water, which creates an emulsion. Therefore, oil in water emulsion was prepared by mixing Fork w2.5 motor cycle oil in distilled water. This oil was selected because its density and viscosity are similar to light crude oil (Table3-3).
Table 3-2: Comparison between light crude oil and Fork w2.5 Motorcycle oils.

<table>
<thead>
<tr>
<th>Specifications</th>
<th>Light crude oil</th>
<th>Fork w2.5 Motorcycle oils</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (kg/L)</td>
<td>0.825</td>
<td>0.827</td>
<td>[151, 152]</td>
</tr>
<tr>
<td>Viscosity (mm²/s)</td>
<td>5.96</td>
<td>6.74</td>
<td></td>
</tr>
</tbody>
</table>

3.3.3 Draw solution

Sodium chloride NaCl was chosen as the draw solute for the study on the fundamental characteristics and applications of the FO process, due to their respective advantages. NaCl has a good solubility in water and is able to generate a high osmotic pressure that is crucial for achieving good water flux. In addition, the simplicity, stability, and ease of handling of NaCl were the reasons for choosing it as the draw solution.

3.4 Experimental protocol

3.4.1 FO Experiments

The feed was prepared by melting sodium acetate (CH₃COONa) into Milli-Q water to generate a concentration of 300 mg/L of acetate (CH₃COO⁻). Either HCl (1M) or NaOH (1M) was used to adjust the pH value of the feed solution. 0.5 M of NaCl was melted in Milli-Q water and prepared as a draw solution. The volume of the feed solution and draw solution were 3 and 1 L, respectively. The temperature of the feed and draw solutions were monitored throughout the experiments 25±2°C using a temperature control unit (Thermo Fisher Scientific, Waltham, MA) in all experiments. Both FO and PRO mode experiments were conducted. In the FO mode experiments, the active layer of the FO membrane was placed against the feed solution, and in the PRO mode experiments the active layer of the FO membrane was placed against the draw solution. A new FO membrane was used and
approximately 2 mL samples were collected for analysis from the feed and draw solution, until the experiment was terminated. Feed samples were drawn directly from the feed and draw reservoirs and were usually kept in the fridge until the following day when they were analysed in an ion chromatography IC.

3.4.2 NF Experiments

Prior to each NF experiment, the membrane was compacted using DI water at a pressure of approximately 18 bar higher than the normal operating pressure of each membrane. Membrane compaction was conducted for at least 1 h until a stable baseline flux was obtained. 300 mg/L of acetate was than melted and added to the feed reservoir, and made up to the total feed volume of 10 L. In all the experiments, the cross-flow velocity and permeate flux were adjusted to be 25 cm/s and 8 L/m² h, respectively. The temperature of the feed solution was kept at 25 ± 1°C throughout the experiment. To assess the impact of solution pH on the rejection of acetate, the solution pH was raised to 9 by adding an appropriate volume of 1 M NaOH, and then the pH was incrementally dropped to pH 4 by adding an appropriate volume of 1 M HCl. Feed and permeate samples were collected for analysis after the filtration system had been established for 1 h. The system was operated under a recirculation mode, where both permeate and concentrate were re-circulated to the feed tank, except for the permeate sample collection.

3.5 Analytical Methods

3.5.1 Acetate analysis

Acetate concentration was analysed using a Shimadzu Ion Chromatography (IC) system (Kyoto, Japan). The IC system consisted of two high pressure pumps (LC-20AD), a degasser unit (DGU-20A3), a SIL-20A auto sampler, a column oven (CTO-20A), and a Dionex
suppressor (SRS 300), as shown in Figure 3-12. An IonPac AS23 column was used for the analysis. The temperature was maintained at 35°C. Calibration standards containing 200, 100, 50, 10, and 1 mg/L of acetate were prepared in 0.5 M NaCl background solution (which was also the draw solution in the FO experiments) by a serial dilution technique. The calibration curve was always linear with an R2 value of above 0.99 (Figure 3-11). IC started with a group of 5 samples. Some parameters such as time and the volume injected were adjusted, and at the end of the experiment each sample was analysed and measured in different areas by the IC. These areas of different concentration were plotted on a spread sheet in order to establish a standard for the acetate which would be used to determine the concentration of acetate in the following experiments. The results of the calibrated acetate are plotted in Figure 3-11.

![Figure 3-11: The standard calibration of acetate (CH₃COO⁻) using IC (in 0.5M NaCl matrix).](image-url)
3.5.2 Basic water quality analysis

3.5.2.1 Water Flux ($J_w$)

The water flux was calculated from the change in weight of the draw solution during each experimental run. As water permeated through the membrane from the feed to the draw side, the weight of the feed solution decreased while the weight of the draw solution increased. The water flux ($J_w$) can be calculated:

$$J_w = \frac{\Delta \text{Weight}}{\text{Membrane Surface Area} \times \Delta \text{Time}}$$

(2)

where $\Delta \text{Weight}$ is the increase in weight of the draw solution, $A$ is the surface area of the membrane, and $\Delta t$ is the differentiation time.

3.5.2.2 Conductivity analysis

Conductivity and pH were measured using a Thermo Scientific conductivity meter (ORION 4 STAR, Singapore). The relationship correlation between the conductivity and salt
concentration (NaCl) was established by measuring the diluted concentrations of NaCl and corresponding conductivity. A 4 g/L (0.068 M) solution of NaCl was prepared and the conductivity was measured as 7.87 mS/cm. The solution was diluted to get a range of molar concentrations, and then the conductivity for each solution was measured. Based on the data obtained, the standard curve of conductivity and salt concentration for NaCl was established (Figure 3-13). The concentration of NaCl in the feed solution can then be determined using the linear relationship presented in Figure 3-13.

**Figure 3-13:** Calibration curve of conductivity versus salt concentration for NaCl.

The reverse salt flux $J_s$ can be determined from an increase in the conductivity of the feed water. The reverse salt flux is in the opposite direction of the water flux. The reverse salt flux is given by [153]:

$$J_s = \frac{\Delta (CV)}{A \times \Delta t}$$

where $\Delta (CV)$ is an increase in salt in the feed, $A$ is the surface area of the membrane, and is $\Delta t$ the differentiation time.

Hence, the rejection of salt by the FO membrane can be calculated by the following Equation.
\[
R = \left[ 1 - \frac{C_P}{C_F} \right] \times 100\% 
\] (4)

Where,

\( R \) = salt rejection of a membrane, %;

\( C_P \) = salt (NaCl) concentration at the permeate side, g/L;

\( C_F \) = salt (NaCl) concentration at the feed side, g/L.

### 3.6 Membrane Characterisation techniques

#### 3.6.1 Zeta potential

The zeta potential of the surface of the membrane was measured by a SurPASS electrokinetic analyser (Anton Paar GmbH, Graz, Austria) (Figure 3-14). The zeta potential of each membrane was calculated from the measured streaming potential using the Fairbrother-Mastin approach. All the measurements of the streaming potential were conducted in a background electrolyte solution that contained 10 mM KCl. Hydrochloric acid and potassium hydroxide was used to adjust the pH by means of automatic titration. The test solution was to thoroughly flush the cell before the pH adjustment for each measurement. All the measurements of the streaming potential were performed at a room temperature of approximately 25 °C, which was monitored by the temperature probe of the instrument.

**Figure 3-14:** A picture of the SurPASS electrokinetic analyser.
3.6.2 A and B values

The measurement of A value (pure water permeability coefficient) and B value (NaCl permeability coefficient) were carried out using the laboratory scale cross flow NF system described above. Prior to each experiment, the membrane was compacted to approximately 16 bars using DI water for at least 1 h. The temperature of the feed reservoir was kept at $25 \pm 1^\circ C$ throughout the experiment, and unless stated otherwise, the permeate was recycled back into the feed reservoir. The system was operated at 14, 12, 10, 8, and 6 bars for one hour respectively by adjusting the pressure valve as required, and for each above operating pressure, the pure water flux data was collected for getting its function to applied pressure. Then the operating pressure was re-adjusted to 10 bars and 2g of NaCl was added into the feed reservoir to make up the total feed volume of 10 L and generate a concentration of 2000 mg/L. The permeate and feed solution conductivity was measured respectively. The relationship between the pressure applied throughout the experiment (bar) and the permeate flux (LMH) was plotted, as it shown in Figure 3-15

$$A = 195.889 \frac{LMH}{10 \text{ bar}} = 19.286 \frac{LMH}{M^2 \text{ bar}^{-1}}$$

![Figure 3-15: Permeate flux as a function of the applied pressure.](image-url)
Whereas the B value was calculated from the following equation:

\[
B = J_w \left( \frac{1 - R}{R} \right) \exp \left( - \frac{J_w}{k} \right)
\]  

(5)

where \( k \) is the mass transfer coefficient of the membrane cell. This was estimated by measuring the water and salt (2000 mg/L NaCl) flux, and NaCl rejection at 10 bars and then calculated using the Suzkot method.
4.1 Membrane Characteristics

The four membranes selected in this study differ from one another in their polymeric composition and internal structure in that the HTI-Pouch and HTI-Cartridge membranes are made of cellulose triacetate. According to the manufacturer, the HTI-Pouch is a thin film composite membrane with a thin layer of cellulose triacetate fused onto a layer of non-woven polyester fibre individually coated with polyethylene. On the other hand, the HTI-Cartridge is a polyester screen mesh embedded within an asymmetric layer of cellulose triacetate [154]. Both the NF-90 and NF-270 are thin film composite membranes with an ultra-thin layer of polyamide skin on top of a supporting layer of microporous polysulphone. Given the difference in their polymeric composition and internal structure, their physio-chemical properties and performance also differs, and hence, their intrinsic separation properties are also expected to be different.

The NaCl rejection of the selected membranes was as follows: HTI-pouch > HTI-cartridge > NF-90 > NF-270 (Table 4-1), which is consistent with the B value of the selected membranes. The NF-270 is considered to be a loose NF membrane with a low rejection of sodium whereas the NF-90 is a tight NF membrane with moderate rejection of sodium (Table 4-1) [155]. The pores of the HTI membranes are comparable in size to the tight NF membranes (NF-90), but are slightly smaller in diameter than the NF-270. Based on the diameter of their pores, it is expected that the HTI FO membranes would achieve better solute separation than a typical NF membrane (Table 4-1). In addition, both HTI membranes have a much lower water
permeability (A value) and salt (NaCl) permeability (B value) compared to the NF-90 and NF-270 membranes (Table 4-1).

**Table 4-1:** Properties of the selected membranes [149, 156-158]

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Water permeability A ((\text{Lm}^{-2} \text{h}^{-1} \text{bar}^{-1}))</th>
<th>NaCl permeability B ((\text{L m}^{-2} \text{h}^{-1}))</th>
<th>Average pore diameter ((\text{nm}))</th>
<th>NaCl retention (%)</th>
<th>Contact angle ((^{\circ}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTI-Pouch</td>
<td>0.745</td>
<td>0.0832</td>
<td>0.70</td>
<td>95-97</td>
<td>65</td>
</tr>
<tr>
<td>HTI-Cartridge</td>
<td>1.13</td>
<td>0.64</td>
<td>0.74</td>
<td>93-95</td>
<td>64</td>
</tr>
<tr>
<td>NF-90</td>
<td>6.4</td>
<td>1.32</td>
<td>0.68</td>
<td>85.0</td>
<td>50.9±2.4</td>
</tr>
<tr>
<td>NF-270</td>
<td>19.29</td>
<td>34.11</td>
<td>0.84</td>
<td>40.0</td>
<td>28.8±4.9</td>
</tr>
</tbody>
</table>

The results of the contact angle measurements show that all the membranes used are hydrophobic, except the NF-270. The hydrophobicity of both NF membranes is less than the HTI FO membranes. The surface charge of the selected membranes is pH dependent; as the pH increases the membranes become more negatively charged (Figure 4-1). Therefore, the electrostatic interaction between the charged organic solutes and the surface of the charged membrane can influence the rejection of organics. Most studies on electrostatic interaction have reported that an increase in the rejection of negatively charged organic solutes resulted from an electrostatic repulsion between the negatively charged membrane and negatively charged organic solute [159, 160]. This rejection, however, is based on the initial feed pH, since both the change on the surface of the membrane and the organic solute vary according to the pH (through a dissociation of the functional groups as a function of their pK\(\text{a}\)) [161].
Figure 4-1: Zeta potential of the selected membranes.

It has been reported that a more negative zeta potential could lead to a higher rejection of salt due to an enhanced electrostatic interaction between the negatively charged surface of the membrane and a negatively charged solute [162]. The zeta potential of the surface of the membrane varies as a function of the solution pH (Figure 4-1). The zeta potential of the membrane in the HTI-Cartridge membrane is not as sensitive to pH as the HTI Pouch. The active and backing layers of the HTI-Cartridge membrane show an almost identical zeta potential profile as a function of pH, while there is a notable difference in the zeta potential profile between the active and backing layers of the HTI Pouch membrane. These results are consistent with the difference in structure of the HTI Cartridge and Pouch membranes as described previously. Both the NF270 and NF90 membranes are much more negatively charged compared to the HTI membranes particularly at above neutral pH. Results reported here suggest that the active skin layers of the two polyamide NF membranes contain significantly more ionisable functional groups than those of the cellulose acetate HTI membranes.
4.2 General behaviour of the HTI membranes

4.2.1 Water flux and reverse salt flux

Both the HTI-Cartridge and HTI-Pouch membranes were investigated under the FO mode (i.e. the active layer facing the feed solution and the backing layer facing the draw solution), using the FO laboratory setup described in Chapter 3. The experimental conditions were maintained the same for all experiments. Feed: 300 mg/L acetate CH₃COO⁻; draw solution: 0.5 M NaCl; cross flow rate: 1 L/min; Temperature: 25 ±2 °C. The water flux and reverse salt flux were calculated based on the amount of water permeating from the feed to the draw solution, and the conductivity measurement respectively using the method described in section 3.4.1. The water fluxes obtained from the HTI-Cartridge and HTI-Pouch membranes in the FO mode are presented in Figure 4-2. The effect of the initial feed pH on the water fluxes by the HTI-Cartridge and HTI-Pouch membranes under the FO mode was insignificant. The water flux by the HTI-Cartridge membrane was higher than that by the HTI-Pouch membrane with the same draw solute concentration of 0.5 M of NaCl. The average water flux obtained by HTI-Cartridge was ~ 6.5 LMH while in HTI-Pouch was ~ 3 LMH. The higher water fluxes observed with HTI-Cartridge membrane compared to the HTI-Pouch membrane can be explained by the different in the membrane structure as described in Section 4.1. Additionally, these results are consistent with the pure water permeability (A value) of these two HTI membranes (see Table 4-1).
Figure 4-2: Water flux as a function of time at different pH values of the feed in the FO mode (draw solution = 0.5 M NaCl, cross flow rate = 1 L/min for both sides, and cross flow velocity = 9 cm/s).

Mass transport in the FO process can be bi-directional [163], and the leakage of salts (or reverse salt flux) can occur with a non-idealised membrane. This reverse salt flux can be measured by monitoring the increase in conductivity in the feed solution using a calibration curve for the NaCl solution that has been explained in Chapter 3. The reverse salt flux is driven by diffusion and can play a significant role in reducing the osmotic difference between the feed and draw solutions. In this study, the reverse diffusion salt flux was calculated based on the concentration and volume of feed at the beginning and end of the FO experiments.

Figure 4-3 shows the reverse NaCl fluxes obtained with the HTI-Cartridge and HTI-Pouch membranes under different initial feed solution pH, namely un-adjusted pH (approximately 6.8 up to 7.3), 4, and 6, respectively. The effect of feed solution pH
on the reverse salt flux by both the HTI-Cartridge and HTI-Pouch membranes is insignificant, which was similar to the observation regarding the water flux. The reverse NaCl fluxes observed with the HTI-Cartridge membrane were significantly higher than those observed with the HTI-Pouch membrane (Figure 4-3). This observation regarding the reverse salt flux is in a good agreement with the B value (salt permeability) of these two membranes that were previously discussed in Section 4-1. It is noteworthy that the water flux of the HTI-Cartridge membrane was also significantly higher than that of the HTI-Pouch membrane (Figure 4-2).

**Figure 4-3:** Water and reverse salt fluxes of NaCl of the HTI-Cartridge and HTI-Pouch membranes.

### 4.2.2 Effects of membrane orientation on water flux and reverse salt flux

#### 4.2.2.1 Water Flux

Of the two membranes specifically designed for the FO applications used in this study, the HTI-Cartridge membrane showed a significantly higher water flux. Thus,
it was selected for further investigation to evaluate the impact of the membrane orientation on water flux and reverse salt flux.

The HTI-Cartridge membrane was used in both the FO and PRO modes using a laboratory FO setup described previously in Section 3. Four experiments were conducted to evaluate the effects of the membrane orientation on the water flux and reverse salt flux. Two values of pH were investigated, un-adjusted pH (which was from 6.7 to 7.3), and pH4. The experimental conditions were maintained the same for all the experiments: Feed: 300 mg/L acetate $\text{CH}_3\text{COO}^-$; draw solution: 0.5 M NaCl; crossflow rate: 1 L/min; Temperature: 25°C ±2. The water flux was calculated based on the amount of water permeating from the feed to the draw solution, using the method described in chapter 3.

Figure 4-4 shows the water fluxes as a function of time when the FO membranes were investigated under the FO mode (i.e., the active layer of the membrane facing the feed solution and the backing layer facing the draw solution), and in the PRO mode (i.e., the backing layer facing the feed solution and the active layer facing the draw solution). By comparing the water fluxes obtained using 0.5 M NaCl in the draw solution at a room temperature of 25 ± 2°C under the PRO mode, it can be seen that water fluxes obtained by the FO membrane under the PRO mode were higher than those obtained under the FO mode, with the same experimental conditions. The average of the water flux obtained FO mode was ~ 6.5 LMH while under PRO mode the water flux was ~ 9 LMH. The higher flux obtained by HTI-Cartridge under PRO mode was due to the internal concentration polarisation (ICP) which is considered to be a unique phenomenon in FO membranes. When a composite or asymmetric membrane consisting of a dense active layer and porous supporting layer is used in FO, two ICP phenomena can occur, depending on the orientation of the membrane.
If the porous support layer on the FO membrane faces the feed solution, a polarised layer is established along the inside of the dense active layer and solute propagates to the porous layer. This phenomenon is referred to as concentrative internal CP [136], that is similar to the concentrative external CP, except that it takes place within the porous layer and cannot be minimised by cross flow.

When the feed solution is against the active layer and the draw solution is against the supporting layer, the ICP phenomenon occurs on the permeate side. This is referred to as dilutive ICP because the draw solution is diluted by the permeate water within the porous support of the membrane. For more details refer to section 2.7.8 in Chapter 2.

![Graph](image)

**Figure 4-4:** Water flux as a function of time at different pH values of the feed in the FO mode. (Initial concentration of acetate in the feed =300mg/L, draw solution = 0.5 M NaCl, cross flow rate = 1 L/min for both sides, and cross flow velocity = 9 cm/s).
4.2.2.2 Reverse Salt Flux

The effects of the membrane orientation on the reverse salt flux (RSF) were investigated in this section. Figure 4-5 shows the comparison between the FO and PRO modes using the same membrane (HTI-Cartridge) and under the same operating conditions. The RSF obtained under the FO mode was consistently less than those obtained under the PRO mode, which is consistent with the results previously obtained by Zhao et al [164].

![Figure 4-5: Reverse salt flux of NaCl for HTI-Cartridge membrane in the FO and PRO modes.](image)

4.3 Solute separation

4.3.1 Effects of pH

The solution pH appears to be a major parameter governing the rejection of acetate by the four FO/NF membranes selected in this study (Figure 4-6). The results presented in Figure 4-6 can be explained by the intricate relationship between the
speciation of acetate, membrane surface charge, and solution pH. Acetate can speciate from a neutral species to a negatively charged acetate ion, as the solution pH increases beyond its pK_a value of 4.7. In addition, an increase in the solution pH can also increase the membrane negatively surface charged density (Figure 4-1), leading to an enhanced electrostatic interaction with charged solute [155].

Figure 4-6: Rejection of acetate as a function of time at different pH values of the feed in the (a) FO mode and (b) RO mode rejection of acetate as a function of pH at the same permeate water flux, feed concentration, and temperature. The FO experimental conditions were as follows: The initial concentration of acetate in the feed =300mg/L, draw solution =0.5 M NaCl, crossflow rate = 1 L/min for both sides, and cross flow velocity = 9 cm/s, temperature = 25± 2°C. The RO experimental conditions were as follows: Initial concentration of acetate in the feed =300 mg/L, water flux = 8 L/m²h, crossflow rate = 1 L/min, crossflow velocity = 25 cm/s, temperature = 25 ± 1°C.

The results reported in Figure 4-6 systematically demonstrate the significance of electrostatic interaction and the major rejection of acetate by the HTI-Cartridge and HTI-Pouch FO membranes under the FO mode. Similar results were obtained by the
FO membrane at a high pH value of 6-9 under the RO mode. It is also noteworthy that the rejection of acetate decreased gradually by decreasing the pH value. A much more dramatic decrease in the rejection of acetate occurred with the NF membranes (NF-90 and NF-270) compared to the other two FO membranes (Figure 4-6). As a result, the differences in the rejection of acetate by all four selected membranes decreased substantially as the feed solution pH increased. The results reported in Figure 4-6 suggest that charged repulsion is a predominant rejection mechanism of acetate at high pH. Furthermore, there is a considerable scope for using the FO membrane for the removal of acetate and other dissolved organic acids in produced water. At pH 6 and un-adjusted pH, the rejection of acetate by the FO membranes (HTI-Cartridge and HTI-Pouch) varied from 92% to 100%. Under the RO mode, acetate rejection of 90% to 100% could be achieved with the HTI-Cartridge and HTI-Pouch membranes. With the NF membranes, size exclusion is always an underlying rejection mechanism. The importance of size exclusion is shown by differences in the rejection of acetate at a certain pH. At any given pH value, the rejection of acetate by NF membranes generally increases as the size of the pores in the membrane decreases (Figure 4-6 and Table 4-1). It is noted that the rejection of acetate by the NF membranes was less than the HTI-FO membranes, even though the zeta potential of the two HTI FO membranes was less negatively charged than the NF membranes (Figure 4-1). In addition, the pore sizes between the FO membranes and those values of the NF90 and NF270 (Table 4-1) are intermediate.

The conductivity of the feed and permeate was monitored every hour during sample collection. Conductivity has a direct relationship on the concentration of salt in the water: A high concentration of salt generates high ionic concentrations in the feed or permeates, which will result in a high conductivity value. The rejection of
conductivity was calculated, and a relationship between the rejection of conductivity and pH value was established for each experiment. Figure 4-7 shows the rejection of conductivity of HTI-Cartridge and HTI-Pouch with the NF-90 and NF-270.

The results of this rejection of the conductivities are in good agreement with the rejection of acetate that was analysed by the IC (Figure 4-6). There was a high rejection of conductivity in the HTI-Cartridge and HTI-Pouch under the RO mode when it operated on FO mode where “the active layer faces the feed solution”. In contrast, the rejection rates by NF-90 and NF-270 were less than the HTI-FO membranes. These results can be explained by the relationship between the solution and membrane surface charge, and the pressure applied, as explained previously in section 4.3.

![Figure 4-7](image_url)

**Figure 4-7:** Rejection of acetate as a function of different pH values of the feed. The RO experimental conditions were as follows: Initial concentration of acetate in the feed =300 mg/L, water flux = 8 L/m²h, crossflow rate = 2 L/min, crossflow velocity = 25 cm/s, temperature = 25 ± 1°C.
Rejections of conductivity by the HTI-Cartridge, HTI-Pouch, and NF90 membranes remained largely constant, despite any changes in the feed solution pH (Figure 4-8). One exception was the NF-270 membrane which showed a considerable decrease in conductivity rejection as the feed solution pH decreased. This can be attributed to the large pore size of this membrane which encourages an increase in the electrical double layer on the surface of the membrane in high pH conditions [165, 166].

4.3.2 Effects of membrane orientation on rejection of acetate

Membrane orientation can exert some impact on the rejection of acetate during the FO and RO modes. Higher rejection obtained in both FO and RO systems when it was run under FO mode (i.e. active layer facing feed solution) (Figure 4-8). The different rejection behaviour of acetate in both systems FO and RO is attributed to the effect of ICP. Because the ICP phenomenon may not significantly impact the osmotic pressure gradient in the PRO mode, the effective mass transfer driving force in the PRO mode is higher than in the FO mode. In addition, in the PRO mode, acetate is subjected to a concentrative ICP within the porous supporting layer of the membrane [167], which leads to a gradient of higher concentration across the dense active layer of the membrane. Therefore, the ICP phenomenon can negatively affect the rejection of acetate in a similar fashion to that caused by the normal concentration polarisation phenomenon. At an un-adjusted pH (pH 6.8 – 7.3), the rejection of acetate in PRO mode was lower than in FO mode. In PRO mode the rejection varied from 100-92 % but under FO mode the rejection was very high, with a figure of 100%. In contrast, the rejection of acetate under RO mode in both sides (FO and PRO) was 10% lower than in the FO mode (Figure 4-7 b). In the FO mode, the supporting layer of the membrane was more negatively charged than the active
layer (Figure 4-1), and thus the rejection of acetate was enhanced by electrostatic repulsion between the negatively charged supporting layer and negatively charged compound.

**Figure 4-8:** (a) Rejection of acetate as a function of time at different pH values of the feed in the FO and PRO modes. The FO experimental conditions were as follows: Initial concentration of acetate in the feed =300 mg/L, draw solution = 0.5 M NaCl, cross flow rate = 1 L/min for both sides, and cross flow velocity = 9 cm/s. Temperature = 25 ± 2 °C. (b) Rejection of acetate as a function of pH values of the feed in the FO and PRO modes. The RO experimental conditions were as follows: Initial concentration of acetate in the feed =300 mg/L. water flux = 8 L/m²h, crossflow rate = 1 L/min, crossflow velocity = 25 cm/s, temperature = 25 ± 1°C.

4.4 Membrane fouling

4.4.1 The FO process of an oily solution

The concentration of oil in produced water often changes due to the effect that processes such as reduction have on the temperature or chemical treatment. Based on the Environmental Protection Agency (EPA), the maximum monthly average of dispersed oil is 30 mg/L, generally the higher the concentration of feed oil in emulsion is, the lower the amount of permeate flux is produced, whereas at a lower feed concentration the permeate flux is higher. The feed concentration has a strong
influence on the size of the oil droplet and its distribution [168]. Hence, the concentration of feed solution has a direct influence on fouling. Fouling is mainly due to the adsorption of oil on the structure of the membrane which effects the pore diameter and reduces its permeability [168]. A high concentration of oil in the feed increases the adsorption of oil and causes more resistance for the permeating water.

FO experiments were conducted using a closed loop bench scale FO membrane system. A detailed description of the FO set up and operating protocol has been provided in Chapter 3 (Figure 3-4). Here the FO system was exposed to a cleaning procedure using Milli-Q water that was carried out for at least one hour before every experiment. The conductivity of the draw solution was measured continuously with a conductivity probe. To maintain a constant draw solution concentration, a peristaltic pump was regulated by a conductivity controller to intermittently dose a small volume of a concentrated draw solution (6 M of NaCl) into the draw solution reservoir. The concentrated draw solution makeup reservoir was also placed on the same digital balance to ensure that the transfer of liquid between the two reservoirs did not interfere with the measurement of permeate flux, and that the system could be operated at a constant osmotic pressure driving force during the experiment.

This part of the study was conducted to investigate membrane fouling. The HTI-Cartridge membrane was used under the FO mode (i.e. active layer facing the feed solution and backing layer facing the draw solution). The experimental conditions were the same for all four tests, except that the concentration of oil varied. Feed: 0, 30, 300, and 3000 mg/L respectively with 30 mg/L NaCl; Draw solution 0.5 M NaCl; room temperature 25 ± 2°C. The system was operated under a constant condition, as
explained above, until 60% of the water had been recovered. Both the flux and reverse salt flux were recorded.

The experimental water fluxes through an HTI-Cartridge are presented in Figure 4-9. Generally, the water flux was not influenced by the concentration of oil in the feed solution (30 mg/L), indicating that the presence of up to 30 mg/L of oil does not change the intrinsic separating properties and structure of FO membranes. These results encouraged us to increase the oil content by 10 times to 300 mg/L, and then in an extreme case, by 100 times to 3000 mg/L (Figure 4-9 b).

**Figure 4-9:** Flux as a function of time (a) initial concentration of NaCl in the feed = 30 mg/L; oil content = 0 mg/L and 30 mg/L; draw solution = 0.5 M NaCl; cross flow rate = 1 L/min for both sides; cross flow velocity = 9 cm/s). While in (b) initial concentration of NaCl in the feed = 30 mg/L and oil content 300 and 3000 mg/L draw solution = 0.5 M NaCl, cross flow rate = 1 L/min for both sides, and cross flow velocity = 9 cm/s).
Despite the fact that the water flux was not influenced by up to 30 mg/L oil in the feed solution, it can be considered that permeate flux depends on the concentration of oil. A lower steady permeate flux was obtained with a higher concentration of oil in the feed solutions, as shown in Figure 4-9 (b), when the concentration was increased to 300 mg/L. Fouling was significant when the oil content was increased up to 3000 mg/L.

4.4.2 Effects of Membrane Fouling on Reverse Salt Flux and Acetate Rejection

4.4.2.1 Acetate removal under fouled conditions

Since the HTI-Cartridge membrane showed a better water flux than the HTI-Pouch membrane, the HTI-Cartridge membrane was further investigated to evaluate the rejection of acetate under pre-fouling conditions. In addition, only the FO mode was investigated further as it has been shown to result in higher acetate rejection than the PRO mode.

Experiments were conducted to evaluate the efficiency of the HTI-Cartridge. Membrane fouling was assessed and evaluated separately and the results showed that the existing allowable oil in water addressed by the Environmental Protection Agency (EPA) did not show any significant fouling (see section 4.4). Experiments were conducted to evaluate the performance of HTI-Cartridge under pre-fouling conditions. These experiments on fouling have been explained in section 4.4, and showed that when the concentration of oil in a feed solution was 300 mg/L, the subsequent fouling was quite significant. Consequently, four experiments were conducted to evaluate the rejection of acetate, flux, and reverse salt flux under fouling conditions.
All four experiments were carried out under stable conditions. Feed: emulsion of 300 mg/L acetate (CH$_3$COO$^-$) and 300 mg/L of oil in 3 L of MilliQ water; draw solution: 0.5 M NaCl in 2 L MilliQ water; cross-flow rate: 1 L/min; temperature: 25±2°C. The water flux and reverse salt flux were calculated based on the amount of water permeating from the feed to the draw solution and the conductivity measurement respectively. The system was operated under a constant condition in FO mode until 1 L of permeate was collected. Samples of water were collected at fixed time intervals for IC analysis.

**Figure 4-10:** Rejection of acetate as a function of time at different pH values of the feed in FO mode. (Initial concentration of acetate in the feed =300mg/L, draw solution =0.5 M NaCl, cross flow rate = 1 L/min for both sides, and cross flow velocity = 9 cm/s). Fouling experiment conditions are as follows: feed contains 300 mg/L acetate and 300 mg/L oil, draw solution = 0.5 M NaCl, crossflow rate = 1L/min for feed and draw solution sides, and cross flow velocity = 9 cm/s.

Figure 4-10 compares the rejection of acetate under pre-fouling conditions with experiments conducted without using oil. These experiments were conducted under
different initial feed pH, un-adjusted pH (6.7-7.3), and pH4 respectively. At pH 4 the concentration of acetate in the draw solution was similar to the results obtained under the same conditions, but the feed solution was without oil (Figure 4-10). Whereas in un-adjusted pH the results matched the same results as the experiment held under the same conditions except that the concentration of oil on the feed side was zero, the results were similar, with values of 100% up to five hours, after which there was a slight decrease in the experiment under pre-fouling conditions (100 to 91%), and then a steady constant at this percentage until the experiment ended. The reduction of ~10% happened because in this experiment the pH measurement varied between 6.3-6.1, except for an initial pH of 7.38. This result shows that the presence of oil in the feed did not affect the acetate’s rejection. This result is in good agreement with results presented in Figure 4-6 “HTI-Cartridge, and pH 6 in FO mode, and supports our outcome that the presence of oil did not affect the rejection of acetate.

This result shows that the presence of oil in the feed did not affect the rejection of acetate.

4.4.2.2 Water flux under pre-fouling condition

The experimental water flux under pre-fouling conditions through HTI-Cartridge is presented in Figure 4-11. The HTI-Cartridge was investigated and compared with the fouled conditions (feed solution 300 mg/L acetate) in the FO mode under similar experimental conditions. Furthermore, the effect of the initial feed pH on the water fluxes by the HTI-Cartridge membrane under FO mode was investigated experimentally.

The results showed that the water flux achieved by the HTI-Cartridge under pre-fouling conditions decreased gradually, whereas, there were higher and constant
water fluxes when the feed solution only contained 300 mg/L acetate. In contrast, the initial feed pH did not show any significant influence on the water fluxes, either under pre-fouling conditions, or when the oil content was zero. For further details regarding the concentration of oil, see section 4.4.1.

![Graph](image)

**Figure 4-11**: Flux as a function of time at different pH values of the feed in FO mode. (Initial concentration of acetate in the feed =300mg/L and 30 mg/L oil, draw solution = 0.5 M NaCl, cross flow rate = 1 L/min for both sides, and cross flow velocity = 9 cm/s) while under pre-fouling conditions (Initial concentration of feed =300mg/L and 300 mg/L oil, draw solution = 0.5 M NaCl, cross flow rate = 1 L/min for both sides, and cross flow velocity = 9 cm/s).

### 4.4.2.3 Reverse salt flux under Pre-fouling condition

Based on the previous results, the HTI-Cartridge membrane was further investigated to evaluate how the flux and reverse salt flux performed under pre-fouling conditions. The HTI-Cartridge was investigated under the FO mode and PRO modes. The effects of the orientation of the membrane on reverse salt flux, and a
comparison of the HTI-Cartridge under the FO mode and PRO modes were carried out. Two experiments were conducted to evaluate the effects of the initial feed pH on the water flux, and reverse salt flux under pre-fouling conditions. Two values of pH were investigated, un-adjusted pH (6.7-7.3), and pH4. All the experiments were conducted under the same conditions. The water flux and reverse salt flux were calculated based on the amount of water permeating from the feed to the draw solution and the conductivity measurement, respectively.

Figure 4-12: Comparison of reverse salt fluxes of NaCl for HTI FO cartridge membrane under pre-fouling and fouled conditions (FO and PRO modes).

Figures 4-12 compares the water flux and reverse salt flux under pre-fouling conditions with experiments conducted without oil, under the same operating conditions. By comparing the reverse salt flux obtained using the FO mode under pre-fouling conditions with those experiments which conducted without oil in the feed solution, it was found that the water flux depended on the concentration of oil.
The water flux observed when the content of oil in the feed solution was zero mg/L was higher, whereas the water flux deceased under pre-fouling conditions when the content of oil was 300 mg/L. In contrast, the reverse salt flux obtained under pre-fouling conditions was always slightly higher than those obtained by the same membrane under similar experimental conditions.
5.1 Conclusion and recommendations

This study investigated the ability of the forward osmosis (FO) process to remove dissolved organics from produced water, with a focus on offshore platforms where seawater can be utilised as the draw solution. This appears to be the first attempt to study the removal of dissolved components from produced water using an FO membrane. This chapter summarises the findings and recommends possible further work that can extend this study.

In the first part of the study, the performance of the FO process in terms of water flux, reverse salt flux, and the rejection of acetate under various experimental conditions, were evaluated under the FO mode. The experimental results showed that the HTI-Cartridge membrane performed better than the HTI-Pouch membrane in terms of water flux, whereas the rejection of acetate by both membranes was largely indifferent.

The transport phenomena for HTI-Cartridge membranes were also investigated under both forward osmosis (FO) and pressure retarded osmosis (PRO) modes because it showed a better water flux than the HTI-Pouch membrane. In the former, the active layer of the membrane is in contact with the feed solution but in the latter, the active layer of the membrane is in contact with the draw solution. The internal and external concentration polarisation phenomena were found to play a major role in influencing the water flux and reverse salt flux. When the FO membranes were operated under the PRO mode, internal CP occurred within the backing layer (loose support layer) of
the FO membranes on the feed side, which decreased the effective driving force. When the FO membranes were operated under FO mode, a more severe internal CP occurred within the backing layer facing the draw solution, which resulted in a higher resistance than the PRO mode.

The experimental results also suggested that the initial feed pH plays a significant role in terms of acetate rejection. The selected membranes were investigated under different initial feed pH (i.e., unadjusted pH (6.7-7.3), pH 4, and pH 6). It can be concluded from the experiments that under unadjusted pH and pH 6 there was a high rejection, but it decreased dramatically at pH 4. This can be explained by the relationship between the solution and the surface charge of the membrane.

The FO membranes (HTI-Cartridge and HTI-Pouch) and the NF membranes (NF-90 and NF-270) were also investigated under reverse osmosis (RO) mode. A comparison between FO and RO mode were held to evaluate the removal efficiency between the selected membranes under FO and RO modes. It was noted that the rejection of acetate by the FO membranes was strongly pH-dependent under both FO and RO modes. At an unadjusted pH which varied from 6.7 to 7.3, and pH 6, the acetate rejected by the HTI-Cartridge and HTI-Pouch membranes under FO mode was between 92-100%, and this rejection decreased dramatically as the feed solution pH decreased to pH 4. Moreover, rejection by the selected membranes was more efficient under FO mode where the active layer faced the feed solution and the backing layer faced the draw solution. Similar results were obtained by the FO membrane at a high pH value of 6-9 under the RO mode. It is also noteworthy that the rejection of acetate decreased gradually by decreasing the pH value. A much more dramatic decrease in the rejection of acetate occurred with the NF membranes.
(NF-90 and NF-270) compared to the other two FO membranes. The differences in the rejection of acetate under RO mode by all four selected membranes decreased substantially as the feed solution pH increased. The rejection of acetate by the NF-270 and NF-90 membranes was considerably lower than the FO membranes, whereas it increased from 55% to 92% with the NF-90 membrane, as the feed pH increased from 4 to 9. Furthermore the acetate rejected by the NF-270 membrane (with a larger size pore than the NF-90 membrane), increased from 2% to 89% as the feed pH increased from pH 4 to pH 9. Acetate rejection in the FO mode was also pH dependent, and was at least 10% higher than in the RO mode. These results can be explained by the relationship between the membrane surface charge and the solute charge, so the relationship between the solution and surface charge of the membrane proved that an increase in the rejection of negatively charged organics was due to electrostatic repulsion between the negatively charged membranes and negatively charged organic solute. In addition, charges on the surface of the membrane were investigated using the zeta potential, with the results showing that the HTI-Cartridge, HTI-Pouch, NF-90 and NF-270, selected for this study were negatively charged at high pH and became more negative as the solution pH increased, whereas at low pH they became positively charged.

In the latter part of this study the experiments conducted on fouling to investigate the water flux and membrane fouling under various experimental conditions – with oil contents of 0, 30, 300, and 3000 mg/L – were investigated. These experiments were held in terms of evaluating whether or not the allowable oil content (30 mg/L) discharged with the produced water would cause significant fouling. The results of these experiments are as follows:
Chapter 5 Conclusion and Recommendations

- An oil content of 30 mg/L did not lead to any significant fouling.
- An oil content of 300 mg/L led to a dramatic decrease in the water flux due to membrane fouling.
- An oil content of 3,000 mg/L led to a significant reduction in the water flux due to membrane fouling.

It can be concluded from these experiments that the water flux was not influenced by up to 30 mg/L of oil in the feed solution, which indicates that this allowable oil content (30 gm/L) does not affect the intrinsic separation properties and structure of the membrane.

The final part of the study was on the effects of membrane fouling on the rejection of acetate. Since the FO mode rejected acetate better than the RO mode, and the HTI-Cartridge membranes showed better water flux than the HTI-Pouch membranes, the HTI-Cartridge membrane was further investigated to evaluate the rejection of acetate under pre-fouling conditions. Several experiments were conducted to evaluate the membrane under pre-fouling conditions, with the results showing that the rejection of acetate under pre-fouling conditions was similar to the experiments held without oil. Therefore, it can be concluded that the rejection of acetate was not affected by the allowable oil content of 30 mg/L in produced water.

Produced water contains various compounds originating from crude oil, such as carboxylic, hydrocarbons, phenols, and BTEX (which is a mixture of benzene, toluene, ethylbenzene and xylene). These dissolved components are considered to be a challenge to remove completely by physico-chemical processes. Consequently, using the FO process to treat produced water offshore offers good prospects because
based on our investigations, FO showed a high removal of acetic acid, which is one of the organic dissolved contaminants in produced water. This encouraging performance of the FO system in treating produced water leads us to recommend that the FO process be investigated using other dissolved components, such as BTEX. This approach would be most interesting due to the increasing concern that discharging produced water containing traces of BTEX into the ocean might have a severe environmental impact. Furthermore, in offshore platforms, seawater can be utilised as a draw solution because it significantly reduces the cost of treatment before discharging the produced water into the ocean.

Further investigation of the following parameters are required for future research, these include the influence of temperature on the FO process, significant differences in the properties of produced water depending on its origin, and varied temperatures of produced water depending on the oil field. Moreover, a further investigation into the fate of concentrated produced water is recommended to re-inject it into the oil reservoir or to recover the hydrocarbon content.
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