A vertical stream of water falls from the top of the frame into a clear glass at the bottom. The water is captured in a way that shows its motion, with a slight blur and splashing at the point of impact. A thin, horizontal line, possibly representing a surface or a measurement, intersects the water stream about halfway down. The background is a light, neutral color.

Hyper-Saline Produced Water Treatment for Beneficial Use

Mustafa Al-Furaiji

HYPER-SALINE PRODUCED WATER TREATMENT FOR BENEFICIAL USE

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DISSERTATION

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1

Introduction

1.1 General introduction

Producing oil and gas is always accompanied with large amounts of effluent water, called “produced water” (PW). Most of the PW is formation water that has accumulated over millions of years with fossil fuels in the geologic formations deep in the earth. Also, PW may contain some surface water that has been injected into the formation for enhanced oil recovery [1]. The injected water becomes necessary with the increase of the oilfield’s age. The oil recovery process goes through three different stages depending on the production phase of the oilfield: primary, secondary and tertiary oil recovery. During the initial phase of production (primary recovery), the pressure in the oil reservoir is sufficient to force the oil to the surface. About 15% of the oil in the formation can be extracted during this stage [2]. In the following phase (secondary recovery), external energy is applied to force the oil to the surface. This is typically done by injecting water to increase the pressure in the reservoir. This method can recover about 30% of the remaining oil after the primary recovery stage [2], this phase is also called Improved Oil Recovery or IOR. After that, more advanced methods (tertiary recovery) are applied to extract more oil from the reservoir. These methods depend on altering the flow properties (e.g. reducing the viscosity) of the crude oil to facilitate oil flow to the surface. This can recover up to 15% of the oil before the oilfield becomes unproductive [2]. This last phase is called Enhanced Oil Recovery or EOR.

In many instances, this produced water is seven to eight times larger by volume than oil produced at any given oilfield [3]. The composition of produced water varies greatly from oilfield to oilfield depending on factors such as geographic location, a method of extraction, chemicals that are used during the production of oil, and contact time with the oil in the formation [4]. In general, it may contain inorganic salts, organic chemicals (mostly

hydrocarbons, but also production chemicals like corrosion inhibitors, hydrate inhibitors, surfactants and polymers), heavy metals, and suspended solids.

Treatment of produced water can provide an additional water resource especially in the arid or semi-arid regions. Iraq is typically such a region with annual rainfall below 150 mm [5]. Water consumption in Iraq depends mainly on two rivers: the Tigris and the Euphrates that are flowing from the Turkish mountains to the south of the country where they meet and finally flow into the Arabian Gulf. However, the quality and quantity of water in these rivers has become insufficient, especially in the south of the country, because most of the water is consumed by the upstream cities and the remaining water gets polluted due to the improper treatment of the municipal and industrial waste waters before discharging to the rivers. Most of the oil and consequently the produced water in Iraq is produced in the southern region of the country. At present, in most cases, large volumes of produced water are injected into the ground or disposed to the surface as untreated effluent fluids.

1.2 Treatment of hyper-saline produced water

The selection of a suitable treatment method depends mainly on the quality of the produced water source. Produced waters from four giant oilfields in the south of Iraq (i.e. Rumaila North, Rumaila South, Al-Zubair and Qurna West) were analyzed by Al-Rubaie et al. The analysis showed that the total dissolved solids (TDS) of PW is extremely high (about 240,000 mg/L) and as such is classified as a hyper-saline produced water [6]. Treatment of such high salinity streams can be a challenge, especially when they also contain hydrocarbons that cause additional problems in the conventional oil/water separation equipment like skimmers, coalescers, filters, and hydrocyclones.

In general, desalination can be done either by thermal processes where heat is involved in the process or by membrane processes where a membrane is used.

1.2.1 Thermal processes

Distillation is the oldest and most commonly used method of desalination. In this process, the saline water is heated to produce water vapor, which is then condensed to produce freshwater [7]. Thermal desalination processes can be classified depending on the method used for the supply of energy.

1.2.1.1 Vapor Compression (VC)

Vapor-compression distillation uses mechanical energy rather than thermal energy. Compressed water vapor is passed through the evaporator bundle, where it condenses and forms distilled water (Figure 1.1A). The heat of condensation can be re-used to evaporate more brine [8]. The vapor-compression process is quite energy efficient and has a low operating cost. However, its capacity is limited, and the quality of the water produced and the maintenance costs do not match those by other distillation processes [9].

1.2.1.2 Multi-Stage Flash Distillation (MSF)

In MSF distillation, water is heated in a series of stages. Typical MSF systems consist of many evaporation chambers, each with successively lower pressures and temperatures that cause flash evaporation of hot brine, followed by condensation on cooling tubes (Figure 1.1B). The steam generated by flashing is condensed in heat exchangers that are cooled by the incoming feed water. This warms up the feed water, reducing the total amount of thermal energy needed [10].

1.2.1.3 Multi-Effect Distillation (ME)

Multi-effect (ME) distillation was the first process used to produce a significant amount of drinking water from sea water. The Multi-effect distillation process takes place in a series of vessels (effects) and uses the principle of reducing the pressure in the various stages in order of their arrangement (Figure 1.1C) [11]. This causes the feed water to undergo boiling in a series

of effects without supplying additional heat after the first effect. Vapor generated in the first effect gives up the heat to the second effect for evaporation and is condensed inside the tubes. This continues for several effects.

Even though thermal desalination processes can treat highly concentrated streams, they require a significant amount of high-grade energy [12]. Also, all evaporation distillation processes can be prone to scaling unless action is taken to prevent it [13]. Scaling is caused by precipitation of salts from the solution because of increased concentration during evaporation of the water or in some cases because of the increased temperature affecting inversely on the solubility of some compounds like calcium carbonate.

Figure 1.1 Schematic diagram of the thermal processes: A) VC, B) MSF and C) ME

1.2.2 Membrane processes

The major commercial membrane processes include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) (Figure 1.2). Two emerging membrane technologies (i.e. forward osmosis and membrane distillation) have been considered for desalination but not commercialized yet on a large scale.

MF membranes have the largest pore size and typically reject large particles and various microorganisms. UF membranes have smaller pores than MF membranes and, therefore, in addition to large particles and microorganisms, they can reject bacteria and soluble macromolecules such as proteins. In NF, organic molecules with molecular weights greater than 200-400 g/mol are rejected. Also, dissolved salts are rejected in the range of 20-98%. Salts which have monovalent anions (e.g. sodium chloride or calcium chloride) have rejections of 20-80%, whereas salts with divalent anions (e.g. magnesium sulfate) have higher rejections of 90-98%. However, MF and UF are not classified as desalination processes as they do not reject the total dissolved solids (TDS). NF is considered as a softening process and can be used as pre-treatment for desalination to reduce the effect of scaling.

Figure 1.2 Range of Nominal Membrane Pore Sizes [14].

1.2.2.1 Reverse Osmosis (RO)

Reverse osmosis was the first membrane process to be widely commercialized [15]. RO membranes are used to separate salts and low molecular weight components from water because they are highly permeable to water and highly impermeable to microorganisms, colloids, salts and organic molecules [16]. In RO, hydraulic pressure is applied in excess of the osmotic pressure of the saline solutions to force the pure water to transfer across the semipermeable membrane. RO has been proven to be efficient in the treatment of streams with concentrations around 35,000 mg/L [17]. At salinities higher than 55,000 mg/L, the hydraulic pressure required

for RO becomes greater than the maximum allowable pressure (65 bars) of membrane modules [18,19].

1.2.2.2 Forward Osmosis (FO)

Forward osmosis is an osmotically driven membrane process that uses the osmotic pressure difference between the feed solution and a highly concentrated solution (called the draw solution) as a driving force for the process. An additional separation step is necessary to extract the product water and recycle the concentrated draw solution to the process (Figure 1.3). The main advantages of using FO are that [20] it operates at low or no hydraulic pressures, it has high rejection of a wide range of contaminants, and it may have a lower membrane fouling propensity than pressure-driven membrane processes, the equipment used is very simple and membrane support is less of a problem (as there is no hydraulic pressure in FO). Also, unlike RO where hydraulic pressure limits its applicability in highly concentrated streams, FO has the ability to treat streams with elevated levels of salinity. However, a draw solution with an osmotic pressure higher than that of the feed solution is a critical aspect in the feasibility of FO.

Figure 1.3 Schematic diagram of the forward osmosis process [21].

1.2.2.3 Membrane Distillation (MD)

Membrane distillation is a thermally driven process, in which water vapor transport occurs through a non-wetted porous hydrophobic membrane. MD is driven by the vapor pressure of the feed solution at the operating temperature. The relatively low dependency of the water vapor pressure on concentration makes MD an option to treat highly concentrated solutions. For instance, the vapor pressure of sodium chloride at a concentration of 5 M is just 20% lower than the vapor pressure of the pure water [22]. Depending on the method of collecting the transported vapor on the permeate side, there are four basic MD configurations (Figure 1.4): direct contact membrane distillation (DCMD), air gap membrane distillation (AGMD), sweeping gas membrane distillation (SGMD) and vacuum membrane distillation (VMD). In DCMD, a cold liquid (usually DI water) in contact with the membrane is used to create the driving force across the membrane. While in AGMD and SGMD, air or inert gas is applied on the permeate side of the membrane to induce the vapor transport through the membrane. The driving force in VMD is maintained by applying vacuum at the permeate side of the membrane. Table 1.1 summarizes the main advantages and disadvantages of the different MD configurations.

Figure 1.4 Illustration of the basic MD configurations: (A) DCMD, (B) AGMD, (C) SGMD and (D) VMD [23].

Table 1.1 main advantages and disadvantages of MD configurations.

MD configuration	Pros	Cons
DCMD	<ul style="list-style-type: none">• Easy and simple	<ul style="list-style-type: none">• High conductive heat loss
AGMD	<ul style="list-style-type: none">• Low conductive heat losses	<ul style="list-style-type: none">• Low permeate flux• Additional resistance to mass transfer is created
SGMD	<ul style="list-style-type: none">• Low conductive heat losses	<ul style="list-style-type: none">• Difficult module design• Difficult heat recovery
VMD	<ul style="list-style-type: none">• High permeate flux	<ul style="list-style-type: none">• Higher possibility of pore wetting

The advantages of using MD over the other mentioned treatment methods are that [24] it works at lower temperature than conventional distillation, it works at lower operating pressures than conventional pressure-driven membrane processes, it has 100% (theoretical) rejection of ions, macromolecules, colloids, cells, and other non-volatiles, and low-grade energy like waste heat or solar energy can be used in MD.

On the other hand, the existence of fouling materials in the feed solution can deteriorate the selectivity of the membrane as they affect the hydrophobicity of the membrane [25]. Typical

produced water contains hydrocarbons and surfactants that cause pore wetting and allows the liquid feed solution to flow directly through the membrane negatively affecting the quality of permeate [26]. Therefore, using MD directly in the treatment of oilfield produced water is impractical unless a pre-treatment step is used to remove the low surface tension contaminants.

In this thesis, a hybrid process consisting of FO and MD processes is proposed as a treatment method for hyper-saline oilfield produced water. In the FO-MD concept, FO acts as a pre-treatment step to protect the MD membrane from the fouling materials that cause pore wetting while MD works as a recovery method for the FO draw solution. The FO-MD combination might be more cost effective for PW treatment if waste or low-grade heat is available nearby the oil extraction facilities.

1.3 Thesis outline

The main objectives of the research described in this thesis are:

1. Estimation of the water shortage in the south of Iraq and how PW can contribute in solving the water scarcity in this region.
2. Investigating the feasibility of treating the hyper-saline PW using an FO-MD hybrid process by studying the performance of each process individually as well.

In order to achieve these objectives, this thesis is divided into chapters as follows:

In **chapter two**, the water available for consumption in the south of Iraq is estimated and compared to the actual water demands in the region. Then the water shortage is calculated from the difference in water supply and demands. Also, the quantity of produced water in the region is estimated and its possible contribution to solving water shortage is determined.

In **chapter three**, FO is studied in the treatment of the hyper-saline produced water. A synthetic produced water is prepared and used as a feed solution for the FO process. A cellulose triacetate

membrane provided by Hydration Technologies Inc. (HTI) is used in this research. In general, the FO draw solutions can be classified based on the separation method of the draw solution into two categories: thermal separation where heat is involved in the process and membrane separation where a membrane is involved. A draw solution from each category is chosen: ammonia-carbon dioxide (thermal separation) and magnesium chloride (membrane separation). Scaling -which is potentially caused by the ions in the produced water- in each draw solution is studied.

In **chapter four**, the direct contact membrane distillation (DCMD) process is studied as a separation method for the FO draw solution using commercial membranes. Three different types of membranes with the same 0.45 μm pore size (i.e. polyvinylidene fluoride (PVDF), polypropylene (PP), and ethylene chloro trifluoro ethylene (ECTFE)) are tested in this research. Also, PP membranes with different pore sizes of 0.45, 0.2, and 0.1 μm are used to study the effect of the pore size of the membrane on the process efficiency. The temperature polarization coefficient (TPC) is used to interpret the difference in performance of the different membranes and how TPC is related to the membranes' properties.

In **chapter five**, a triple layer nanofiber based membrane is fabricated and tested in DCMD for treating highly concentrated solutions. PVDF nanofibers are electrospun on both sides of commercial polyether sulfone (PES) nanofibers. This membrane combines the advantages of the high hydrophobicity of PVDF and the good mechanical strength of PES. The performance of the fabricated membrane is tested for treating of a highly concentrated solution of 5 M NaCl and compared to the performance of the commercial PVDF membrane.

In **chapter six**, the integrated forward osmosis-membrane distillation process is used in treating the hyper-saline produced water. Four different draw solutions (i.e. NaCl, KCl, LiCl, and MgCl_2) with different physical and chemical properties are tested to select the most appropriate draw solution for the FO-MD process. The different behavior of the draw solutions is explained

by the difference in driving forces of the FO and MD processes (i.e. osmotic pressure and vapor pressure respectively).

In **chapter seven**, the reflections of the results obtained in this thesis on the management and treatment of the hyper-saline produced water are presented. This is followed by an outlook in which some recommendations for future work are given.

1.4 References

- [1] K. Lee, J. Neff, *Produced Water: Environmental Risks and Advances in Mitigation Technologies*, Springer Science & Business Media, New York, 2011. doi:10.1007/978-1-4614-0046-2.
- [2] E. Tzimas, A. Georgakaki, G.C. Cortes, S.D. Peteves, *Enhanced Oil Recovery using Carbon Dioxide in the European Energy System*, 2005.
- [3] M. Çakmakce, N. Kayaalp, I. Koyuncu, *Desalination of produced water from oil production fields by membrane processes*, *Desalination*. 222 (2008) 176–186. doi:10.1016/j.desal.2007.01.147.
- [4] C. Murray-Gulde, J.E. Heatley, T. Karanfil, J.H. Rodgers, J.E. Myers, *Performance of a hybrid reverse osmosis-constructed wetland treatment system for brackish oil field produced water*, *Water Res.* 37 (2003) 705–713. doi:10.1016/S0043-1354(02)00353-6.
- [5] H. Partow, J.M. Jaquet, *Iraqi Marshlands Observation System*, (2005) 86. <http://imos.grid.unep.ch/>.
- [6] M.S. Al-Rubaie, M.A. Dixon, T.R. Abbas, *Use of flocculated magnetic separation technology to treat Iraqi oilfield co-produced water for injection purpose*, *Desalin. Water. Treat.* 53 (2015) 2086–2091. doi:10.1080/19443994.2013.860400.
- [7] N.D.F.R. Dos Anjos, *Source Book of Alternative Technologies for Freshwater Augmentation in Latin America and the Caribbean*, 1998. doi:10.1080/07900629849277.
- [8] S. Jenkins, *Water Treatment Handbook*, Degremont 1979. Fifth English Edition. FIRMIN-DIDOT S.A. PARIS, 1186 pp., *Water Res.* 14 (1980) 93. doi:10.1016/0043-1354(80)90053-6.
- [9] A.H. Khan, *Desalination Processes and Multistage Flash Distillation Practice*, 1986.
- [10] H. Cooley, P.H. Gleick, G. Wolff, *Desalination, With A Grain Of Salt A California Perspective*, 2006.
- [11] K.S. Spielgler, A.D.K. Laird, *Principles of Desalination*, 2nd ed., Academic Press, 1980. doi:10.1016/B978-0-12-656701-4.50001-2.
- [12] J.E. Miller, *Review of water resources and desalination techniques*, *Sand Rep.* (2003) 1 – 54. doi:sand 2003-0800.
- [13] S. Vigneswaran, ed., *Waste Water Treatment Technologies - Volume III, Encyclopedia of Life Support Systems (EOLSS)*, 2009.
- [14] D.W. Green, R.H. Perry, *Perry's chemical engineers' handbook*, 8th ed., McGraw-hill, New York, 2008.
- [15] P. Ferguson, *The first decade of commercial reverse osmosis desalting 1968–1978*, *Desalination*. (1980). doi:10.1016/S0011-9164(00)86001-4.
- [16] E.A. Mason, H.K. Lonsdale, *Statistical-mechanical theory of membrane transport*, *J. Memb. Sci.* 51 (1990) 1–81. doi:10.1016/S0376-7388(00)80894-7.
- [17] C. Fritzmann, J. Löwenberg, T. Wintgens, T. Melin, *State-of-the-art of reverse osmosis desalination*, *Desalination*. 216 (2007) 1–76. doi:10.1016/j.desal.2006.12.009.
- [18] S.H. Kim, S.H. Lee, J.S. Yoon, S.Y. Moon, C.H. Yoon, *Pilot plant demonstration of energy reduction for RO seawater desalination through a recovery increase*, *Desalination*. 203 (2007) 153–159. doi:10.1016/j.desal.2006.01.035.
- [19] L.F. Greenlee, D.F. Lawler, B.D. Freeman, B. Marrot, P. Moulin, *Reverse osmosis desalination: Water sources, technology, and today's challenges*, *Water Res.* 43 (2009) 2317–2348. doi:10.1016/j.watres.2009.03.010.
- [20] S. Zhao, L. Zou, C.Y. Tang, D. Mulcahy, *Recent developments in forward osmosis : Opportunities and challenges*, *J. Memb. Sci.* 396 (2012) 1–21. doi:10.1016/j.memsci.2011.12.023.
- [21] J.R. McCutcheon, R.L. McGinnis, M. Elimelech, *A novel ammonia-carbon dioxide forward (direct) osmosis desalination process*, *Desalination*. 174 (2005) 1–11. doi:10.1016/j.desal.2004.11.002.

- [22] Y. Guan, J. Li, F. Cheng, J. Zhao, X. Wang, Influence of salt concentration on DCMD performance for treatment of highly concentrated NaCl, KCl, MgCl₂ and MgSO₄ solutions, *Desalination*. 355 (2015) 110–117. doi:10.1016/j.desal.2014.10.005.
- [23] P. Wang, T. Chung, Recent advances in membrane distillation processes : Membrane development , configuration design and application exploring, *J. Memb. Sci.* 474 (2015) 39–56. doi:10.1016/j.memsci.2014.09.016.
- [24] K.W. Lawson, D.R. Lloyd, Membrane distillation, *J. Memb. Sci.* 124 (1997) 1–25. doi:10.1016/S0376-7388(96)00236-0.
- [25] M. Gryta, Fouling in direct contact membrane distillation process, *J. Memb. Sci.* 325 (2008) 383–394. doi:10.1016/j.memsci.2008.08.001.
- [26] D.L. Shaffer, L.H. Arias Chavez, M. Ben-Sasson, S. Romero-Vargas Castrillón, N.Y. Yip, M. Elimelech, Desalination and reuse of high-salinity shale gas produced water: Drivers, technologies, and future directions, *Environ. Sci. Technol.* 47 (2013) 9569–9583. doi:10.1021/es401966e.

2

Evaluation of water demand and supply in the south of Iraq

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Abstract

This chapter presents results from the first study that focuses on water resources availability and demand for different purposes in the four oil-rich provinces of southern Iraq. The region accounts for 23% of the surface area and 18% of the country's population, but holds 88% of its oil. A water shortage of 430 Mm³/year for 2010 is estimated for this region where irrigation accounts for 81% of the total water demand. Dhi Qar is the largest agricultural producer and water consumer with Al Basrah and Al Muthanna having the highest water shortages among the four provinces. The interrelationship of energy-water production and utilization is discussed and the annual water balance for irrigation, industrial, domestic and livestock usage in the different provinces determined. On these basis, recommendations are made for treating and utilizing the steadily increasing amounts of water produced from the oilfields to supplement the other sustainable water resources in that region.

2.1 Introduction

Water self-sufficiency is essential to ensure food security and so it is one of the most important pillars for a developed and sustainable economy anywhere in the world. This is especially true in arid and semi-arid regions that are strongly dependent on water resources controlled from beyond their international borders, which is the case in Iraq.

Since ancient times the main water supply in Iraq has been provided by the Rivers Tigris and the Euphrates. These two rivers gave Iraq the Greek name Mesopotamia (the land between two rivers). The headwaters of the River Tigris and River Euphrates are in the Turkish mountains meeting in the Shatt-el-Arab river at the southern tip of Iraq, before finally discharging into the Arabian (Persian) Gulf. About 98% of the water consumption in Iraq is dependent on these two rivers and their branches [1].

Recently, Iraq has passed through exceptionally long, dry and warm seasons with frequent dust storms and the lowest river levels in centuries. Water inflow and quality monitored through 2014, have significantly reduced and salinity in Shatt-el-Arab river has deteriorated to alarming levels [2]. Several studies discussed in details the causes and the size of major upstream developments along the Tigris and Euphrates leading to the present situation [3-7]. Other causes include poor water management and global warming. Intrusion from the Arabian (Persian) Gulf has increased the salt content of the rivers and groundwater and brought unprecedented water crises deep into the southern region of Iraq. In this chapter, we will quantify the shortages by analyzing the water supply and demand in the south of Iraq focusing on the existing and outlook of potential water sources and use.

The southern region of Iraq comprises four provinces: Al Basrah, Al Muthanna, Dhi Qar, and Maysan (Figure 2.1). These four provinces cover 23 % of the total area of the country, provide homes for 18% of Iraq's population (i.e. 5.7 million inhabitants) while holding over 80% of

Iraq's petroleum wealth [8]. Al Basrah, with its harbor on the Arabian Gulf and its oil fields, is on the verge of becoming an international hub of industrial, agricultural, transport, construction and commercial activities. With this comes the need for alternative fresh water supply in large quantities in an area that is confronted with a significant and persistent decline in water quantity and quality. This situation will become worse by an anticipated threefold increase in oil production by the end of this decade, rapid industrialization, and growth in irrigation to secure economic development and food supply for a high-rate growing population demanding a better quality life.

The main objective of this study is to assert the best estimates for the water demand and supply in the south of Iraq for the various purposes in the present time and in the future. We argue here that the current supply and demand can be partially balanced in that region by available strategic water resources that are not yet utilized and through the rational use of water from recycling/treatment of these unexploited water resources, specially produced water (PW). We justify this by showing that the region has a large footprint from the demand side, with so far only a single source from the supply side, and that supplying sufficient quantity and quality PW is a good and a manageable option. This is shown by calculating demand and supply for irrigation, industry, domestic and livestock purposes to determine the water balance and water shortages, based on information from the scientific literature, data from international and national organizations and institutes, and sometimes local information sources. This is the first study that quantifies the water demand and supply for the south of Iraq and proposes possible solutions to the increasing water scarcity in the region.

Figure 2.1 Map of Iraq showing the four southern provinces comprising the study area of this thesis (FAO 2008).

2.2 Data and methods

Water demand and supply were estimated for 2010 as a baseline for the calculations. To determine the water needed for irrigation in south Iraq, we first need to specify the most important crops (we only considered the crops with the production of more than 1000 ton/year) that are cultivated there. For this, we rely on governmental data which are accessible from the Central Organization of Statistics and Information Technology (COSIT). The main crops in the south of Iraq in 2010 were (in descending order of production ton/year): tomato, wheat, alfalfa, barley, date, okra, sugarcane, maize, lettuce, green beans, eggplant, onion, garlic, rice, turnip, carrot. These crops represent 99.9% of the total crops produced in the south of Iraq [9]. Mekonnen & Hoekstra (2011) [10] calculated the blue water footprint (BWF, which is defined by Hoekstra *et al.* (2011) as the use of blue water resources - surface and groundwater - along the supply chain of a product) for the various crops at national and subnational levels for the period from 1996 to 2005 [11]. We used the BWF data of the Iraqi provinces to estimate the irrigation water needed in the south of Iraq for the crops produced in 2010. To estimate the water demand for irrigation, we divided the BWF by the irrigation efficiency (the fraction of water diverted from the water source that is actually available for crop evapotranspiration) of Iraq which was obtained from [12]. Since there are no BWF data available for dates, sugarcane and alfalfa for Iraq, we used the standard estimates of Bhat *et al.* (2012) [13] and Morton (1987) [14] for dates and Brouwer and Heibloem (1986) [15] for sugarcane and alfalfa to calculate irrigation water needs.

To determine the water demand for industrial purposes, we first identified the industrial plants for the four provinces in the south of Iraq. We used the official data (which are published on the websites of Iraqi Ministry of Industry and Minerals and its directorates) for the production of the various industrial plants. Information about oil production from the southern oil fields

were obtained from the South Oil Company SOC and Maysan Oil Company MOC official websites. Water consumption estimates have been made based on the standard estimates from various sources [16-20], for the petrochemical industries, data was taken from [21].

The amount of water supplied in the south of Iraq for domestic purposes was obtained from COSIT. The domestic water demands were calculated based on the standard of Iraq for daily consumption of domestic water which is 392 L/day/capita [22].

Detailed data for the various species of livestock in Iraq are available from COSIT for 2008 for all eighteen Iraqi provinces [23]. Although we considered 2010 as a baseline for our estimations, we used the provincial proportion of livestock from the COSIT data for 2008 and the overall FAO 2010 data to estimate the livestock for the southern province in Iraq. Water consumption data – both drinking and servicing - per animal were obtained from [24].

Information on water supply was obtained from the water resources authorities in the relevant provinces [25-28]. Part of the total run-off of a river (the so-called environmental flow) should be kept to sustain freshwater and estuarine ecosystems. Smakhtin *et al.* (2004) estimated the environmental flow requirements for the rivers Tigris and the Euphrates at 26% of the total runoff [29]. Thus, the utilizable water is calculated as the total run-off of the river in a province minus the environmental water requirements. We estimated water demands in Iraq for the period from 2005-2020 based on FAO data for the period from 1990-2000 using linear extrapolation. Water availability information for the period from 1990 to 2020 was obtained from [30].

2.3 Water demand

2.3.1 Irrigation

Agriculture is a primary reason for water stress in the entire Arab region in general and in Iraq in particular [31]. Water needs for growing crops depend mainly on crop type and climate

conditions. Such water can be supplied to the crops by rainfall, irrigation, or a combination of the two. Water supply for agriculture in the south of Iraq relies mainly on surface water, Figure 2.2 shows the distribution of water resources for agricultural water demand. It shows that surface water provides about 85 % of the water consumption by agriculture. Moreover, rainfall is not reliable for irrigation, since the majority of the country is arid or semi-arid. Precipitation in the south of Iraq is in the order of just 100-200 mm per annum, and is also highly irregular [32].

Figure 2.2 Sources of irrigation water in the southern provinces in Iraq [33].

We estimated the detailed water demands for irrigation of various crops that are grown in the four provinces in the south of Iraq. We can see from Table 2.1 that barley, wheat, and date consume most water in this region, about 89% of the total water required for irrigation. It was estimated that irrigation needed about 6017 Mm³/year of surface and groundwater in the south of Iraq in 2010.

Table 2.1 Agricultural production and water demands for irrigation in the south of Iraq.

	Al Basrah		Al Muthanna		Dhi Qar		Maysan		Total	
	Production (ton/year) ^a	Water Needs (Mm ³ /year)	Production (ton/year) ^a	Water Needs (Mm ³ /year)	Production (ton/year) ^a	Water Needs (Mm ³ /year)	Production (ton/year) ^a	Water Needs (Mm ³ /year)	Production (ton/year)	Water Needs (Mm ³ /year)
Alfalfa	4144	7	29358	26	148747	43	16728	14	198977	89
Barley	3927	41	30987	368	89694	1065	66864	674	191472	2148
Carrot	61	0.111	0	0	1110	2	88	0.2	1259	2
Date	54513	608	19513	318	32674	505	7580	83	114280	1514
Eggplant	298	0.23	842	0.64	9660	7	1532	1	12332	9
Garlic	81	0.10	0	0.00	6300	8	63	0.1	6444	8
Green beans	133	0.16	505	0.59	3800	4	8400	9	12838	14
Lettuce	252	0.32	0	0.00	8568	10	4636	5	13456	16
Maize	0	-	11	0.05	2666	13	16016	74	18693	87
Okra	22085	0.16	3613	0.59	15843	4	9368	9	50909	14
Onion	0	-	38	0.05	10328	12	1358	2	11724	14
Rice	0	-	4150	60	776	12	170	3	5096	74
Sugarcane	0	-	0	-	0	-	29350	60	29350	60
Tomato	360888	274	11589	8	12502	9	6681	4	391660	295
Turnip	3	0.01	91	0.17	1183	2	564	1	1841	3
Wheat	16900	138	26500	215	92000	730	81400	587	216800	1670
Total	463285	1068	127197	997	435851	2426	250798	1526	1526	6017

^a [23]

2.3.2 Industry

The geographical location directly on waterways and the Arabian Gulf and the availability of raw materials make the south of Iraq a good place for many industrial activities. The southern region of Iraq contains some of the key industrial plants in the country such as iron and steel, cement, fertilizer, paper, petrochemicals, and sugar factories. Furthermore, in 2010 more than 80% of Iraqi oil was produced in this region and four oil refineries are located there. Currently, some of these industrial plants are non-functioning due to power shortages, outdated equipment, and acts of sabotage after the invasion of Iraq in 2003. In Table 2.2 we specified the industrial plants in the south of Iraq, showing that Al Basrah accounts for the biggest portion of the industrial plants and consequently consumes most of the water which is required for industry. A lumped amount of 616 Mm³/year of water is required to supply the industrial activities in the southern region of Iraq (see Table 2.2). This amount is anticipated to increase in the next years, especially when the non-functioning plants return to work and new factories are built as planned by the Iraqi government.

Table 2.2 The key industrial plants in the south of Iraq and their water demands.

Province	The industrial plant	Production	Water demands (Mm ³ /year)
Al Basrah	The state company of fertilizers-Basrah	1000 ton/day	28
	The State Company for Petrochemical Industries (Ethylene)	79200 ton/year	110
	The State Company for Petrochemical Industries (HDPDE)	16650 ton/year	10
	The State Company for Petrochemical Industries (LDPE)	33300 ton/year	26
	The State Company for Petrochemical Industries (Chlorine)	9500 ton/year	3
	The State Company for Petrochemical Industries (Caustic soda)	19000 ton/year	-
	The State Company for Petrochemical Industries (MVC & PVC)	0 ton/year	-
	Oil	2150000 bbl/day	187
	Refinery	140000 bbl/day	90
	Paper	0 ton /year	-
	State company for iron and steel	440000 ton/year	57
	State company for iron and steel (pipes)	200000 ton/year	26
	Um Qasr cement plant (grilling of clinker)	360000 ton/year	-
	Alhartha thermal power plant	130 MW	1
	Alnajibiyah thermal power plant	150 MW	1
	Khor Al-Zubair gas station	380 MW	-
	Alshiaibah gas station	73 MW	-
	Petrochemical gas station	80 MW	-
	Al Fao salt recovery plant	0 ton/year	-
Total Al Basrah			539
Al Muthanna	Al Muthanna cement plant (dry method)	241860 ton/year	-
	Samawa (south) cement plant (wet method)	365000 ton /year	-
	Salt recovery plant	137000 ton /year	Rain and groundwater
	Oil	0 bbl/year	-
	Refineries	25000 bbl/day	16
	Samawa gas station	60 MW	-
Total Al Muthanna			16
Dhi Qar	Nasiriyah thermal power station	500 MW	3
	Refinery	30000 bbl/day	19
	Oil	35000bbl/day	3
Total Dhi Qar			25
Maysan	Sugar	0 ton/year	-
	Paper	0 ton /year	-
	Plastic	20 ton/year	-
	vegetable oils	35 ton/week	-
	refinery	30000bbl/day	19
	Oil	200000 bbl/day	17
	Bazergan gas station	80 MW	-
Total Maysan			36
Total			616.13

2.3.3 Domestic

Domestic water demand includes the use for drinking, preparing food, bathing, washing clothes and dishes, air-conditioning, gardening and other household purposes. Domestic water in the south of Iraq is mainly supplied by the Tigris and its tributaries except in Al Muthanna where the Euphrates supplies it. It appears that, as shown in Table 2.3, most of the population does not have access to safe drinking water where they use either untreated water or insufficient amount of water (below the standard limit of 392 L/day/capita [22]).

Table 2.3 Domestic water supply and demands.

Province	Population	Amount of water provided for domestic use (Mm ³ /year) ^a	Amount of water required for domestic use (Mm ³ /year)
Al Basrah	2409391	280	345
Al Muthanna	684367	77	98
Dhi Qar	1745800	160	250
Maysan	924300	150	132
Total	5763858	667	825

2.3.4 Livestock

Water is essential for livestock farming and breeding. About 15% of the total livestock in Iraq is in the southern region of the country. To assess this issue quantitatively, we estimated the water required for livestock farming and breeding. This water is made up of drinking water and service water (it is the water that is used to clean the farmyard, wash the animals and other necessary services). Detailed data for the various species of livestock in Iraq are available from COSIT for 2008 for all eighteen Iraqi provinces. Table 2.4 shows that Dhi Qar has the largest number of livestock and consumes about 38% of the total water required for livestock. Our calculations revealed that a quantity of about 12.8 Mm³/year is required to maintain the current livestock in the south of Iraq in an acceptably healthy condition. In general, this amount is negligible compared to the demand for the other purposes, especially irrigation. Nevertheless, the percentage of farmers that were forced to sell their livestock due to water scarcity in Al

Basrah and Maysan was significantly above the figure for Iraq as a whole. In Al Muthanna and Dhi Qar, most of the livestock faced water-related health problems like sickness and even death (see Figure 2.3).

Table 2.4 Number of animals and corresponding water needs in the south of Iraq.

	Al Basrah		Al Muthanna		Dhi Qar		Maysan		Total	
	Number of animals	Water Needs (Mm ³ /year)	Number of animals	Water Needs (Mm ³ /year)	Number of animals	Water Needs (Mm ³ /year)	Number of animals	Water Needs (Mm ³ /year)	Number of animals	Water Needs (Mm ³ /year)
Buffalo	59590	1.5	7080	0.2	51035	1.3	25075	0.63	142780	3.6
Cows	33127	0.5	26817	0.4	105692	1.5	82030	1.14	247666	3.4
Goats	9114	0.03	44051	0.14	74431	0.23	25823	0.08	153419	0.5
poultry	138000	0.01	2403000	0.24	407000	0.04	252000	0.02	3200000	0.3
Sheep	56000	0.24	280000	1.21	400000	1.72	400000	1.72	1136000	5
Total	295831	2.23	2760948	2.13	1038158	4.74	784928	3.59	4879865	12.8

Figure 2.3 Effect of water scarcity on livestock in Iraq [31].

2.4 Water supply and shortage

The key source of water supply in the south of Iraq is surface water from the Tigris, the Euphrates, and their tributaries. More than 90% of the marshes in the south of Iraq was drained in the 1990s [34]. Groundwater has limited use in Iraq because it is pumped at rates faster than

it is being replenished by rainfall. However, in the regions that are far from the rivers, groundwater resources are of more significance.

Agreed water quota from the Tigris and the Euphrates are used to distribute water among the various provinces. The southern provinces take the least amount of water due to their downstream location as well as due to the presence of several dams which are situated upstream and controlled by the upstream provinces.

2.4.1 Al Basrah

Al Basrah is the economic center of Iraq with the largest oil fields, Iraq's main harbors, and major industrial plants like oil, petrochemical, iron, steel, fertilizers, and paper are located here. It produces more than three-quarters of the oil produced in the country. In terms of population, it is the third province in Iraq with 2.4 million inhabitants in 2009. However, Al Basrah has the worst water situation in Iraq in terms of quantity and quality. It is the last province in the downstream area of the Tigris, and the Euphrates which means it receives all the irrigation return flows from the upstream provinces and most of the water is used by the upstream cities. Water quota of Al Basrah is 50 m³/s which is provided mainly by the River Tigris. It has been reported that the quality of larger parts of Shatt-el-Arab River is not suitable for domestic and irrigation uses [35]. Freshwater supply to Al Basrah is below the actual needs: we found that an amount of about 790 Mm³/year was estimated as water shortage in 2010 in Al Basrah (Table 2.5). Currently, the people of Al Basrah either do not get enough water or they use poor quality water like that from Shatt-el-Arab river for the domestic and irrigation purposes. Agricultural lands, especially in the south of Al Basrah, have decreased due to the water shortage in terms of quality and quantity [35].

2.4.2 Al Muthanna

Al Muthanna lies on the Euphrates river and uses its water as the main source for various purposes. The province has the lowest population, the smallest agricultural and industrial sector and the lowest water demand for livestock of the four provinces. Water quota of the province (which is $16.8 \text{ m}^3/\text{s}$) is also the least among the southern provinces. Poor quality of the Euphrates is recorded starting from Al Muthanna to its confluence with the Tigris at Al Qurna [36]. It was found that water supply to Al Muthanna province is less than half of its water demands. This water shortage has affected the agriculture to a great extent. According to the water resources department in Al Muthanna, about 30 % of the agricultural lands is at stake if the province water quota does not increase to a value of $28 \text{ m}^3/\text{s}$.

2.4.3 Dhi Qar

The province of Dhi Qar has the highest water quota among the other provinces because it has the highest agricultural area. Dhi Qar relied on the Euphrates water as the main source for water supply until the mid-1970s and now depends on the Al Gharraf River, a side branch of the Tigris [37]. This is due to the low flow rate and the increasing salinity of the Euphrates which reached $5,500 \text{ mg/L}$ in 2002 in Dhi Qar [36]. The reasons for the increased salinity are irrigation return flows, the decrease in discharge of the river, and passage of the river through the salty area in Al Muthanna. Water quota of Dhi Qar from Al Gharraf River is $140 \text{ m}^3/\text{s}$ which is regulated by Al Kut Barrage.

2.4.4 Maysan

After the disastrous drainage of marshes in the 1990s, Maysan has lost most of its agricultural lands and the main dependence of water supply became on the Tigris river. Since it is the last province in the stream of the Tigris before meeting the Euphrates in Al Qurna (100 km

Southward), Maysan receives poor quality water with low discharge [37]. Water quota for the province of Maysan as specified by the water resources authorities is 95 m³/s. Our calculation shows that this amount is sufficient for the current water demands (Table 2.5). However, water demands will increase when the non-functioning industrial plants in Maysan like sugar, paper, and plastic are back to work as planned for the next years. Moreover, part of Maysan water supply goes to the marshes refurbishment project, but we have no information about the water quantities used for this purpose.

Water demands and supply results in the south of Iraq are summarized in Table 2.5, overall water deficit estimated is about 430 Mm³/year, this amount can be balanced by using proper water management and alternative water resources.

Table 2.5 Total water supply and demands for the different purposes.

	Water supply Mm ³ /year	Utilizable water Mm ³ /year	Total demands Mm ³ /year	The difference Mm ³ /year
Al Basrah	1577	1167	1954	-787
Al Muthanna	530	392	1114	-722
Dhi Qar	4415	3267	2707	560
Maysan	2996	2217	1698	519
Total	9518	7043	7473	-430

2.5 Water management solutions

In this section, we introduce sustainable solutions which might help to improve the water situation in the south of Iraq. Based on our findings, we can discern that water problems in the south of Iraq are not just a matter of quantity but also of the management of water resources in this region. We make the recommendations outlined below:

1. Treat oilfield PW and use it for one or more of many useful purposes such as industrial applications, irrigation, rangeland restoration, cattle and other animal consumption, and even domestic water use for washing, air-conditioning, gardening, and even for drinking. Waisi *et al.* (2015) estimated an amount of PW of 54 Mm³/year in the south of Iraq, most

of this amount is currently either reinjected into the ground or put in evaporation ponds [38]. This amount is anticipated to increase by the end of this decade as oil production is planned to reach three times its current production and due to the fact that PW quantities increase with the age of a given oilfield.

2. Desalination of the Arabian Gulf water can be a significant and stable water source for Al Basrah which can be used for various purposes. A seawater desalination plant is to be constructed in the south of Iraq to provide the required water for injection in the oil industry [20]. This option is not practical for the other provinces because of the long distance.
3. Reclaim municipal wastewater using efficient modern technologies such as Membrane bioreactors (MBR) and moving bed bioreactors (MBBR) followed by a disinfection step (UV or chemical disinfection by peracetic acid or chlorine dioxide).
4. Consider groundwater as an additional water resource, because 7 billion m³ of groundwater was available for extraction in 2010 in Iraq [39].
5. Rainwater harvesting is one of the methods that can ensure availability of water for winter crops. By this technique, the excess rainwater (runoff) is stored in small reservoirs or dams of different sizes to be supplied later when required to satisfy the crops requirements [40].
6. Increase efforts to the marshes refreshment to enhance the agricultural activities and livestock farming in the marshlands.
7. Consider more efficient irrigation techniques like drip irrigation and sprinkle irrigation instead of surface irrigation (flood irrigation) which is the main method that is currently used in the south of Iraq. Surface irrigation consumes a huge amount of water and

produces high salinity water -as a result of high evaporation rates- which drains back to the surface water as return flow.

8. Consider water allocation rule between the Euphrates-Tigris river basin countries. Sakamoto *et al.* (2013) investigated the application of a game theoretical approach to water resources allocation for agricultural purposes in the Euphrates-Tigris river basin [41].

The possible solutions to solve water scarcity will be different for the various provinces as shown in Table 2.6. These solutions depend on the location of the province, the available resources in this province like oilfield PW and sea water, and the need due to water shortage. Here, we describe how we constructed Table 2.6. For instance, PW is a promising solution for Al Basrah and Maysan where the oil is extracted, while for Al Muthanna and Dhi Qar it is not the best choice because of the large distance from the giant oilfield in Al Basrah of 300 km and 200 km, respectively. Desalination of seawater is a possible solution for Al Basra because it is the closest city in Iraq to the sea. A giant Common Seawater Supply Facility (CSSF) to treat seawater from the Arabian Gulf is planned to be built in 2017 to provide the required water for the oilfields in Al Basra [38]. The anticipated capacity of the CSSF is 10-12 Mbbl/d. This solution has the benefits of providing a secure water supply, independent of future water availability; it also reduces stress on freshwater resources, freeing them for other uses [20]. Groundwater could be an important resource in the desert of Al Muthanna, Mohammed (2008) reported that the renewable reserve of the groundwater in the desert of Al Muthanna is 250 Mm³/year with a total dissolved solids (TDS) of 2000 mg/L in the south and west of the desert which is suitable for irrigation and livestock [42]. Although rainfall is of low value in the southern region, rainwater harvesting in the desert of Al Muthanna could contribute to the water resources in the region. Reuse of municipal wastewater has most potential in Al Muthanna where currently no central wastewater treatment plant is available. The daily amount of 10,000

m³ municipal wastewater in Al Muthanna [9] can be used for irrigation purposes instead of discharging it to the river or directing it to evaporation ponds. This will also better serve the environment. Since in the other provinces, where central wastewater treatment plants do exist, the effluent is also discharged to the river, we consider it as a potential solution for all provinces.

Table 2.6 The possible options for the alternative water resources for the four provinces in the south of Iraq.

	Groundwater	Arabian Gulf	Marshes	Water harvesting	Produced water	Wastewater
Al Basrah		✓			✓	✓
Al Muthanna	✓			✓		✓
Dhi Qar	✓		✓	✓		✓
Maysan			✓		✓	✓

2.6 Produced water as a potential solution to water scarcity in Iraq

Production of oil and gas is always accompanied by large amounts of effluent water, called "produced water". These huge quantities of water can be used (if treated efficiently and economically) for many useful purposes like industrial applications, irrigation, cattle and animal consumption, and domestic water use for washing, air-cooling, gardening, and even for drinking. PW is most often considered as waste water, but industrial companies and policy makers have started to see it as a sustainable source of water. However, the handling of this water requires special attention. The treatment of PW has the potential to produce a valuable product rather than waste. Selection of PW treatment options is a challenging problem that is steered by the overall treatment objective, the quantity, and quality of the PW. Besides the oil constituents, one of the most important concerns of PW is its high salinity [43]. The salt content of the PW in the south of Iraq reaches elevated levels of more than 240 g/L [44]. Advanced technologies are necessary to treat the PW to the desired water quality levels. Recent studies showed that some technologies can handle such hyper-saline PW like forward osmosis and membrane distillation [45].

2.7 Water-energy nexus

The water need for energy production will be increasingly important. About 15% of the global water use in 2010 is related to energy production [20]. Water availability can be the limiting factor for electric power in Iraq.

In the south of Iraq, energy is produced either by thermal power plants or gas power plants. The thermal power plant consumes water explicitly to generate steam which is used to drive a turbine generating the electricity, while in the gas power plant fuel is used to heat up gasses which are driving the turbines. In the gas power plant, water is implicitly included in the fuel which consumes water in the different stages of extraction and refining. At the same time, energy is required to produce freshwater from the various sources like surface water, groundwater, and wastewater.

During the production life of an oil well, this interrelation manifests strongly in the lifecycle of PW in production, re-injection or dumping as waste water, recycling, purification and subsequent injection for enhancing oil and gas recovery. Energy in return is required to deal with this water reuse whether in the energy industry or the other sectors.

Planners have to take into account this nexus when planning for energy production or water treatment. To produce one kWh, 0.757 m³ of fresh water is needed [18], while to provide 1 m³ of fresh water from surface water resources like rivers, 0.5 kWh is needed [46]. Accordingly, it is very important to think about alternative water resources which can be used for various purposes using less energy consuming techniques or renewable energy resources.

2.8 Discussion

Water consumption by the agricultural sector in the south of Iraq accounts for about 81% of the total water consumption, which is larger than the average figure of the country of about 72% (calculated from Table 2.7). This result is compatible with the fact that the southern region contains the majority of the agricultural land in Iraq. While industry consumes about 20% of the total water demands in Iraq, it accounts for 8% in the southern provinces. This is most likely because the majority of the industrial plants are situated in Baghdad.

Water demands in Dhi Qar occupy about 40% of the total water demands in the south of Iraq, as shown in Figure 2.4. This since Dhi Qar has the highest agricultural production among the four provinces. Also, our estimations showed that more than 80% of the industrial activities in the south are currently based in Al Basrah. These findings can be used in the management of available freshwater resources, as discussed previously.

Table 2.7 Past, current, and future water demands and availability in Iraq.

	1990	1995	2000	2005	2010	2015	2020
Total water demand							
billion m ³ /year ^a	42.8	54.4	66	77.6	89.2	100.8	112.4
Domestic demand							
billion m ³ /year ^a	1.28	2.79	4.3	5.81	7.32	8.83	10.34
Industrial demand							
billion m ³ /year ^a	2.14	5.92	9.7	13.48	17.26	21.04	24.82
Irrigation							
billion m ³ /year ^a	39.38	45.69	52	58.31	64.62	70.93	77.24
Water availability							
m ³ /year/capita ^b	6029		3100		2400		1900

^a 1990-2000 estimations from [47], 2005-2020 our estimations using linear extrapolation

^b [30]

The water situation in Iraq is anticipated to worsen in the next years because water demands in the country are going to increase as shown in Table 2.7, whereas water supply is going to decrease due to upstream damming of the Tigris and the Euphrates, and climate change.

Figure 2.4 Water consumption by the various purposes and different provinces in the south of Iraq (Note the log scale).

Population and industrial growth mainly drives the increase in water demand. The water needed for irrigation may also increase due to climate change besides the effect of population growth, however, in Iraq the effect of population growth on water demand will be much larger than that of climate change [48].

Despite the current and future water shortage in Iraq, the annual water availability per capita in Iraq is the highest among the other Arabian countries [30]. However, international organizations reported that if the current water management situation continues, the Tigris and the Euphrates will dry up by 2040 [49]. So it is critical to begin immediately with the utilization of alternative water resources and new technologies as suggested in previous sections, to guarantee a secure water demand-supply balance through a rational use of all the available water resources.

2.9 Conclusions

Water shortage in the south of Iraq is a serious issue that is only expected to become the worst in the future because of population growth, increased abstractions upstream, poor management of the available water resources and climate change. The utilizable water for consumption in the south of Iraq was estimated at 7043 Mm³/year compared to 7473 Mm³/year for water demand. A current water deficit was calculated of 430 Mm³/year for the four southern provinces. Irrigation claims about 81% of the consumed water in the south of Iraq where the province Dhi Qar is the main consumer. The worst water situation was reported in Al Muthanna and Al Basrah, while the other two provinces of the southern region (Maysan and Dhi Qar) suffer from poor quality water rather than insufficient water quantity. This can be dealt with by application of modern water treatment techniques.

There are some potential solutions that can be applied to overcome water scarcity in the south of Iraq like the treatment of oilfield PW and municipal waste water, desalination of Arabian Gulf water, groundwater abstraction, rainwater harvesting, and using modern irrigation techniques. There is no unique solution for this problem but considering a combination of various potential solutions will lead to sustainable use of water. PW can be an important water resource in the region, modern technologies that are more efficient and consume less energy need to be applied to provide clean water that can be used for irrigation and industrial consumption and even other purposes. The water-energy nexus should be taken into account when dealing with water and energy management issues.

2.10 References

- [1] A. H. Al Bomola, 2011 Temporal And Spatial Changes In Water Quality Of The Euphrates River - Iraq. Ph.D. Thesis, Division of Water Resources Engineering Department of Building and Environmental Technology, Lund University.
- [2] D. A. Abdullah, I. Masih, P. Vander Zag, U. F. A. Karim, I. Popescu, Q. Al Suhail, 2015 The Shatt al Arab System under Escalating Pressure: a preliminary exploration of the issues and options for mitigation. *International Journal of River Basin Management*, 13 (2015) 215-227.
- [3] A. Tilmant, J. Lettany, R. Kelman, Hydrological risk assessment in the Euphrates-Tigris river basin: A stochastic dual dynamic programming approach. *Water International* **32** (2007) 294-309.
- [4] N. Shamout, G. Lahn, 2015 The Euphrates in Crisis Channels of Cooperation for a Threatened River. Energy, Environment and Resources research paper, Chatham House, UK,
- [5] C. Jones, M. Sultan, E. Yan, A. Milewski, M. Hussein, A. Al-Dousari, S. Al-Kaisy, R. Becker, Hydrologic impacts of engineering projects on the Tigris–Euphrates system and its marshlands. *Journal of Hydrology* 353 (2008) 59– 75.
- [6] I. H. Olcay Ünver, Southeastern Anatolia Project (GAP). *International Journal of Water Resources Development* 13 (1997) 453-484.
- [7] I. Yuksel, Southeastern Anatolia Project (GAP) For Irrigation and Hydroelectric Power in Turkey. *Energy Exploration & Exploitation* 24 (2006) 361-370.
- [8] Ministry of Oil 2013. <http://www.oil.gov.iq/> (accessed July 25, 2013).
- [9] COSIT 2010 Environmental Survey in Iraq 2010 (Water- Sewage- Municipality services) June 2011. www.cosit.gov.iq/english/pdf/2011/env2010_E.pdf.
- [10] M. M. Mekonnen, A. Y. Hoekstra, The green, blue and gray water footprint of crops and derived crop. *Hydrology and Earth System Sciences* 15 (2011) 1577–1600.
- [11] A. Y. Hoekstra, A. K. Chapagain, M. M. Mekonnen, 2011 The water footprint assessment manual: Setting the global standard. London: Earthscan.
- [12] J. Rohwer, D. Gerten, W. Lucht, 2007 Development of functional types of irrigation for improved global crop modeling. Potsdam: Potsdam Institute for Climate Impact Research.
- [13] N. R. Bhat, V. S. Lekha, M. K. Suleiman, B. Thomas, S. I. Ali, P. George, L. Al-Mulla, Estimation of Water Requirements for Young Date Palms Under Arid Climatic Conditions of Kuwait. *World Journal of Agricultural Sciences* 8 (2012) 448-452.
- [14] J. F. Morton, 1987 Fruits of warm climates. Miami: Julia F. Morton.
- [15] C. Brouwer, & M. Heibloem, 1986 Irrigation Water Management: Irrigation Water Needs, Training manual no. 3. Rome: FAO.
- [16] L. E. Otts, 1963 Water requirements of the petroleum refining industry. Washington: United States Government Printing Office.
- [17] F. B. Walling, L. E. Otts, 1967 Water Requirements of the Iron and Steel Industry. Washington: United States Government Printing Office.
- [18] EPRI 2002 Water & Sustainability (Volume 3): U.S. Water Consumption for Power Production—The Next Half Century. California: Palo Alto.
- [19] European Commission 2010 Reference Document on Best Available Techniques in Cement, Lime and Magnesium Oxide Manufacturing Industries.

- [20] IEA 2012 Iraq Energy Outlook- World energy, special report Paris: Corlet.
- [21] MoEnv & MoInd, Ministry of Environment and Ministry of Industry 2008 The environmental situation of the chemical industries in Iraq. Ministry of Environment.
- [22] UN 2013 Water in Iraq Factsheet. UN Iraq.
- [23] Y. Al-Fahad, T. Abbas, 2011 Agricultural statistical atlas. Roadmap for Agricultural Development (green economy). COSIT, Baghdad (in Arabic).
- [24] A. K. Chapagain, A. Y. Hoekstra, 2003 Virtual water flows between nations in relation to trade in livestock and livestock products. Value of Water Research Report Series No. 13, Delft: UNESCO-IHE.
- [25] Al Muthanna Governorate. July 18, 2010. <http://muthana.gov.iq/ar/index.php> (accessed -July 25, 2013) (in Arabic).
- [26] Al Nasiriya electronic newspaper. Ministry of Water Resources agrees to increase the water quota of Dhi Qar and takes several steps to address water scarcity in the province. 1, 17, 2012. <http://www.nasiriae.com> (accessed July 25, 2013) (in Arabic).
- [27] Shafaaq News. Water scarcity hinders the implementation of Maysan's agricultural plan. December 7, 2010. <http://www.shafaaq.com> (accessed July 25, 2013) (in Arabic).
- [28] IMN February 7, 2013 Increasing water releases to the marshes of Maysan from Kut Barrage. <http://www.center-imn.net> (accessed July 25, 2013) (in Arabic).
- [29] V. Smakhtin, C. Revenga, P. Döll, A pilot global assessment of environmental water requirements and scarcity. *Water International* 29 (2004) 307–317.
- [30] M. Tolba, N. Saab, 2008 Arab Forum for Environment and Development: Arab Environment: Future Challenges. Beirut.
- [31] WWAP 2012 The United Nations World Water Development Report 4: Managing Water under Uncertainty and Risk. Paris: UNESCO.
- [32] UNEP 2007 UNEP in Iraq Post-Conflict Assessment, Clean-up and Reconstruction. Nairobi: United Nations Environment Programme.
- [33] IOM 2012 IOM-Iraq Special Report- Water Scarcity. International Organization for Migration – Iraq mission.
- [34] Canada-Iraq Marshlands Initiative 2010 Atlas of the Iraqi Marshes. Victoria: Hemlock.
- [35] A. Al-Hamad, Effect of Irrigation Water Quality of Al-Sidoor and Al-Thanaab Locations on Some Productivity Properties for Date Palm. *Journal of Al Basrah Research* 36 (2010) 57-65.
- [36] K. A. Rahi, T. Halihan, 2010 Changes in the salinity of the Euphrates River system in Iraq. *Regional Environmental Change* 10 (2010) 27–35.
- [37] B. J. Al-Sabah, A. T. Halboose, S. A. Al-Gaffor, T. K. Hassan, A. J. Mohammed, A. L. Sajjet, Seasonal Alteration of Some Nutrient Elements for Tigris River in Misan. *Journal of Dhi Qar Science* 2 (2011), 127-133.
- [38] B. I. H. Waisi, U. F. A. Karim, D. C. M. Augustijn, M. H. O. Al-Furaiji, S. J. M. H. Hulscher, A study on the quantities and potential use of produced water in southern Iraq. *Water Science & Technology: Water Supply*, 15 (2015), 370-376.
- [39] H. M. Al-Hadawi, L. J. Abbod, M. M. Al-Alaak, T. A. Salman, 2011 Priority environment and sustainable development indicators in Iraq. Baghdad: Central Statistical Organization- Ministry of Planning.
- [40] R. Mohammed, The environmental and natural data for the western plateau in Al- Muthana province and it's effect on practicing agricultural and pastoral activity. *Journal of Al Qadisiyah for Humanity Science* 11 (2008), 293-311.

- [41] S. Zakaria, 2012 Rain Water Harvesting and Supplemental Irrigation at Sinjar District in Northwest Iraq, Licentiate thesis. Lulea University of Technology, Sweden.
- [42] M. Sakamoto, Y. Tanaka, , K. Salewicz, M. Nakayama, (2013, October). Game Theoretical Analysis of Water Allocation Rule in Lower Basin of Euphrates and Tigris Rivers. IEEE International Conference on Systems, Man, and Cybernetics (SMC), 2013 (pp. 2042-2049). IEEE.
- [43] F. Ahmaduna, A. Pendashteh, L. C. Abdulla, D. Biak, S. Madaeni, Z. Abidin, Review of technologies for oil and gas produced water treatment. *Journal of Hazardous Materials* 170 (2009) 530-551.
- [44] M. S. Al-Rubaie, M. A. Dixon, T. R. Abbas, Use of flocculated magnetic separation technology to treat Iraqi oilfield co-produced water for injection purpose. *Desalination and Water Treatment* 53 (2015), 2086-2091.
- [45] D. L. Shaffer, L. H. Arias Chavez, S. R. Castrillón, M. Ben-Sasson, N. Y. Yip, M. Elimelech, Desalination and Reuse of High-Salinity Shale Gas Produced Water: Drivers, Technologies, and Future Directions. *Environmental Science and Technology* 47 (2013) 9569–9583.
- [46] G. Olsson, 2012 The Water and Energy Nexus-Framing the Context. EEA. Copenhagen.
- [47] FAO, Aquastat 2013. <http://www.fao.org/nr/water/aquastat/data/query/results.html> (accessed July 25, 2013).
- [48] J. Chenoweth, P. Hadjinicolaou, A. Bruggeman, J. Lelieveld, Z. Levin, M. Lange, E. Xoplaki, M. Hadjikakou, 2011 Impact of climate change on the water resources of the eastern Mediterranean and Middle East region: Modeled 21st century changes and implications. *Water Resources Research* 47 (2011) 1-18.
- [49] UNCT 2013 Iraq Facts & Figures. <http://iq.one.un.org/Facts-and-Figures> (accessed September 1, 2013).

3

Use of forward osmosis in treatment of hyper-saline produced water

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Use of Forward Osmosis in Treatment of Hyper-Saline Iraqi Produced Water

Abstract

Produced water is the largest waste stream in the oil and gas industry. The quality of produced water varies greatly, from near drinkable to containing large amounts of salts and organics. Some of the most challenging produced waters in the world today are found in Iraq, where concentrations of dissolved solids can exceed 200,000 ppm and oil content can be near 100 ppm. In this work, forward osmosis is investigated as a suitable treatment method for hyper-saline produced water. Two draw solutions, ammonia-carbon dioxide ($\text{NH}_3\text{-CO}_2$) and magnesium chloride (MgCl_2), were evaluated for dewatering these brines. The $\text{NH}_3\text{-CO}_2$ draw solution, though easily recycled, showed low flux and substantial scaling issues caused by pH changes and carbonate fluxes. MgCl_2 showed substantially higher fluxes due to higher osmotic efficiency and lower scaling propensity.

3.1 Introduction

Potable water scarcity is of global concern, especially in arid areas like Iraq where about 97% of the country is in an arid land with low and erratic rainfall [1]. Iraq's freshwater resources primarily come from the Tigris and Euphrates rivers that run through the center of the country. About 98% of the water consumption in Iraq depends on these two rivers, their tributaries, and their associated marshes. The country has recently passed through exceptionally dry and warm years with the lowest river discharges in decades [2]. This is caused partly by Turkish, Syrian, and Iranian dams built over the past thirty years leading to a significant decrease in average water levels of the two rivers. This combined with a lack of proper water management, high rate of evaporation, desertification, climate change, and inward flow of the Gulf Sea waters have increased the salt content of the rivers bringing an unprecedented water crisis into the southern region of Iraq. An annual water shortage of 430 million cubic meters was estimated in this region [3].

Despite this severe water shortage, large amounts of oilfield wastewater are produced every day accompanied by the production of oil in Iraq (produced water). This waste water may be used as a new water resource, if treated efficiently and economically, for many different purposes including irrigation, rangeland restoration, cattle and animal consumption, cooling towers, or enhanced oil recovery.

One of the greatest challenges in treating produced water, especially those waters produced in Iraq, is its high salinity [4]. Salinity level often determines the choice of produced water management practices, because many practices might become uneconomical or impractical for highly saline produced waters [5]. These waters are notoriously risky to work with. Some risks include [6]: (1) degradation of ground and surface water quality; (2) death of plants and destruction of soil textures; (3) erosion of soils and siltation of nearby waterways; (4) blockage

of produced water equipment; and (5) adverse effects on ecosystems. In Iraq, produced waters in some oil fields can reach levels of salinity more than 240 g.L⁻¹ of total dissolved solids (TDS). Desalination of such hyper-saline water is considered as extraordinarily expensive because of large energy requirements [7].

Highly saline produced water often renders conventional desalination technologies, like reverse osmosis, unusable due to high hydraulic pressure demand. Forward osmosis (FO) circumvents this issue by using osmotic pressure instead of hydraulic pressure to drive water across a selective membrane. Using a high concentration draw solution, osmotic potential can force osmotic flow from even the highest salinity solutions [8]. The draw solution can then be subsequently regenerated (or used) by another process chosen specifically for that draw solute. While forward osmosis will not use less energy than other technologies, it does have the capability of using lower quality energy or operating with other advantages (low fouling propensity, for instance). FO achieves this while relying on an osmotic potential gradient generated by a concentrated draw solution across a semi-permeable membrane.

Forward osmosis (FO) has been touted as being capable of treating moderate to high salinity waters in recent years [9][10]. One such study describes using forward osmosis in the treatment of drilling mud and hydraulic fracturing wastewater (with a TDS of 6750 ppm) [11]. They found that FO could recover more than 80% of the water from drilling wastewater and reduce its volume by more than three times. Another, two projects were performed on a pilot scale to investigate using of forward osmosis in the treatment of produced water in a scalable and movable plant. The first one is the Green Machine which was built by HTI (Hydration Technology Innovations). This system was tested with a feed solution from Haynesville shale gas field (3500 ppm TDS). Its results showed that the system recovered 85% of the feed solution using 1M NaCl draw solution and produced highly purified water for reuse [12]. The other pilot plant used the ammonia-carbon dioxide draw solution in the treatment of high salinity produced water (about

75000 ppm TDS) from the Marcellus shale region [13]. This plant was able to run with energy 2.3 times less than that of the conventional mechanical vapor compression process for the same feed salinity. An additional stage after the draw solution recovery was necessary to remove the salts which crossed the membrane from the feed solution to the draw solution. The final product (permeate) was of high quality with a TDS of about 300 ppm.

These early studies on using FO in produced water treatment have been limited to water streams with salinity less than 100,000 ppm. In this work, the feasibility of using FO in the treatment of produced water with TDS of about 240,000 ppm was studied. At the time of publication, this represents the first study that explores the use of FO with such a high salinity feed. The focus of this chapter will be on testing two different draw solutions and studying the inorganic scaling potential in both draw solutions. The results of this study can be valuable in designing an integrated process of treatment of hyper-saline streams and deciding the required pre-treatment steps and preferred properties of a chosen draw solute.

3.2 Materials and method

3.2.1 Forward osmosis membrane

The membrane used in this work was CTA (cellulose triacetate) forward osmosis membrane. This membrane was provided by HTI (Hydration Technology Innovations Inc., Albany, OR). The CTA membrane has been used successfully in a wide range of FO applications such as seawater desalination [14], wastewater treatment [15], and advanced life support systems [16]. Properties of the membrane as well as the cross-sectional image are provided elsewhere [17].

3.2.2 Feed solution

Produced water analyses (Table 3.1) was taken from [18]. These analyses represent the four giant oilfields in Iraq which stand for about 85% of the total Iraqi oil production [3]. These produced waters have very high TDS (about eight times the salinity of seawater) and relatively low oil content. To study the effect of the different salts in the produced water on the FO process, we prepared feed solutions with different compositions (Table 3.2). NaCl (99.9% Fisher), CaCl₂ (Fisher), MgCl₂.6H₂O (99% Acros Organics), MgSO₄.7H₂O (99.3% Fisher), NaHCO₃ (99%, J.T. Baker), and FeCl₃.6H₂O (99+% Acros Organics) were used to prepare the feed solution. We tested the described recipe (PW-Full) and then individual recipes with a single component removed (such as Ca, Mg, SO₄, etc.). For instance, PW-Ca lacks calcium, PW-Mg lacks Magnesium, PW-SO₄ lacks Sulfate, PW-HCO₃ lacks bicarbonate, and PW-Fe lacks iron. In each solution, the osmotic pressure was kept constant by compensating the removed salt by adding NaCl. The modified Van't Hoff equation [19] was used to calculate the osmotic pressures and retune the feed recipe after removal of one of the components.

Table 3.1 Characteristics of the produced water in the south of Iraq. TDS: total dissolved salts, TH: total hardness [18].

Analysis	North Rumaila	South Rumaila	Al-Zubair	West Qurna
pH	4.8	4.1	6.62	4.9
Conductivity ($\mu\text{S.cm}^{-1}$)	280,000	278,000	268,000	300,000
TDS (mg.L^{-1})	247,000	246,000	238,000	264,000
TH (mg.L^{-1}) as CaCO ₃	54,000	40,000	50,000	43,000
Alkalinity (mg.L^{-1}) as HCO ₃ ⁻	238	110	262	347
Oil content (mg.L^{-1})	36	53	66	57
SO ₄ ⁻² (mg.L^{-1})	108	116	104	94
Total Fe (mg.L^{-1})	98	110	50	2.4
Ca ⁺² (mg.L^{-1})	17,234	12,826	14,028	12,024
Mg ⁺² (mg.L^{-1})	2,655	1930	3,632	3,148
Na ⁺ (mg.L^{-1})	89,000	91,000	87,000	98,000
Cl ⁻ (mg.L^{-1})	138,000	141,000	134,000	151,000

Table 3.2 Composition of the synthetic produced water and the corresponding osmotic pressure.

Component	Concentration (g.L⁻¹)						
	Baseline	PW-full	PW-Ca	PW-Mg	PW-SO ₄	PW-HCO ₃	PW-Fe
NaCl	223	185	215	192	185	185	185
CaCl₂	-	45	-	45	45	45	45
MgCl₂	-	10	10	-	10	10	10
MgSO₄	-	0.12	0.12	-	-	0.12	0.12
NaHCO₃	-	0.25	0.25	0.25	0.25	-	0.25
FeCl₃	-	0.05	0.05	0.05	0.05	0.05	-
Total	223	240.42	225.23	237.71	240.36	240.33	240.41

Component	Osmotic pressure (atm)						
	Baseline	PW-full	PW-Ca	PW-Mg	PW-SO ₄	PW-HCO ₃	PW-Fe
NaCl	200.88	167	194	174	167	167	167
CaCl₂	-	26.92	-	26.92	26.92	26.92	26.92
MgCl₂	-	6.64	6.64	-	6.64	6.64	6.64
MgSO₄	-	0.05	0.05	-	-	0.05	0.05
NaHCO₃	-	0.15	0.15	0.15	0.15	-	0.15
FeCl₃	-	0.03	0.03	0.03	0.03	0.03	-
Total	200.88	200.88	200.88	200.88	200.88	200.88	200.88

3.2.3 Draw solutions

Two types of draw solutions were used in this study. A 6 M ammonia-carbon dioxide draw solution was prepared by dissolving ammonium bicarbonate NH_4HCO_3 in a mixture of ammonium hydroxide (29%, Fisher) and deionized water (DI) to get $\text{NH}_3\text{-CO}_2$ molar ratio of 2.2/1. Higher ratios of NH_3/CO_2 are required to prepare higher concentrations of $\text{NH}_3\text{-CO}_2$ draw solution [14]. A 4.8 M MgCl_2 solution was prepared by dissolving the appropriate amount of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (99%, Acros Organics) in DI water which was provided from a Millipore Integral 10 water system (Millipore Corporation, Billerica, MA, USA).

3.2.4 Forward osmosis tests

The FO experiments were run on a bench-scale laboratory system, a schematic diagram of the laboratory scale unit used in this study is provided elsewhere [20]. The weight change of the feed

solution was measured using a digital balance (Denver Instruments PI-4002, Denver Instruments Bohemia, NY) connected to a computer. The average water permeation flux was calculated as follows:

$$J_w = \frac{\Delta w}{\rho A t} \quad (1)$$

where J_w is the water flux ($\text{L}\cdot\text{m}^{-2}\cdot\text{hr}^{-1}$), Δw is the weight change of the feed solution (g), ρ is the density of water ($\text{g}\cdot\text{L}^{-1}$), A is the effective membrane area ($20\cdot 10^{-4} \text{ m}^2$), and t is the time of the experiment (20 hr.).

Feed and draw solutions were maintained at $30\pm 1^\circ\text{C}$. The pressure on both sides was three psi ($\Delta p = 0$). Cross-flow velocities of both the feed and draw solutions were $0.25 \text{ m}\cdot\text{s}^{-1}$. After each experiment, the membrane was flushed with DI water and dried to prepare it for Scanning Electron Microscopy (SEM) imaging. All experiments were conducted in the FO mode (the active layer facing the feed solution). A baseline test using a NaCl feed solution with an equivalent osmotic pressure to the produced water was used as a control for the experiment. All experiments were run in duplicate and the error bars are the standard deviations of experimental data.

3.2.5 Analytical methods

The membrane surface was analyzed by Scanning Electron Microscopy-Energy Dispersive X-ray Apparatus JSM-6335F (FESEM, JEOL Ltd., Japan). Prior to imaging, the samples were sputter coated with a thin layer of gold. Imaging was done using an accelerating voltage of 10 kV and current of 12 μA . Reverse ammonia/ammonium flux during the FO tests was measured gravimetrically using sodium tetraphenyl boron to precipitate dissolved ammonia species as ammonium tetraphenylborate as described by Arena et al. [21]. The pH of the feed solutions

before and after the experiments was measured by a *pH* meter (accumet excel XL 50, Fischer Scientific) calibrated using five buffer solutions of *pH* 2, 4, 7, 10, and 12.

3.2.6 Langelier Saturation Index (LSI)

The *LSI* is calculated number used to predict the calcium carbonate stability in water. It indicates whether the CaCO_3 will precipitate, dissolve, or be in equilibrium. Precipitation occurs when $LSI > 0$ [22] [23]. The value of *LSI* is calculated from the following equation:

$$LSI = pH - pH_s \quad (2)$$

where *pH* is the *pH* value of the feed solution and pH_s is the saturation *pH* which was calculated using Lenntech calculator [24].

3.3 Results and discussion

3.3.1 $\text{NH}_3\text{-CO}_2$ as a draw solution

3.3.1.1 Feed solution composition effect

Figure 3.1 shows the average water flux in LMH ($\text{L.m}^{-2}.\text{hr}^{-1}$) for different feed compositions using $\text{NH}_3\text{-CO}_2$ as the draw solution for 20 hr. of operation. Details of the feed compositions are given in Table 3.2. As expected, the highest fluxes were observed in the baseline test which was a NaCl solution of 223 g.L^{-1} (equivalent osmotic pressure as the produced water recipe). Comparatively, the water flux when using a full composition feed solution (PW-full) was 60% lower than the baseline which contained only NaCl as the feed solution. When individual components of the PW were removed and replaced with NaCl, a number of conclusions can be drawn. Upon removing the divalent cations (i.e. calcium and magnesium) the water flux increased by about 72% compared to the water flux observed for the full composition feed solution. The behavior was particularly dependent on the presence of calcium within the solution

and this suggests that calcium is mainly responsible for flux decline in this process. The flux decline is likely due to calcium scaling and more evidence will be discussed in the following sections. The omission of the anions (SO_4 and HCO_3) and iron from the feed solution showed minimal changes in the water flux. This is most likely because the saturation limits for these salts are higher than their concentrations in the feed solution.

Figure 3.1 Water flux at different feed solution compositions. Experimental conditions: 6 M $\text{NH}_3\text{-CO}_2$ draw solution, HTI-CTA membrane, FO mode, cross-flow velocity of feed and draw $0.25 \text{ m}\cdot\text{sec}^{-1}$, Temp 30°C , zero transmembrane pressure. Results are an average of three experiments with different coupons. Error bars indicate standard deviation.

3.3.1.2 Ammonia flux

Figure 3.2 shows the ammonia flux for the different feed solution compositions. The ammonia flux was measured between 1 and $2.5 \text{ mol.m}^{-2}.\text{hr}^{-1}$. Ammonia flux from the draw into the feed solution will create substantial changes in feed solution chemistry during the course of a test.

The mechanism of mass transfer (water and ammonia fluxes) in the CTA membrane is governed by diffusion that happens due to the concentration difference across the membrane [25].

Interestingly, the ammonia flux results followed a similar trend to that of the water flux. The highest ammonia flux was for the baseline test while the lowest was for the full composition feed solution (PW-full). The difference in ammonia flux was most likely caused by scaling, which adds a layer of resistance to ammonia transport on the active layer of the membrane.

Figure 3.2 solute flux at different feed solution. Experimental conditions: 6 M $\text{NH}_3\text{-CO}_2$ draw solution, HTI-CA membrane, FO mode, cross-flow velocity of feed and draw 0.25 m.sec^{-1} , Temp 30° C , zero transmembrane pressure. Results are an average of three experiments with different coupons. Error bars indicate standard deviation.

3.3.1.3 Scaling when using $\text{NH}_3\text{-CO}_2$ as draw solution

Scaling was observed on the active layer side of the membrane surface upon the removal of the membrane from the test cell when using $\text{NH}_3\text{-CO}_2$ as a draw solution. The main component of the scaling in this process is calcium carbonate (CaCO_3). There is an abundance of carbonate ions (i.e. 6 M) in the $\text{NH}_3\text{-CO}_2$ draw solution which will diffuse into the feed solution where the concentration of carbonate ions is relatively low (i.e. 250 ppm).

Figure 3.3 shows the scaling layer which formed on the membrane surface with PW-full as the feed solution. The composition of this layer as illustrated by the EDX is the calcium carbonate. The solubility of CaCO_3 depends largely on the pH of the solution with higher pH lowering the solubility [26]. During the test, the pH of the feed solution increased from 6 to more than 8 (Figure 3.4). This is due to the ammonia flux through the membrane. The precipitation of CaCO_3 is supported by the Langelier Saturation Index (LSI). The LSI of the feed solution increased from -0.44 to 1.7 after the FO experiment for 20 hr. confirming that the feed solution reached the supersaturation limit of CaCO_3 . Further confirmation that the scaling is indeed CaCO_3 is demonstrated by the fact that when Ca was removed from the feed, no scaling was observed (Figure 3.5). This lack of scaling is likely part of the reason why the average fluxes from these tests were higher than with feed solutions containing Ca.

Figure 3.3 SEM image of CTA membrane at a magnification of a) 100X, b) 500X, c) 5000X, d) EDX of the scaling. Experimental conditions: PW-full feed solution, 6 M $\text{NH}_3\text{-CO}_2$ draw solution, HTI-CA membrane, FO mode, cross-flow velocity of feed and draw $0.25 \text{ m}\cdot\text{sec}^{-1}$, Temp 30°C , zero transmembrane pressure.

Figure 3.4 pH change of the feed solution for the different feed solution compositions. Experimental conditions: 6 M $\text{NH}_3\text{-CO}_2$ draw solution, HTI-CA membrane, FO mode, cross-flow velocity of feed and draw $0.25 \text{ m}\cdot\text{sec}^{-1}$, Temp 30°C , zero transmembrane pressure. Results are an average of three measures. Error bars indicate standard deviation.

Figure 3.5 SEM image of CTA membrane at a magnification of a) 200X, b) 500X. Experimental conditions: PW-Ca feed solution, 6 M $\text{NH}_3\text{-CO}_2$ draw solution, HTI-CA membrane, FO mode, Cross-flow velocity of feed and draw $0.25 \text{ m}\cdot\text{sec}^{-1}$, Temp 30°C , zero transmembrane pressure.

When feed solutions without bicarbonate were evaluated, scaling was still observed (Figure 3.6a-c). At first, one might think that this scaling is from CaSO_4 , however, EDX detected no sulfur (Figure 3.6d). This suggests that bicarbonate is diffusing into the feed from the draw solution, which contains 6 M carbonate species. A similar mechanism of scaling formation was reported by Li et al. when using $\text{NH}_3\text{-CO}_2$ draw solution in desalination of seawater [27].

Figure 3.6 SEM image of CTA membrane at a magnification of a) 100X, b) 500X, c) 5000X, d) EDX of the scaling. Experimental conditions: PW- HCO_3 feed solution, 6 M $\text{NH}_3\text{-CO}_2$ draw solution, HTI-CA membrane, FO mode, cross-flow velocity of feed and draw $0.25 \text{ m}\cdot\text{sec}^{-1}$, Temp 30°C , zero transmembrane pressure.

3.3.2 MgCl_2 as a draw solution

MgCl_2 has been considered by a number of groups to be a high-performance draw solution [28] [29] [30]. This draw solute is simple compared to the complex speciation of the ammonia-carbon dioxide system. For instance, it lacks pH changing species like ammonia and scalable species like carbonate, both of which have been confirmed to cause scaling with these produced waters.

Moreover, a 4.8 M MgCl_2 solution has an osmotic pressure of 1057 atm (based on modified Van't Hoff equation) compared to 250 atm for 6 M of $\text{NH}_3\text{-CO}_2$ [14]. From an application perspective, recycling MgCl_2 has its challenges. Nanofiltration has been reported as an efficient method to concentrate solutions up to 0.6 M MgCl_2 [30], but this would not be suitable for high salinity feeds. Membrane distillation can be used for separation of very high concentration solutions, but the energy requirement for doing so would exceed that of recycling the $\text{NH}_3\text{-CO}_2$ for the same feed concentration [7]. Nevertheless, it is worth exploring this draw solution to identify better draw solution properties that are preferred for treating high salinity waters with scalable components.

Figure 3.7 shows the water flux for the two different draw solutions when using PW-full as feed solution. The MgCl_2 draw solution produced higher water flux than the $\text{NH}_3\text{-CO}_2$ solution because it generates a higher osmotic pressure and there is substantially less scaling. The *pH* of the feed solution (Figure 3.8) did not change in the feed solution during the test. This allowed the LSI of the feed solution to remain negative (changed from -0.44 to -0.29) which indicates that the feed solution is not saturated with CaCO_3 . The lack of scale is noticeable in the SEM image (Figure 3.9) which shows a clean active side of the CTA membrane.

Figure 3.7 Comparison between NH₃-CO₂ and MgCl₂ as draw solutions in CTA membrane. Experimental conditions: Feed solution PW-full, FO mode; cross-flow velocity of 0.25 m.sec⁻¹; Temp 30° C; zero transmembrane pressure. Results are an average of three experiments with different coupons. Error bars indicate standard deviation.

Figure 3.8 pH change of the feed solution. Experimental conditions: PW-full feed solution, 4.8M MgCl₂ draw solution, HTI-CA membrane, FO mode, Cross-flow velocity of feed and draw 0.25 m.sec⁻¹, Temp 30° C, zero transmembrane pressure. Results are an average of three measures. Error bars indicate standard deviation.

Figure 3.9 SEM image of CTA membrane at a magnification of a) 100X, b) 500X, c) 5000X, d) EDX of the scaling. Experimental conditions: PW-full feed solution, 4.8 MgCl₂ draw solution, HTI-CA membrane, FO mode, Cross-flow velocity of feed and draw 0.25 m.sec⁻¹, Temp 30° C, zero transmembrane pressure.

3.4 Conclusions

FO is a feasible and reliable treatment option for the hyper-saline produced water where other treatment methods fail or consume a high amount of energy. Although NH₃-CO₂ has the advantage of being economically separable and recyclable to the FO process, it has high reverse solute flux across the membrane. Ammonia flux has a negative effect on the process as it raises the *pH* of the feed solution which promotes scaling of carbonate species. Reverse carbonate flux can also promote scaling. In both cases, loss of the draw solution either requires expensive resupply or stripping of the brine to recover the lost solute. Controlling the *pH* of the feed solution may help to reduce the scaling as it affects the solubility of the CaCO₃. It is possible that designing more selective membranes could reduce solute transport. While this is likely possible for retaining carbonate and bicarbonate, retaining ammonia can be quite difficult due to its size

and uncharged nature. Softening the produced water could also prevent scaling, but these waters are exceptionally hard. Our results show that using simpler draw solutions, such as MgCl_2 , may be a better option since it eliminates the pH changes and complexities of the system. However, the lack of economic recycling options for very high concentrations of MgCl_2 is a concern that would have to be addressed.

3.5 References

- [1] T.M. Omer. Country Pasture/Forage Resource Profiles-Iraq; FAO: Rome, Italy, 2011.
- [2] M. Tolba, N. Saab. Arab Forum for Environment and Development: Arab Environment: Future Challenges; Beirut, 2008.
- [3] M.H. Al-Furaiji, U.F. Karim, D.C.M. Augustijn, B.I. Waisi, S.J.M.H. Hulscher, Evaluation of water demand and supply in the south of Iraq, *Journal of water desalination and reuse* 6 (2016) 214-226.
- [4] F.R. Ahmadun, A. Pendashteh, L.C. Abdullah, D.R. Biak, S.S. Madaeni, Z.Z. Abidin, Review of technologies for oil and gas produced water treatment, *Journal of Hazardous Materials* 170 (2009) 530-551.
- [5] A Guide to Practical Management of Produced Water from Onshore Oil and Gas Operations in the United States; U.S. Department of Energy: National Petroleum Technology Office, 2009.
- [6] J. Environmental Aspects of Produced-water Salt Releases in Onshore and Coastal Petroleum-producing Areas of the Conterminous U.S. – A Bibliography; U.S. Geological Survey Open-File report: Virginia, 2006.
- [7] D.L. Shaffer, H. Arias Chavez, M., S.R.V. Castrillón, Y.N. Yip, M. Elimelech, esalination and Reuse of High-Salinity Shale Gas Produced Water: Drivers, Technologies, and Future Directions, *Environ. Sci. Technol* 47 (2013) 9569-9583.
- [8] T.Y. Cath, A.E. Childress, M. Elimelech, Forward osmosis: Principles, applications, and recent developments, *Journal of Membrane Science* 281 (2006) 70-87.
- [9] Oil Wastewater Treatment & Gas Wastewater Treatment: Green Machine. <http://www.htiwater.com/divisions/oil-gas/photos.html> (accessed Aug 8, 2014).
- [10] Produced Water Case Studies in the Marcellus Shale and Permian Basin. <http://oasyswater.com/case-study> (accessed Aug 8, 2014).
- [11] K.L. Hickenbottom, N.T. Hancock, N.R. Hutchings, E.W. Appleton, E.G. Beaudry, P., T.Y. Cath, Forward osmosis treatment of drilling mud and fracturing wastewater from oil and gas operations, *Desalination* 312 (2013) 60-66.
- [12] B.D. Coday, P., E.G. Beaudry, J., K., T. Hancock, Y. Cath, The sweet spot of forward osmosis: Treatment of produced water, drilling wastewater, and other complex and difficult liquid streams, *Desalination* 333 (2014) 23-35.
- [13] R.L. McGinnis, N.T. Hancock, M.S. Nowosielski-Slepawron, G.D. McGurgan, Pilot demonstration of the NH₃/CO₂ forward osmosis desalination process on high salinity brines, *Desalination* 312 (2013) 67-74.
- [14] J.R. McCutcheon, R.L. McGinnis, M. Elimelech, Desalination by ammonia-carbon dioxide forward osmosis Influence of draw and feed solution concentrations on process performance, *Journal of Membrane Science* 278 (2006) 114-123.
- [15] W. Holloway, E. Childress, E. Dennet, Y. Cath, Forward osmosis for concentration of anaerobic digester centrate, *Water Research* 41 (2007) 4005-4014.
- [16] Y. Cath, , G. Beaudry, T. Flynn, V., E. Childress, Membrane contactor processes for wastewater reclamation in space Part I. Direct osmotic concentration as pretreatment for reverse osmosis, *Journal of Membrane Science* 257 (2005) 85-98.

- [17] J.R. McCutcheon, R.L. McGinnis, M. Elimelech, A novel ammonia--carbon dioxide forward (direct) osmosis desalination process, *Desalination* 174 (2005) 1-11.
- [18] M.S. Al-Rubaie, M.A. Dixon, T.R. Abbas, Use of flocculated magnetic separation technology to treat Iraqi oilfield co-produced water for injection purpose, *Desalin. Water. Treat.*, 53 (2015) 2086-2091. doi:10.1080/19443994.2013.860400.
- [19] R.A. Robinson, H.R. Stokes. *Electrolyte Solutions*; Dover: New York, 2002.
- [20] J.R. McCutcheon, M. Elimelech, Influence of membrane support layer hydrophobicity on water flux in osmotically driven membrane processes, *Journal of Membrane Science* 318 (2008) 458-466.
- [21] J.T. Arena, S.S. Manickam, K.K. Reimund, B.D. Freeman, J.R. McCutcheon, Solute and water transport in forward osmosis using polydopamine modified thinfilm composite membranes, *Desalination* 343 (2014) 8-16.
- [22] *Handbook of Air Conditioning System Design*; McGraw-Hill Books: New York, 1965.
- [23] K. Rafferty. *Scaling In Geothermal Heat Pump Systems*; U.S. Department of Energy: Idaho, 1999.
- [24] Ionic Strength, activity coefficient and solubility. <http://www.lenntech.com/> (accessed 2014).
- [25] W.A. Phillip, J.S. Yong, M., Reverse Draw Solute Permeation in Forward Osmosis: Modeling and Experiments, *Environ. Sci. Technol* 44 (2010) 5170-5176.
- [26] B. Coto, C. Martos, J. Pena, R. Rodriguez, G. Pastor, Effects in the solubility of CaCO₃: Experimental study and model description, *Fluid Phase Equilibria* 324 (2012) 1-7.
- [27] Z. Li, V. Linares, S. Bucs, C. Aubury, N. Ghaffour, J. Vrouwenvelder, G. Amy, Calcium carbonate scaling in seawater desalination by ammonia-carbon dioxide forward osmosis: Mechanism and implications, *Journal of Membrane Science* No. 481 (2015) 36-43.
- [28] K.Y. Wang, R.C. Ong, T.S. Chung, Double-Skinned Forward Osmosis Membranes for Reducing Internal Concentration Polarization within the Porous Sublayer, *Industrial Engineering Chemistry Research* No. 49 (2010) 4824-4831.
- [29] Q. Yang, K.Y. Wang, T.S. Chung, Dual-Layer Hollow Fibers with Enhanced Flux As Novel Forward Osmosis Membranes for Water Production, *Environmental Science and Technology* No. 43 (2009) 2800-2805.
- [30] C.H. Tan, H.Y. Ng, A novel hybrid forward osmosis - nanofiltration (FO-NF) process for seawater desalination: Draw solution selection and system configuration, *Desalination and Water Treatment* 13 (2010) 356-361.

4

Application of DCMD for treating high salinity solutions: Impact of membrane structure and chemistry

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M. Al-Furaiji, N. Benes, A. Nijmeijer, J. McCutcheon, Application of direct contact membrane distillation for treating high salinity solutions: Impact of membrane structure and chemistry.

Abstract

Direct contact membrane distillation (DCMD) has promise as a technology for concentrating high salinity brines. The literature lacks, however, systematic studies on how membrane structural properties (pore size, thickness) and chemistry impacts the performance of brine concentration. In this work we examine membranes consisting of different materials (polyvinylidene fluoride (PVDF), polypropylene (PP), and ethylene chloro trifluoro ethylene (ECTFE)) with different pore sizes (0.45, 0.2, and 0.1 μm) and thicknesses (105, 115, and 50 μm). The objective is to elucidate structure- and chemical-property relationships of DCMD for brine concentration using three different salts (MgCl_2 , KCl , or NaCl) at near saturation conditions (up to 5 M). All membranes show excellent performance (high water flux and salt rejection above 99.5% for each salt). In general, the thinnest membranes exhibit the highest flux while lower porosity membranes have lower flux. Pore size is shown to have only a modest impact on performance. Solutes also play an important role in MD water flux. For example, at equal concentrations, KCl solutions exhibit a higher water flux than either NaCl or MgCl_2 . These differences are attributed to differences in solution vapor pressure and viscosity.

4.1 Introduction

Membrane distillation (MD) is a thermally driven membrane separation technology that has the ability to concentrate highly concentrated solutions. This ability is derived from its reliance on vapor pressure to drive water vapor across the membrane rather than hydraulic pressure (as in reverse osmosis) to overcome osmotic pressure. The unique ability to handle high salinity brines makes MD a promising technology for treating a variety of high salinity waters, including oily wastewaters from oil and gas production, industrial wastewaters, mining wastes, amongst others. Most of these studies have considered direct contact membrane distillation (DCMD) as the most promising of multiple MD approaches because of its simplicity and stable performance.

A challenge with using DCMD directly to treat these various salty and often dirty waters is that MD membranes foul rapidly due to their hydrophobicity. Fouling leads to wetting of the membrane and loss of selectivity. MD has been considered more viable when coupled with another process, such as forward osmosis (FO). In such FO-MD systems, FO acts as a pretreatment for the MD system, removing essentially all foulants, while the MD concentrates the brine that serves as the draw solution for FO. Such systems have been considered in previous studies [1–3], yet only a few researchers have described the use of MD for concentrating very high concentration brines [4,5]. In such a hybrid process, multiple types of salt solution can be considered.

So far only very few papers reported on the impact of membrane properties when using DCMD in treating highly concentrated solutions. It has been mentioned in the literature that the DCMD flux increases with the increase of the pore size [6,7]. However, the literature still lacks clear experimental study that illustrates the role of pore size on DCMD performance especially in the treatment of the highly concentrated solutions. Alkhudhiri et al. studied the effect of pore size (0.2 and 0.45 μm) when using air gap membrane distillation (AGMD) in treating NaCl, MgCl_2 , Na_2CO_3 , and Na_2SO_4 solutions

[8]. The role of thickness in MD has not been clearly specified in the literature as stated by Drioli et al. in a recently published review paper [9].

In this chapter, we systematically investigate the impact of membrane properties and brine solution type on DCMD performance (flux, selectivity) in the treatment of highly concentrated solutions. Included in this study is the performance of previously untested membranes from 3M made from ethylene chloro trifluoro ethylene (ECTFE). All of the tested membranes exhibited superb selectivity for a variety of salts (near 100% rejection). A substantial difference in water flux is observed for different membranes and salt type. In all, for the size of membranes tested in this study, thinner membranes are preferable as they exhibit lower mass transfer resistance. Heat transfer is more substantial with these membranes but of less importance when testing at this coupon size.

4.2 Materials and method

4.2.1 Materials

Sodium chloride (NaCl), potassium chloride (KCl), and magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), were analytical reagents purchased from Fisher Scientific. The PVDF-HVHP microporous flat sheet membrane (0.45 μm pore size) was purchased from Millipore. The ECTFE membrane (pore size 0.45 μm) was provided by 3M. PP membranes with different pore sizes (0.45, 0.2 and 0.1 μm) were acquired from 3M. Detailed characterization of the membranes used in this research is provided in Table 4.1.

4.2.2 Membrane characterization

The surface of the different membranes was examined by scanning electron microscopy (SEM) using a cold cathode field emission scanning electron microscope JSM-6335F (FESEM, JEOL Ltd., Japan). Prior to imaging, the samples were sputter coated with a thin layer of gold. Imaging was done using an accelerating voltage of 10 kV and current of 12 μA . A CAM 101 series contact angle goniometer

was used to measure the contact angles of the membranes at 5 different locations for each sample. The thickness of the membranes was measured at no less than 5 different locations of the membrane using a digital micrometer (Mitutoyo, series 293 IP65).

4.2.3 Membrane distillation test protocol

The DCMD tests were carried out using the experimental set-up shown in Figure 4.1. The installation consists of two tanks: one for the feed solution and the other for permeate. Feed solution and permeate were pumped to the membrane cell using variable speed peristaltic pumps from Cole-Parmer. A detailed description with pictures of the membrane cell is given elsewhere [10]. The flow of the feed and permeate was controlled by flow meters and the pressure is monitored by pressure gauges on both lines. Four thermocouples, connected to a 4-channel temperature controller from Sper Scientific Direct, were used to measure the temperature at the inlets and the outlets of the membrane cell. The temperature of the feed solution was kept at 50 °C using a heater (Fisher Scientific) while permeate was kept at 20 °C using a chiller (Fisher Scientific).

The water flux was calculated based on the weight change of the collected permeate over the experiment time (6 h). The salt rejection (R) was calculated from the following equation:

$$R = \left(1 - \frac{C_p}{C_{f,i}}\right) \times 100\% \quad (1)$$

where $C_{f,i}$ (g/L) is the initial concentration of the solute in the feed solution, and C_p (g/L) is the solute concentration in the permeate calculated from:

$$C_p = \frac{C_{p,f}(V_{p,i} + \Delta V) - C_{p,i}V_{p,i}}{\Delta V} \quad (2)$$

In this equation $C_{p,i}$ and $C_{p,f}$ are the initial and final solute concentration at the permeate side, $V_{p,i}$ is the initial permeate volume and ΔV is the permeate volume change during the experiment. The

concentration of the solute in the permeate tank was calculated from measuring the conductivity of permeate using a YSI 3200 conductivity meter.

Figure 4.1 Schematic diagram of the DCMD bench-scale test unit.

4.3 Theory

4.3.1 Heat transfer

The temperature polarization coefficient (*TPC*) is used to quantify the difference between the temperatures on the membrane surfaces and that in the bulks of both the feed solution and permeate. A membrane with a higher *TPC* (for the same operation and hydrodynamic conditions) provides better insulation between the feed solution and permeate and consequently better performance (higher water flux). In order to calculate the temperature polarization coefficient, we used the equations:

$$TPC = \frac{T_{fm} - T_{pm}}{T_f - T_p} \quad (3)$$

where T_f , T_p are the bulk temperatures of the feed solution and permeate, T_{fm} , T_{pm} are the temperature of the feed solution and permeate at the membrane surfaces and can be derived from the basic conduction and convection heat transfer equations:

$$h_f \times (T_f - T_{f,m}) = J \times \Delta H_v(T_{ave}) + \frac{k_m \times (T_{f,m} - T_{p,m})}{\delta_m} \quad (4)$$

$$h_p \times (T_{p,m} - T_p) = J \times \Delta H_v(T_{ave}) + \frac{k_m \times (T_{f,m} - T_{p,m})}{\delta_m} \quad (5)$$

where J is the water flux which was obtained from the experiment, $\Delta H_v(T_{ave})$ is the latent heat of vaporization at the average temperature of the feed and permeate which can be calculated from [11]

$$H_v(T) = 1.7535 \times T + 2024.3 \quad (6)$$

k_m is the thermal conductivity of the membrane which is expressed as [12]:

$$k_m = \varepsilon k_a + (1 - \varepsilon) k_p \quad (7)$$

where ε is the membrane porosity, k_a and k_p are the thermal conductivities of air and the polymer of the membrane respectively.

Heat transfer coefficients on the feed solution and permeate sides (h_f and h_p) under laminar flow conditions can be calculated from the Nusselt number (Nu) correlation for laminar flow in rectangular channel [13]:

$$Nu = 0.13 Re^{0.64} Pr^{0.38} \quad (8)$$

where Re is the Reynolds number and Pr is the Prandtl number.

4.3.2 Mass transfer

The effective driving force for the mass (water vapor) transfer through the membrane is the difference between the vapor pressures of the feed and the permeate solution at the membrane surface. The membrane distillation coefficient (MDC) can be used as an indicator of how well the membrane performs given the effective driving force.

The MDC in DCMD is calculated from the linear relation between the water flux and the driving force across the membrane [14]:

$$MDC = \frac{J}{(p_{mf} - p_{mp})} \quad (9)$$

where p_{mf} and p_{mp} are the partial pressures of the feed and permeate sides evaluated from temperatures at the membrane surfaces (T_{mf} and T_{mp}).

The mechanism of mass transfer in a microporous membrane can be determined from Knudsen number (K_n) which is the ratio between the mean free path (λ) and the pore size diameter (d_p) [11]:

$$K_n = \frac{\lambda}{d_p} \quad (10)$$

λ is calculated from the following expression [15]:

$$\lambda = \frac{k_B T}{\sqrt{2} \pi p_m (\sigma_m)^2} \quad (11)$$

where k_B is the Boltzmann constant ($1.38 \times 10^{-23} \text{ m}^2 \text{ kg} \cdot \text{s}^{-1} \cdot \text{K}^{-1}$), T is the absolute temperature, p_m is the mean pressure within the membrane pores and σ_m is the collision diameter of water molecules (2.641 Å).

4.4 Results and discussion

4.4.1 Effect of membrane characteristics on the MD process

Table 4.1 shows the properties of the commercial membranes used in this study. It should be noted that the 3M membranes have a higher porosity than the Millipore membrane. PP membranes exhibit higher contact angles due to their higher hydrophobicity. The 0.45 μm ECTFE and 0.1 PP membranes have thicknesses of about half than that of the other membranes. The morphology of the different membrane materials is shown in Figure 4.2. Each membrane has a nodular structure that provides surface roughness and regular pore size to prevent wetting.

Table 4.1 Properties of membranes used in this study.

	Manufacturer	Pore size (μm) ^a	Porosity (%) ^a	Thickness (μm) ^b	Contact angle ^b
0.45 PVDF	Millipore	0.45	75	105	115 $\pm$ 7
0.45 ECTFE	3M	0.45	81	50	103 $\pm$ 10
0.45 PP	3M	0.45	85	115	126 $\pm$ 7
0.2 PP	3M	0.2	85	114	130 $\pm$ 6
0.1 PP	3M	0.1	70	57	117 $\pm$ 5

^a From the manufacturer^b Our measurements **Figure 4.2 SEM images of the different membrane materials used in this study. a) 0.45 PVDF, b) 0.45 ECTFE and c) 0.45 PP.**

4.4.2 Membrane material type

To compare the different membrane's performance in DCMD, we considered a single brine, 5M NaCl, as a feed solution. This concentration was chosen to cover the whole range of concentrations of the draw solutions that can be used for FO. It can be seen from Figure 4.3 that 0.45 μm ECTFE membrane had the highest flux. The polypropylene membrane exhibited statistically a similar flux, but the 0.45 μm PVDF membrane exhibited less than half of this flux. This result is attributed to the difference in structural properties between the membranes. The ECTFE membrane is half as thick as the PVDF membrane. It has been reported that a thin membrane is favorable in MD as it poses less mass transport resistance [16]. Interestingly enough, the PP membrane is actually thicker than the PVDF, though it is reported to have a higher porosity as well. Membranes with higher porosity offer more surface for vapor generation [17] while at the same time have lower heat conduction through the membrane. It is important to note, however, that even though these membranes had different fluxes, all exhibited complete salt rejection during the 6 hr test.

Figure 4.3 Effect of membrane type on the water flux and the rejection. Experimental conditions: feed solution: 5M NaCl, permeate: DI water, feed temperature: 50 °C, permeate temperature: 20 °C, cross-flow velocity of feed and permeate 0.25 m.sec⁻¹. Results are an average of three experiments with different coupons. Error bars indicate standard deviation.

The thickness differences highlight an important tradeoff between mass transfer and thermal efficiency in MD. A thinner membrane generally yields higher fluxes because the membrane offers less resistance to the mass transfer. However, a thinner membrane shows higher heat loss due to conduction and thus a more severe temperature polarization effect. Figure 4.4 shows the calculated values of the *TPC* and *MDC* for the different membranes. Even though the 0.45 µm ECTFE membrane shows the highest flux, it has the lowest *TPC* and consequently less thermal efficiency. However, the 0.45 µm ECTFE membrane has a higher *MDC* indicating its good mass transfer performance.

Figure 4.4 TPC and MDC for the different membranes

4.4.3 Pore size effect

The effect of pore size on *DCMD* performance was investigated using 3M PP membranes with different pore sizes (i.e. 0.45, 0.2, and 0.1 μm). Figure 4.5 shows that only small differences in water flux between the membranes and that these differences are statistically not significant (especially between the 0.45 μm and the 0.2 μm PP membranes). No difference in salt rejection was detected for the three membranes either. Theoretically, large pore size is favorable for a high water flux due to lower mass transport resistance, but the pores must always be small enough to prevent pore wetting [18]. Slight difference in the flux performances between the 0.1 μm PP membrane and the other two membranes could be attributed to the porosity and thickness differences (membranes that only differed in pore size were unfortunately not available). The thin 0.1 μm pore size membrane had a more severe *TPC* but had a higher *MDC* (Figure 4.6). These trends match those found in Figure 4.4.

Based on the Knudsen number (Table 4.2) the dominant mechanism of mass transfer for the 0.1 μm PP membrane is Knudsen diffusion, implying that the diffusing molecules collide with the walls of the pores much more frequently than they collide with other molecules [19]. For the 0.45 μm and the 0.2 μm membranes the contribution of molecular diffusion to transport is slightly larger. The additional friction on the permeating water, associated with molecular diffusion, can result in an increased overall resistance to mass transfer [20,21]; the faster mass transfer due to a larger pore size may be negatively outweighed by the additional resistance associated with the molecular diffusion. This could explain the lower calculated *MDC* values observed for the larger pore size membranes (Figure 4.6).

Figure 4.5 Effect of pore size on the water flux and the rejection. Experimental conditions: feed solution: 5 M NaCl, permeate: DI water, feed temperature: 50 °C, permeate temperature: 20 °C, cross-flow velocity of feed and permeate 0.25 m.sec⁻¹. Results are an average of three experiments with different coupons. Error bars indicate standard deviation.

Figure 4.6 - TPC and MDC for the PP membrane at different pore sizes

Table 4.2 Knudsen number for the different PP membranes

Membrane	K_n	Mechanism
0.45 PP	0.32	Combined
0.2 PP	0.71	Combined
0.1 PP	1.42	Knudsen

4.4.4 Effect of salt type

Figure 4.7 shows the water flux and salt rejection of the 0.45 PVDF membrane, for three different highly concentrated (4 M) salt solutions. The KCl solution shows the highest water flux, followed by the NaCl solution. For MgCl_2 , a relatively low flux is observed. For all three solutions a salt rejection $> 99\%$ is observed. The differences in the fluxes are caused by the differences in vapor pressure of the different solutions. Figure 4.8 shows the vapor pressure of the solutions at 50°C , over a range of concentrations. At 4 M concentration the vapor pressure of MgCl_2 is lower than that of NaCl and KCl. The low vapor pressure of the MgCl_2 solution explains its lower water flux. Furthermore, the viscosity of the MgCl_2 solution is much higher (6.2 cP) than the viscosity of NaCl (1.37 cP) and KCl (1.07 cP) solutions. Higher viscosity increases the resistance to the mass and heat transfer in the feed solution boundary layer [4,5].

Figure 4.7 Effect of salt type on the water flux and the salt rejection. Experimental conditions: 0.45 PVDF membrane, permeate: DI water, feed temperature: 50°C , permeate temperature: 20°C , cross-flow velocity of feed and permeate $0.25\text{ m}\cdot\text{sec}^{-1}$. Results are an average of three experiments with different coupons. Error bars indicate standard deviation.

Figure 4.8 Vapor pressure of the different salt solutions at 50 °C. [22–24]

4.5 Conclusions

This systematic study demonstrated that certain structural characteristics of commercial membranes, in particular their thickness, contribute to substantial differences in their flux performance in DCMD. The data suggest that reducing the thickness of a membrane results in a complex interplay between reduced mass transfer resistance and enhanced heat transfer. In most membrane processes, reducing mass transfer resistance without sacrificing selectivity is of paramount importance. However, in applications like DCMD, lower mass transfer resistance may lead to higher heat flux, which lowers overall driving force. The calculated values of *TPC* and *MDC* for the membranes with different thicknesses confirmed that mass transfer is more dominant than heat transfer. Interestingly, pore size was shown to have only limited impact on DCMD performance over the range of pore sizes measured even though it substantially impacts resistance in pressure driven systems. Strikingly, even for highly concentrated solutions, the salt rejections are near 100%. While proving that all of the membranes tested never wetted and lost selectivity, this also suggests that DCMD can be a promising option for hybridization with forward osmosis where retention of the draw solute is critical to system performance. Lastly, the ECTFE membranes, which have yet to be reported on, performed quite well during our testing suggesting their utility for DCMD applications.

4.6 Nomenclature

$C_{f,i}$	Initial concentration of the solute in the feed solution (g.L^{-1})
C_p	Solute concentration at the permeate (g.L^{-1})
$C_{p,f}$	Final solute concentration at the permeate side (g.L^{-1})
$C_{p,i}$	Initial solute concentration at the permeate side (g.L^{-1})
d_p	Pore diameter (μm)
ECTFE	Ethylene Chloro Tri Fluoro Ethylene
h_f	Heat transfer coefficient of the feed side ($\text{W.m}^{-2}.\text{K}^{-1}$)
h_p	Heat transfer coefficient of the permeate side ($\text{W.m}^{-2}.\text{K}^{-1}$)
J	Mass flux ($\text{kg.m}^{-2}.\text{h}^{-1}$)
k_a	Thermal conductivity of air ($\text{W.m}^{-1}.\text{K}^{-1}$)
k_B	Boltzmann constant ($1.38*10^{-23} \text{ kg.m}^2.\text{s}^{-1}.\text{K}^{-1}$)
k_m	Thermal conductivity of membrane ($\text{W.m}^{-1}.\text{K}^{-1}$)
k_p	Thermal conductivity of polymer ($\text{W.m}^{-1}.\text{K}^{-1}$)
M	Molecular weight of water (kg. mol^{-1})
MDC	MD coefficient ($\text{kg.m}^{-2}.\text{s}^{-1}.\text{Pa}^{-1}$)
Nu	Nusselt number
p_m	The mean pressure within the membrane pores (Pa)
p_{mf}	Partial pressure of water at the feed side (Pa)
p_{mp}	Partial pressure of water at the permeate side (Pa)
PP	Poly Propylene
Pr	Prandtl number
PVDF	Polyvinylidene Fluoride
R	Salt rejection
Re	Reynolds number
T_f	Bulk temperature of the feed side (K)
$T_{f,m}$	Membrane surface temperature at the feed side (K)
T_p	Bulk temperature of the permeate side (K)
$T_{p,m}$	Membrane surface temperature at the permeate side (K)
TPC	Temperature polarization coefficient
$V_{p,i}$	Initial permeate volume (L)
δ_m	Membrane thickness (μm)
ΔH_v	Latent heat of vaporization (kJ.Kg^{-1})
λ	Mean free path (nm)
σ_w	Collision diameter of water molecule ($2.641 \text{ \AA}^\circ$)

4.7 References

- [1] S. Zhang, P. Wang, X. Fu, T.-S. Chung, Sustainable water recovery from oily wastewater via forward osmosis-membrane distillation (FO-MD), (2014). doi:10.1016/j.watres.2013.12.044.
- [2] Q. Ge, P. Wang, C. Wan, T.-S. Chung, Polyelectrolyte-Promoted Forward Osmosis–Membrane Distillation (FO–MD) Hybrid Process for Dye Wastewater Treatment, (n.d.). doi:10.1021/es300784h.
- [3] M. Xie, L.D. Nghiem, W.E. Price, M. Elimelech, S. Water, N. Haven, Toward Resource Recovery from Wastewater: Extraction of Phosphorus from Digested Sludge Using a Hybrid Forward Osmosis–Membrane Distillation Process, *Environ. Sci. Technol. Lett.* 1 (2014) 191–195. doi:10.1021/ez400189z.
- [4] J. Li, Y. Guan, F. Cheng, Y. Liu, Treatment of high salinity brines by direct contact membrane distillation: Effect of membrane characteristics and salinity, *Chemosphere.* (2015). doi:10.1016/j.chemosphere.2014.12.006.
- [5] Y. Guan, J. Li, F. Cheng, J. Zhao, X. Wang, Influence of salt concentration on DCMD performance for treatment of highly concentrated NaCl, KCl, MgCl₂ and MgSO₄ solutions, *Desalination.* 355 (2015) 110–117. doi:10.1016/j.desal.2014.10.005.
- [6] M.S. El-Bourawi, Z. Ding, R. Ma, M. Khayet, A framework for better understanding membrane distillation separation process, *J. Memb. Sci.* 285 (2006) 4–29. doi:10.1016/j.memsci.2006.08.002.
- [7] A. Alkhudhiri, N. Darwish, N. Hilal, Membrane distillation: A comprehensive review, *Desalination.* 287 (2012) 2–18. doi:10.1016/j.desal.2011.08.027.
- [8] A. Alkhudhiri, N. Darwish, N. Hilal, Treatment of high salinity solutions: Application of air gap membrane distillation, *Desalination.* 287 (2012) 55–60. doi:10.1016/j.desal.2011.08.056.
- [9] E. Drioli, A. Ali, F. Macedonio, Membrane distillation : Recent developments and perspectives, *Desalination.* 356 (2015) 56–84. doi:10.1016/j.desal.2014.10.028.
- [10] D. Anastasio, J. R. McCutcheon, Using forward osmosis to teach mass transfer fundamentals to undergraduate chemical engineering students, *Desalination.* 312 (2013) 10–18. doi:10.1016/j.desal.2012.10.037.
- [11] P. Termpiyakul, R. Jiraratananon, S. Srisurichan, Heat and mass transfer characteristics of a direct contact membrane distillation process for desalination, *Desalination.* 177 (2005) 133–141. doi:10.1016/j.desal.2004.11.019.
- [12] J. Phattaranawik, R. Jiraratananon, a. . Fane, Heat transport and membrane distillation coefficients in direct contact membrane distillation, *J. Memb. Sci.* 212 (2003) 177–193. doi:10.1016/S0376-7388(02)00498-2.
- [13] M. Gryta, M. Tomaszewska, A. Morawski, Membrane distillation with laminar flow, *Sep. Purif.* 5866 (1997) 2–6. doi:10.1016/S1383-5866(97)00002-6.
- [14] M. Qtaishat, T. Matsuura, B. Kruczek, M. Khayet, Heat and mass transfer analysis in direct contact membrane distillation, *Desalination.* 219 (2008) 272–292. doi:10.1016/j.desal.2007.05.019.
- [15] M. Khayet, T. Matsuura, *Membrane Distillation: Principles and Applications*, 2011. doi:10.1016/B978-0-444-53126-1.1.0010-7.
- [16] M. Essalhi, M. Khayet, Self-sustained webs of polyvinylidene fluoride electrospun nanofibers at different electrospinning times: 1. Desalination by direct contact membrane distillation, *J. Memb. Sci.* 433 (2013) 167–179. doi:10.1016/j.memsci.2013.01.023.
- [17] E. Curcio, E. Drioli, Membrane Distillation and Related Operations—A Review, *Sep. Purif. Rev.* 34 (2005) 35–86. doi:10.1081/SPM-200054951.
- [18] K.W. Lawson, D.R. Lloyd, Membrane distillation, *J. Memb. Sci.* 124 (1997) 1–25. doi:10.1016/S0376-7388(96)00236-0.
- [19] E. Cussler, *Diffusion: mass transfer in fluid systems*, Third edit, Cambridge University Press, 2009.
- [20] M. Khayet, T. Matsuura, J.I. Mengual, Porous hydrophobic/hydrophilic composite membranes: Estimation of the hydrophobic-layer thickness, *J. Memb. Sci.* 266 (2005) 68–79. doi:10.1016/j.memsci.2005.05.012.
- [21] S. Adnan, M. Hoang, H. Wang, Z. Xie, Commercial PTFE membranes for membrane distillation application : Effect of microstructure and support material Hydrophobic Membrane Hot feed Feed y layer Permeate, *DES.* 284 (2012) 297–308. doi:10.1016/j.desal.2011.09.015.
- [22] E.C.W.C. and D.N. Glew, Evaluation of the Thermodynamic Functions for Aqueous Sodium Chloride from Equilibrium and Calorimetric Measurements below 154 °C, *J. Phys. Chem. Ref. Data.* 14 (1985).

doi:<http://dx.doi.org/10.1063/1.555730>.

- [23] D.W. Green, R.H. Perry, Perry's chemical engineers' handbook, 8th ed., McGraw-hill, New york, 2008.
- [24] K.R. Patil, A.D. Tripathi, G. Pathak, S.S. Katti, Thermodynamic properties of aqueous electrolyte solutions. 2. Vapor pressure of aqueous solutions of sodium bromide, sodium iodide, potassium chloride, potassium bromide, potassium iodide, rubidium chloride, cesium chloride, cesium bromide, cesium iodide, J. Chem. Eng. Data. 36 (1991) 225–230. doi:10.1021/je00002a021.

5

Triple layer nanofiber membrane for treating high salinity brines using DCMD

This chapter will be submitted t as:

M. Al-Furaiji, J. Arena, J. Ren, N. Benes, A. Nijmeijer, J. McCutcheon, Triple layer nanofiber membrane for treating high salinity brines using direct contact membrane distillation.

Abstract

A composite, three-layered membrane for membrane distillation was prepared from electrospun polyvinylidene fluoride (PVDF) nanofibers supported by commercial polyethersulfone (PES) nanofiber nonwoven from DuPont. The membranes were tested in direct contact membrane distillation (DCMD) using a 5 M sodium chloride brine as a feed solution. The triple-layer membrane combines the hydrophobicity of PVDF and the robustness of the PES. The triple-layer membrane demonstrated excellent performance in DCMD (i.e. relatively high water flux compared to the commercial PVDF membrane and complete salt rejection of the brine) with good mechanical properties imparted by the PES layer. The triple-layer membrane with a thickness of 115 micron showed the highest water flux. The membrane with higher or lower thickness (145 micron and 85 micron respectively) presented lower water flux compared to the 115 micron membrane. This study indicates that there is an optimum thickness that provides the best performance in terms of water flux due to the opposing effects of thickness on mass transfer and thermal insulation for membranes with different thicknesses.

5.1 Introduction

Direct contact membrane distillation (DCMD) is a thermally driven membrane process in which water vapor transport occurs through a non-wetted porous hydrophobic membrane. In DCMD, a hot feed solution flows on one side of a membrane while a cold solution flows on the opposite side creating a driving force of vapor pressure difference across the membrane. DCMD has been considered as an alternative to distillation to treat highly concentrated solutions and brines [1]. These brines may include reverse osmosis reject [2], produced water [3], forward osmosis draw solutions [4] and hyper saline lakes [5].

A suitable membrane for membrane distillation should have high porosity, low tortuosity, and high thermal, mechanical and chemical stability [6]. Conventional commercial membranes that are typically prepared by phase inversion have been investigated for the treatment of highly concentrated solutions by membrane distillation [7,8]. Recently, nanofiber membranes have been considered for MD [9–11] because of their intrinsically high porosity and low tortuosity [12]. These properties facilitate vapor transport through a membrane. This high porosity, however, often leads to a lack of mechanical strength which limits their usefulness to more conventional cast membranes [13].

Adding additional layers to a membrane, such as a supporting scrim, is common with membranes intended for pressurized membrane processes (such as reverse osmosis). Layering MD membranes for the purpose of increasing mechanical integrity has been less common. Prince and co-workers, for example, have studied multi-layered membranes for MD in two different configurations. The first membrane consists of a selective top layer of electrospun PVDF nanofibers, a middle layer that is made of PVDF formed by immersion precipitation, and a bottom PET support layer [14]. The second membrane consists of a hydrophobic PVDF nanofiber layer on the top and a modified PVDF hydrophilic nanofiber layer on the bottom of

a PVDF casted layer [15]. This membrane was tested in DCMD configuration so both sides of the membrane were made hydrophobic. Both membranes showed improved performance in MD over the nanofiber single layer PVDF membrane due to the increase in liquid entry pressure of the triple-layer membrane.

We take this concept a step further by considering a commercial nanofiber as a supporting material for a triple-layer MD membrane. For the first time, a PES nanofiber material available from DuPont is used to support two PVDF nanofiber layers (on either side of the PES layer). The resulting membrane is entirely nanofibrous, thereby retaining high porosity while garnering strength from the PES and hydrophobicity of the PVDF nanofibers on both sides.

5.2 Materials and methods

5.2.1 Materials

Sodium chloride (NaCl, crystalline, certified ACS) was obtained from Fisher Scientific (Pittsburgh, PA). Acetone and dimethylformamide (DMF) were purchased from Sigma-Aldrich (St. Louis, MO). The polymer used in this study was Solef L3 polyvinylidene fluoride generously provided by Solvay Specialty Polymers (Alpharetta, GA). PVDF-HVHP membrane with 0.45 μm pore size was purchased from Millipore and used as a control. This membrane has a porosity of 75% and thickness of 105 μm . Water used in this study was ultrapure Milli-Q (18.2 M Ω) water produced by a Millipore Integral 10 water system, (Millipore Corporation, Billerica, MA).

5.2.2 Membrane fabrication

To prepare the triple-layer MD membrane, a solution of 11.1% PVDF dissolved in 4:1 DMF and acetone was electrospun directly onto a commercially produced nonwoven PES support from DuPont (Wilmington, DE). This support was made of PES fibers spun using a proprietary

technique. This material was selected as the support because it can be produced at scale, it has substantially higher strength than lab-made electrospun nanofibers, and the PES and PVDF have a common solvent in DMF. This last feature is important since the PVDF nanofibers will adhere to the PES support as residual solvent promotes fiber bonding. The finished structure consisted of a layer of PVDF fibers on both sides of the PES.

The PVDF fiber was prepared using a lab-scale electrospinning system described in our previous studies [12,16,17]. The PVDF solution was dispensed through a 20 gauge blunt needle at $5 \text{ mL} \cdot \text{h}^{-1}$ with an 18kV potential and a tip-to-target distance of 26 cm. The needle rasters side-to-side and the collector surface is a grounded rotating drum that was wrapped with the PES support. Spinning was done at room temperature and 65-75% relative humidity (controlled by compressed air). To study the effect of thickness and its impact of the performance of these membranes in DCMD, three different thicknesses were prepared: 85 micron, 115 micron and 145 micron. The thickness of the membrane was controlled by the volume of the PVDF polymeric solution that was spun on both sides of the PES fibers. As a control membrane for some of the characterizations perform, a mat consisting of only PVDF fibers with thickness 85 micron was spun directly onto a polypropylene nonwoven at 18 kV and 65-75% relative humidity.

5.2.3 DCMD performance tests

The DCMD tests were carried out using the experimental set-up shown in Figure 4.1. The installation consists of two tanks: one for the feed solution and the other for permeate. Feed solution and permeate were pumped to the membrane cell using variable speed peristaltic pumps from Cole-Parmer. 5 M NaCl solution was used as a feed in all experiments while DI water was used as permeate. A detailed description with pictures of the membrane cell is given elsewhere [18]. The flow of the feed and permeate was controlled by flow meters and the

pressure is monitored by pressure gauges on both lines. Four thermocouples, connected to a 4-channel temperature controller from Sper Scientific Direct, were used to measure the temperature at the inlets and the outlets of the membrane cell. The temperature of the feed solution was kept at 50 °C using a heater (Fisher Scientific) while permeate was kept at 20 °C using a chiller (Fisher Scientific).

The water flux was calculated based on the weight change of the collected permeate over the experiment time (6 h). The salt rejection (R) was calculated as described in chapter 4.

5.2.4 Membrane characterization

Scanning electron microscopy (SEM) was carried out using low vacuum capable field emission guns FEG-SEM to evaluate fiber size and the surface morphology of the PVDF and PES membranes. Prior to imaging, the samples were sputter-coated with a thin layer of gold. Imaging was done using an accelerating voltage of 20 kV and current of 1.6 nA. Energy-dispersive X-ray spectroscopy (EDS) mapping was conducted using silicon drift detector series EDS (EDAX SDD-EDS). A CAM 101 series contact angle goniometer was used to measure the contact angles of water drops on the PVDF and the PES nanofibers at five different locations for each sample. The thickness of the different samples was measured at no less than 5 different locations of each sample using digital micrometer (Mitutoyo, series 293 IP65). The mechanical properties of the different membranes were obtained from the tensile tests in air at 25 °C using an Instron microforce tester. A dynamic mechanical analysis (DMA) controlled force module was selected and a minimum of three strips (with the size of 40 mm x 5.5 mm) were tested for each type of membrane.

The porosity of the membranes was estimated using a gravimetric method. The membrane was cut into disks with a diameter of 2.54 cm (1 in) and weighed (W_{dry}). Isopropyl alcohol (IPA)

was used as a wetting agent and the membrane weighed after immersed in IPA (W_{wet}). The porosity (ε) was calculated from the following equation [20]:

$$\varepsilon = \frac{\left(\frac{W_{wet} - W_{dry}}{\rho_{IPA}} \right)}{V} \times 100\% \quad (1)$$

where ρ_{IPA} is the density of IPA and V is the total volume of the sample. Each membrane was tested at least three times.

5.3 Results and discussion

5.3.1 Membrane characterization

Table 5.1 shows the properties of the membranes used in this research. The thickness of the membranes was controlled by the amount of the PVDF polymer that was spun on the PES layer. It can be seen that adding the PVDF nanofibers increases the average porosity from 60% to about 90%. While the porosity of the membrane increased, the added layer of PVDF fibers to both faces of the PES layer increased the thickness of the membrane from 32 to 85, 115 and 145 micron. The triple-layer membranes showed superior hydrophobicity compared to the PES membrane.

Table 5.1 Properties of membranes used in this research.

Membrane	Thickness (micron)	Porosity (%)	CA (°)
TL-85	85	87.8 ±1	130 ±2
TL-115	115	88.6 ±4	128 ±5
TL-145	145	88.8 ±2	129 ±3
SL-85	85	92 ±2	132 ±4
PES-DuPont	32	60 ±1.5	87 ±1
PVDF-HVHP	105	75	115 ±7

TL: Triple-layer, SL: Single-layer

The cross-sectional SEM image and the EDS map of the triple-layer membrane are shown in Figure 5.1. Here the three distinct layers of the triple-layered membrane can be seen. The

distribution of the fluoride and the sulfur through the cross section of the membrane highlight the PVDF and the PES layers respectively. The solvent in the PVDF solution (i.e. DMF/acetone) might result in dissolving or softening some of the nanofibers and enhances binding between the PVDF and PES fibers. The surface SEM images (Figure 5.2) shows the nanofibrous structure of the PVDF and the PES layers. It can be seen that the pore size of the PES layer is smaller than that of the PVDF layer. This is beneficial for MD as it increases the liquid entry pressure of water through the membrane [6]. The contact angle measurements confirm the superhydrophobicity of the PVDF nanofibers and hydrophilicity of the PES membrane.

Figure 5.1 SEM image and EDS mapping of the cross section of the TL-115 membrane. Magnification x230, the yellow color of the fluoride and the purple for the sulfur.

Figure 5.2 Surface SEM images of the a) PVDF and b) PES membranes at a magnification of 5000x.

Mechanical properties of the membrane under tension are shown in Figure 5.3. The PES membrane alone has a tensile strength that far exceeds the PVDF nanofiber nonwovens on their own. Interestingly, after deposition of the PVDF nanofibers onto the PES, the membrane was weaker than the PES membrane alone. These differences, however, are due to an increased thickness of the material after adding PVDF nanofibers. Essentially, the tensile test continues until reaching the tensile strength which is the maximum stress that can be achieved before breaking. This method measures the force at break divided by the cross-sectional area of the sample. This means that the PVDF fibers add less to the mechanical strength of the membrane than they add to its thickness. Normalizing for the cross-sectional area gives the force at break which makes more sense comparison. We present the same data but normalized for the cross-sectional area in Figure 5.4. Here, the triple-layer membrane is shown to withstand a higher force at break and confirms its robustness over the PES or PVDF nanofibers alone.

Figure 5.3 Stress-strain curve of the triple-layer membrane, PES and the single-layer PVDF membrane

Figure 5.4 Force at break of the triple-layer membrane, PES and the single layer PVDF membrane. Results are an average of three measurements with different coupons. Error bars indicate standard deviation.

5.3.2 Membrane performance by DCMD

DCMD performance was conducted for all the membranes using a 5 M NaCl feed at a 30 °C temperature differential. Testing the base PES membrane showed that it cannot be used for membrane distillation as the PES was sufficiently hydrophilic that the membrane wetted out immediately. Also a single layer of PVDF electrospun nanofibers was tested in DCMD (Figure 5.5). A similar water flux to the triple-layer membrane was observed but the rejection was lower. The lower rejection indicates that the single layer PVDF membrane was wetted out during the 6 hr. of the experiment. This is most likely caused by the relatively large pore size and small thickness (85 micron) of the PVDF membrane. The variability in the results of the single layer PVDF membrane could be attributed to its poor mechanical properties and therefore being not stable in the membrane cell unit during the test.

Figure 5.5 DCMD water flux and rejection for single-layer PVDF membrane. Experimental conditions: feed solution: 5M NaCl, permeate: DI water, feed temperature: 50 °C, permeate temperature: 20 °C, volumetric flowrate of feed and permeate 0.4 L.min⁻¹. Results are an average of three experiments with different coupons. Error bars indicate standard deviation.

The triple-layer membrane at all thicknesses (Figure 5.6) demonstrated fluxes between 6 and 9 kg/m².hr and nearly complete salt rejection. The water flux and salt rejection were stable over 6 hours of operating time. In general, our triple-layer membranes exhibited higher flux than the commercial PVDF-HVHP membrane. The TL-115 membrane showed water flux twice than that of the PVDF-HVHP membrane. This is due to the high porosity of the triple-layer membrane (around 90%) compared to the PVDF-HVHP membrane (75%).

However, it is interesting to note that increasing membrane thickness from 85 micron to 115 micron results in higher water flux but after increasing the thickness to 145 micron the flux dropped to about the same value. This can be explained considering the interplay between heat and mass transport in membrane distillation. There is a trade-off between mass and heat transfer for the membrane with different thicknesses. A thinner membrane provides a higher rate of mass transport but it also increases the rate of heat transfer by conduction which increases the detrimental effect of temperature polarization [11]. Increasing a membrane's thickness reduces the temperature polarization but also increases the mass transfer resistance. This is valid for the membrane that consists of a single material. The added layer in this research is highly porous. So, increasing the thickness of the membrane (from 32 micron to 85 or 115 micron) will increase the porosity and consequently the evaporation area and enhance the mass transfer. However, for thicker membranes (from 115 micron to 145 micron), the reduced mass transport caused by a thicker membrane overcomes the positive effect of the higher porosity and resulted in lower water flux. Our results showed that there is an optimum value for membrane thickness which can assure good thermal insulation combined with a high mass transfer rate.

Figure 5.6 DCMD water flux and rejection for the prepared membranes with different thicknesses. Experimental conditions: feed solution: 5M NaCl, permeate: DI water, feed temperature: 50 °C, permeate temperature: 20 °C, volumetric flowrate of feed and permeate 0.4 L.min⁻¹. Results are an average of three experiments with different coupons. Error bars indicate standard deviation.

5.4 Conclusions

Triple-layer nanofibers membranes were investigated in this chapter. Commercial PES nanofibers, having good mechanical strength, were used to support the superhydrophobic PVDF nanofibers. The triple-layer membrane showed better performance over both the PES and PVDF single-layer membranes. The results showed that the thickness of the membrane should be chosen carefully because there is a complex interplay between mass transfer and heat transfer effects. There is an optimum thickness which gives the best performance in terms of water flux by limiting heat transfer by conduction. Long term tests are recommended to study the wettability over a longer period than that used in this work (6 hr.).

5.5 References

- [1] E.C.W. Clarke, D.N. Glew, Evaluation of the Thermodynamics Functions for Aqueous Sodium Chloride from Equilibrium and Calorimetric Measurements below 154C, *J. Phys. Chem. Ref. Data.* 14 (1985) 489–610. doi:http://dx.doi.org/10.1063/1.555730.
- [2] S. Lattemann, T. Höpner, Environmental impact and impact assessment of seawater desalination, *Desalination.* 220 (2008) 1–15. doi:10.1016/j.desal.2007.03.009.
- [3] B.I.H. Waisi, U.F. a. Karim, D.C.M. Augustijn, M.H.O. Al-Furaiji, S.J.M.H. Hulscher, A study on the quantities and potential use of produced water in southern Iraq, *Water Sci. Technol. Water Supply.* 15 (2015) 370. doi:10.2166/ws.2014.122.
- [4] H. Luo, Q. Wang, T.C. Zhang, T. Tao, A. Zhou, L. Chen, et al., A review on the recovery methods of draw solutes in forward osmosis, *J. Water Process Eng.* 4 (2014) 212–223. doi:10.1016/j.jwpe.2014.10.006.
- [5] X. Wang, J.D. Miller, F. Cheng, H. Cheng, Potash flotation practice for carnallite resources in the Qinghai Province, PRC, *Miner. Eng.* 66 (2014) 33–39. doi:10.1016/j.mineng.2014.04.012.
- [6] L.D. Tijing, J.S. Choi, S. Lee, S.H. Kim, H.K. Shon, Recent progress of membrane distillation using electrospun nanofibrous membrane, *J. Memb. Sci.* 453 (2014) 435–462. doi:10.1016/j.memsci.2013.11.022.
- [7] J. Li, Y. Guan, F. Cheng, Y. Liu, Treatment of high salinity brines by direct contact membrane distillation: Effect of membrane characteristics and salinity, *Chemosphere.* 140 (2015) 143–149. doi:10.1016/j.chemosphere.2014.12.006.
- [8] Y. Guan, J. Li, F. Cheng, J. Zhao, X. Wang, Influence of salt concentration on DCMD performance for treatment of highly concentrated NaCl, KCl, MgCl₂ and MgSO₄ solutions, *Desalination.* 355 (2015) 110–117. doi:10.1016/j.desal.2014.10.005.
- [9] J. A. Prince, G. Singh, D. Rana, T. Matsuura, V. Anbharasi, T.S. Shanmugasundaram, Preparation and characterization of highly hydrophobic poly(vinylidene fluoride) - Clay nanocomposite nanofiber membranes (PVDF-clay NNMs) for desalination using direct contact membrane distillation, *J. Memb. Sci.* 397-398 (2012) 80–86. doi:10.1016/j.memsci.2012.01.012.
- [10] Y. Liao, R. Wang, M. Tian, C. Qiu, A.G. Fane, Fabrication of polyvinylidene fluoride (PVDF) nanofiber membranes by electro-spinning for direct contact membrane distillation, *J. Memb. Sci.* 425-426 (2013) 30–39. doi:10.1016/j.memsci.2012.09.023.
- [11] M. Essalhi, M. Khayet, Self-sustained webs of polyvinylidene fluoride electrospun nanofibers at different electrospinning times: 1. Desalination by direct contact membrane distillation, *J. Memb. Sci.* 433 (2013) 167–179. doi:10.1016/j.memsci.2013.01.023.
- [12] N.N. Bui, J.R. McCutcheon, Hydrophilic nanofibers as new supports for thin film composite membranes for engineered osmosis, *Environ. Sci. Technol.* 47 (2013) 1761–1769. doi:10.1021/es304215g.
- [13] L. Huang, J.T. Arena, S.S. Manickam, X. Jiang, B.G. Willis, J.R. McCutcheon, Improved mechanical properties and hydrophilicity of electrospun nanofiber membranes for filtration applications by dopamine modification, *J. Memb. Sci.* 460 (2014) 241–249. doi:10.1016/j.memsci.2014.01.045.
- [14] J. a. Prince, V. Anbharasi, T.S. Shanmugasundaram, G. Singh, Preparation and characterization of novel triple layer hydrophilic–hydrophobic composite membrane for desalination using air gap membrane distillation, *Sep. Purif. Technol.* 118 (2013) 598–603. doi:10.1016/j.seppur.2013.08.006.
- [15] J.A. Prince, D. Rana, T. Matsuura, N. Ayyanar, T.S. Shanmugasundaram, G. Singh, Nanofiber based triple layer hydro-philic/-phobic membrane - a solution for pore wetting in membrane distillation, *Sci. Rep.* 4 (2014) 6949. doi:10.1038/srep06949.
- [16] L. Huang, N.N. Bui, S.S. Manickam, J.R. McCutcheon, Controlling electrospun nanofiber morphology and mechanical properties using humidity, *J. Polym. Sci. Part B Polym. Phys.* 49 (2011) 1734–1744. doi:10.1002/polb.22371.

- [17] L. Huang, S.S. Manickam, J.R. McCutcheon, Increasing strength of electrospun nanofiber membranes for water filtration using solvent vapor, *J. Memb. Sci.* 436 (2013) 213–220. doi:10.1016/j.memsci.2012.12.037.
- [18] D. Anastasio, J. R. McCutcheon, Using forward osmosis to teach mass transfer fundamentals to undergraduate chemical engineering students, *Desalination*. 312 (2013) 10–18. doi:10.1016/j.desal.2012.10.037.
- [19] M. Al-Furaiji, N. Benes, A. Nijmeijer, J. McCutcheon, Application of direct contact membrane distillation for treating high salinity solutions: Impact of membrane structure and chemistry, Unpublished. (2016).
- [20] M. Khayet, T. Matsuura, *Membrane Distillation: Principles and Applications*, 2011. doi:10.1016/B978-0-444-53126-1.10010-7.

6

Use of an FO-MD integrated process in the treatment of high salinity produced water

This chapter will be submitted as:

M. Al-Furaiji, N. Benes, A. Nijmeijer, J. McCutcheon, Use of a FO-MD integrated process in the treatment of high salinity produced water.

Abstract

Oilfield produced water (PW) can be considered as a potential water resource if treated efficiently and economically. However, its high salinity and complex chemistry can limit treatment options. In this work, the feasibility of using a hybrid forward osmosis (FO) - membrane distillation (MD) process for treating of hyper-saline produced water with total dissolved salts (TDS) of about 240,000 ppm was studied. MD is applied as a separation method for the draw solution of the forward osmosis process. Four draw solutions (i.e., sodium chloride (NaCl), potassium chloride (KCl), lithium chloride (LiCl) and magnesium chloride (MgCl_2)) at concentrations near to their saturation limits were considered. Results showed that each draw solution behaved quite differently in both FO and MD due to substantial differences in solubility, activity, and solution viscosity. LiCl has high solubility in water and can generate very high osmotic pressure (at 10 M), which was the reason for getting a relatively high FO flux (more than $6 \text{ L.m}^{-2}.\text{hr}^{-1}$). However the MD water flux for the 10 M LiCl was relatively low due to the low vapor pressure. NaCl and KCl showed different behavior of a high MD flux and low or negative FO flux. MgCl_2 at a concentration of 4.8 M showed comparable fluxes for both FO and MD over 20 hr. of operation. Both FO and MD water fluxes appear to be the limiting factor of design, especially when using membrane modules with the same effective area. We also found that no oil contaminated the draw solution, assuring that the MD process would be protected from oil fouling.

6.1 Introduction

With the increasing stress on the conventional water resources, the need arose to think of unconventional water resources such as oilfield-produced water (PW). The quantity of PW varies greatly depending on the location of the oilfield and the age of the reservoir. In many instances, this waste stream is seven to eight times larger by volume than oil produced at any given oilfield [1]. In the United States, for example, the oil and gas industry produces about 57 million barrels of water per day [2]. PW is most often considered as waste water, but industrial companies and policy makers have started to see it as a sustainable source of water. However, the handling of this water requires special attention. The treatment of produced water has the potential to produce a valuable product rather than waste. However, the selection of a produced water treatment option is a challenging problem that is steered by the composition of the PW and the overall treatment objective.

The combination of forward osmosis (FO) and membrane distillation (MD) can be a suitable option for the treatment of hyper-saline PW. FO has the ability to deal with extremely saline solutions that also contains a certain level of hydrocarbons. MD is used in this process (i.e. FO-MD) for the regeneration of the draw solution. It has been proven that MD can treat solutions at concentrations near their saturation limits [3]. The use of the FO-MD process in the treatment of produced water has been studied by Zhang et al. These authors used synthetic produced water with a salinity of about 12,000 ppm and an oil content of 4,000 ppm as the feed solution and 5 M NaCl as the draw solution for the FO-MD experiment. Both FO and MD showed more than 99.9 % rejection for the oil and the salt [4].

Besides, the FO-MD process has been investigated for other applications like wastewater reclamation [5,6], reverse osmosis (RO) brine treatment [7], sewer mining [8], dye wastewater treatment [9] and the concentration of protein solutions [10].

In this research, the hybrid FO-MD process is used for the treatment of extremely saline produced water. The focus of this work will be in testing four draw solutions with different physical and chemical properties to select the most appropriate draw solution for the FO-MD process. To the best of our knowledge, this is the first trial to use the FO-MD hybrid system for treating streams with such high levels of salinity.

6.2 Theory

Osmotic pressures of the feed solution (i.e. the synthetic produced water (SPW)) and the different draw solutions were calculated using the modified Van't Hoff equation [11]. Vapor pressures of the draw solutions and permeate at different temperatures were calculated based on the data from different references [12–15]. The temperature polarization effect and the temperature polarization coefficient (*TPC*) at the MD side was determined using equations derived from the heat balance across the MD membrane. All the used equations and the detailed procedure of the calculations are described in chapter 4.

6.3 Materials and method

6.3.1 Materials

A thin film composite (TFC) membrane from Hydration Technology Innovations (HTI) was used in the FO tests. A polypropylene microporous flat sheet membrane with 0.45 μm pore size was provided by 3M[®] for the MD experiment. A detailed description and SEM images of these membranes are provided in our pervious publications [3,16]. Petroleum (~18% aromatics basis, Sigma-Aldrich, boiling point 180-220 °C) and Tween 80 (average molecular weight 1310, Sigma-Aldrich) were used to prepare the synthetic produced water. Sodium chloride (NaCl), potassium chloride (KCl), lithium chloride (LiCl) and magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), were analytical reagents and were purchased from Fisher Scientific. Deionized

(DI) water -which was used as permeate to recycle in the MD part of the system and to prepare the feed and draw solutions- was provided from a Millipore Integral 10 water system (Millipore Corporation, Billerica, MA, USA).

6.3.2 FO-MD test protocol

The FO-MD experiments were conducted using the experimental set-up shown in Figure 6.1. The system consists of an FO system and an MD system connected together. The FO side of the system consists of two tanks: one for the feed solution and the other for the draw solution. The MD experiment uses the draw solution tank as the feed for the process, while the condensate is collected in the permeate tank. The FO and the MD membranes were installed in two separate and identical cell units with the same effective area of $20 \cdot 10^{-4} \text{ m}^2$. The FO and MD fluxes were calculated from the weight change of the feed solution and permeate respectively. Detailed descriptions of the individual systems are given in our previous publications [3,17].

Synthetic produced water (SPW) with a salinity of 240,000 ppm and an oil content of 100 ppm was used as the feed solution for the FO-MD experiment. The composition of the SPW was prepared based on the analysis of the PW in Iraq where some of the largest oilfields in the world are located (i.e. North Rumaila, South Rumaila, Al-Zubair and West Qurna) [18]. Emulsion was prepared by mixing the oil and the emulsifier at a ratio of 9:1 with DI water in a blender (Waring Products Division, Torrington, CT, USA) at the speed of 20,000 rpm for 3 minutes. Then, the emulsion was mixed with the solution that contains the other salts described in Table 3.2 to form the synthetic produced water. Four draw solutions (i.e. NaCl, KCl, LiCl and MgCl_2) were tested separately in FO mode (i.e., membrane active layer faces feed solution).

Figure 6.1 Schematic diagram of the FO-MD bench-scale test unit

6.4 Results and discussion

6.4.1 NaCl

Figure 6.2 shows the water flux results when using 5 M NaCl as draw solution. It can be seen that the water flux in MD is much higher (about eight times) than the water flux in FO. This large difference in water fluxes is unfavorable in the FO-MD process. During the experiment, the concentration of the draw solution increases because it becomes more concentrated by MD than it becomes diluted by FO. After four hr. of operation, the NaCl draw solution started to crystalize as it reached its solubility limit.

Figure 6.2 Water flux in FO-MD experiments. Experimental conditions: feed solution: SPW, draw solution: 5 M NaCl, permeate: DI water, feed temperature: 20 °C, draw solution temperature: 50 °C, permeate temperature: 20 °C, Cross-flow velocity of feed, draw and permeate 0.25 m.sec⁻¹. Results are an average of three experiments with different coupons. Error bars indicate standard deviation.

The difference in water fluxes can be explained by looking to the driving forces for FO and MD. The driving force in FO is quite different from the driving force in MD. FO is driven by the osmotic pressure difference across the membrane [19] while MD is driven by vapor pressure difference [20]. Figure 6.3a indicates that the osmotic pressure difference between the feed solution (SPW) and the 5 M NaCl draw solution is small explaining the low FO water flux. The vapor pressure difference between the draw solution at 50 °C and permeate at 20 °C is relatively large, which explains the high MD water flux. However, the actual driving force is less due to the temperature polarization effect [21]. Figure 6.3b shows the vapor pressures of the draw solution and permeate calculated at 44 °C and 25 °C respectively after taking the temperature polarization effect into consideration. Nevertheless, the vapor pressure difference still large enough to provide the high MD water flux.

Figure 6.3 Osmotic pressure and vapor pressure of NaCl at different concentrations. a) Vapor pressures of the draw solution and permeate are calculated at 50 °C and 20 °C respectively, b) Vapor pressures of the draw solution and permeate are calculated at 44 °C and 25 °C respectively (temperature polarization effect). Osmotic pressure of the draw solution is calculated at 50 °C and of SPW at 20 °C.

6.4.2 KCl

KCl has lower solubility than NaCl [22]; so it was tested at 4 M concentration instead of 5M as used for NaCl. The KCl draw solution provided high MD water flux. However, in FO, it was observed that the water transferred in the opposite direction (from the draw solution to the feed solution). This clearly appears in Figure 6.4 as a negative flux.

Figure 6.4 Water flux in FO-MD experiments. Experimental conditions: feed solution: SPW, draw solution: 4 M KCl, permeate: DI water, feed temperature: 20 °C, draw solution temperature: 50 °C, permeate temperature: 20 °C, Cross-flow velocity of feed, draw and permeate 0.25 m.sec⁻¹. Results are an average of three experiments with different coupons. Error bars indicate standard deviation.

The vapor pressure of the 4 M KCl draw solution is higher than that of the DI water even with the effect of temperature polarization (Figure 6.5a and Figure 6.5b). The driving force of the FO process was estimated at approximately zero where the osmotic pressure of the feed solution (SPW) and the 4 M KCl curves meet at the same point (about 200 atm). It has been reported that both external and internal concentration polarization negatively impact osmotic driving force [23]. This can explain the negative water flux in Figure 6.4.

Figure 6.5 Osmotic pressure and vapor pressure of KCl at different concentrations. a) Vapor pressures of the draw solution and permeate are calculated at 50 °C and 20 °C respectively, b) Vapor pressures of the draw solution and permeate are calculated at 44 °C and 26 °C respectively (temperature polarization effect). Osmotic pressure of the draw solution is calculated at 50 °C and of SPW at 20 °C.

6.4.3 LiCl

Lithium chloride has the advantage of enabling highly concentrated solutions (more than 14 M) [22]. LiCl as the draw solution was tested at two concentrations: 4.8 M and 10 M for 20 hr. as it is possible here to work with wide range of concentrations.

The results for the 4.8 M LiCl draw solution (Figure 6.6a) were similar to that of NaCl with a high MD flux and a low FO flux. It was also noticed that the MD flux decreases and the FO flux increases slightly with time. This is due to the fact that the concentration of the draw solution increases during the course of the experiment as a result of the faster concentration due to the higher MD flux compared to the dilution by the FO process. A completely contrary

behavior was observed with the 10 M LiCl draw solution (Figure 6.6b) with higher, but slightly decreasing flux in FO and lower, but slightly increasing flux in MD.

Figure 6.6 Water flux in FO-MD experiments. Experimental conditions: feed solution: SPW, draw solution: a) 4.8 M LiCl b) 10 M LiCl, permeate: DI water, feed temperature: 20 °C, draw solution temperature: 50 °C, permeate temperature: 20 °C, Cross-flow velocity of feed, draw and permeate 0.25 m.sec⁻¹. Results are an average of three experiments with different coupons. Error bars indicate standard deviation.

Figure 6.7a illustrates this different behavior of the LiCl draw solution in FO-MD operation. At 4.8 M LiCl, the osmotic driving force is much lower than that at 10 M LiCl while the thermal driving force is much higher. Interestingly, the 4.8 M LiCl draw solution ($TPC=0.5$) shows a more severe temperature polarization effect than the 10 M LiCl draw solution ($TPC=0.73$) as shown in Figure 6.7b and Figure 6.7c. This is mostly related to the difference in water flux. At a lower MD water flux (at 10 M LiCl) the decrease in the feed temperature at the membrane surface is less compared to the case of high water flux (4.8 M LiCl). A similar temperature polarization behavior at different concentrations for a NaCl solution was reported by Termpiyakul et al. [24].

Figure 6.7 Osmotic pressure and vapor pressure of LiCl at different concentrations. a) Vapor pressures of the draw solution and permeate are calculated at 50 °C and 20 °C respectively, b) Vapor pressures of the 4.8 M LiCl draw solution and permeate are calculated at 41 °C and 26 °C respectively (temperature polarization effect), c) Vapor pressures of the 10 M LiCl draw solution and permeate are calculated at 46 °C and 24 °C respectively (temperature polarization effect). Osmotic pressure of the draw solution is calculated at 50 °C and of SPW at 20 °C.

6.4.4 MgCl₂

Figure 6.8 presents the FO-MD results of the MgCl₂ draw solution at two concentrations: 4 M and 4.8 M. With the 4 M MgCl₂ draw solution, the MD flux was higher than the FO flux while the 4.8 M MgCl₂ draw solution showed comparable and stable flux for both FO and MD over the 20 hr. of operation. In general, the MgCl₂ draw solution has the advantage of being able to generate a high osmotic pressure as it has three ions compared to the other solutions with only two ions. It can provide more than 1000 atm at a concentration of 4.8M as seen in Figure 6.9a. Similar to LiCl, the polarization effect (Figure 6.9b and Figure 6.9c) at the 4 M was more than

that of 4.8 M. The *TPC* for the 4 M MgCl_2 solution was calculated at 0.6 whereas for the 4.8 M MgCl_2 solution it was 0.67.

Figure 6.8 Water flux in FO-MD experiments. Experimental conditions: feed solution: SPW, draw solution: a) 4 M MgCl_2 b) 4.8 M MgCl_2 , permeate: DI water, feed temperature: 20 °C, draw solution temperature: 50 °C, permeate temperature: 20 °C, Cross-flow velocity of feed, draw and permeate 0.25 m.sec⁻¹. Results are an average of three experiments with different coupons. Error bars indicate standard deviation.

Figure 6.9 Osmotic pressure and vapor pressure of MgCl_2 at different concentrations. a) Vapor pressures of the draw solution and permeate are calculated at 50 °C and 20 °C respectively, b) Vapor pressures of the 4 M MgCl_2 draw solution and permeate are calculated at 42 °C and 24 °C respectively (temperature polarization effect), c) Vapor pressures of the 4.8 M MgCl_2 draw solution and permeate are calculated at 43 °C and 23 °C respectively (temperature polarization effect). Osmotic pressure of the draw solution is calculated at 50 °C and of SPW at 20 °C.

6.5 Discussion

Neither FO nor MD can be used alone to treat the hyper-saline PW. FO is only producing a diluted draw solution that needs to be treated to extract the pure water from it. The hydrophobic nature of the MD membrane makes it highly susceptible to fouling. We have tested MD with the SPW as the feed and we noticed that the conductivity of permeate increased rapidly after some minutes. This indicates that the membrane was wetted and lost all of its selectivity due to the existence of the oil in the feed solution. Placing an FO unit up front as a pretreatment step can protect the MD from fouling. MD revealed near complete rejection with the all four tested draw solutions and produced high-quality water with a conductivity of about two micro Siemens.

To achieve a stable operation in FO-MD, it is necessary to get similar transfer rates in both FO and MD so the water transferred by FO is extracted by MD at the same rate. Otherwise, the draw solution either will be diluted and lose its osmotic efficiency or concentrated until reaching saturation. The MgCl_2 draw solution at a concentration of 4.8 M showed the best results with no significant decrease or increase in flux during the time of the experiment. This is applicable when using FO and MD modules with the same effective membrane area. Otherwise, the transfer rates can be balanced by changing the membrane areas. If the FO is the slowest step, FO membrane area has to be increased and if the MD is the slowest step, the MD membrane area has to be increased.

To make a comparison, the four draw solutions have been tested in FO-MD operation at the same concentration. The maximum common concentration that can be prepared is 4.8 M. The

order of the FO water fluxes (Figure 6.10) follows the same order of the osmotic pressures of these solutions.

As stated above, the driving force for the MD process is the vapor pressure difference across the membrane. To discuss the difference in vapor pressure between the different solutions at the same concentration, the hydrated radius and the hydration free energy of the ions should be considered. Ions with higher hydra-ability (larger hydrated radius) would require more hydration free energy and so it will have lower water activity [25,26]. It can be concluded from Table 6.1 that the water activity of the draw solutions lies in the following order: $\text{KCl} > \text{NaCl} > \text{LiCl} > \text{MgCl}_2$. The Mg^{+2} ion has a much higher hydration free energy compared to the other ions. This explains the low vapor pressure of the MgCl_2 draw solution and hence the lower MD water flux. Moreover, the difference in viscosity of the draw solutions (Figure 6.11) can also explain the difference in MD water flux. MgCl_2 has a much higher viscosity than the other solutions. A high viscosity increases the temperature polarization effect as it reduces the heat transfer coefficient on the hot solution side of MD.

Figure 6.10 Water flux in FO-MD experiments of the different draw solutions. Experimental conditions: feed solution: SPW, permeate: DI water, feed temperature: 20 °C, draw solution temperature: 50 °C, permeate temperature: 20 °C, Cross-flow velocity of feed, draw and permeate 0.25 m.sec⁻¹. Results are an average of three experiments with different coupons. Error bars indicate standard deviation.

Table 6.1 Hydrated radius and hydration free energy of the different ions of the different ions [27].

	Hydrated radius (nm)	Hydration free energy (KJ/mol)
Li ⁺	0.36	-530
Mg ⁺²	0.43	-1900
Na ⁺	0.3	-400
K ⁺	0.23	-300

The hydration free energies are negative as this is always an exothermic process.

Figure 6.11 Viscosities of the different draw solutions at concentration of 4.8M and temperature of 50 °C.

6.6 Conclusions

In this chapter, the performance of a hybrid FO-MD process in the treatment of hyper-saline produced water is reported. Results show that the FO-MD process can produce high-quality water from highly polluted wastewater streams. The performance of the FO-MD process was evaluated using four different draw solutions (i.e. NaCl, KCl, MgCl₂ and LiCl) and commercially available membranes (HTI-TFC membrane for FO and 3M-PP membrane for MD). There was a substantial difference between the FO and the MD water flux for the tested draw solutions and this difference was attributed to the difference in osmotic pressure and vapor

pressures of these draw solutions respectively. The 4.8 M MgCl_2 draw solutions showed the best performance with stable fluxes for both FO and MD for 20 hr. of operation.

6.7 References

- [1] M. Çakmakce, N. Kayaalp, I. Koyuncu, Desalination of produced water from oil production fields by membrane processes, *Desalination*. 222 (2008) 176–186. doi:10.1016/j.desal.2007.01.147.
- [2] C. Clark, J. Veil, Produced water volumes and management practices in the United States., (2009). <http://www.osti.gov/scitech/biblio/1007397> (accessed January 28, 2016).
- [3] M. Al-Furaiji, N. Benes, A. Nijmeijer, J. McCutcheon, Application of direct contact membrane distillation for treating high salinity solutions: Impact of membrane structure and chemistry, Unpublished. (2016).
- [4] S. Zhang, P. Wang, X. Fu, T.-S. Chung, Sustainable water recovery from oily wastewater via forward osmosis-membrane distillation (FO-MD), *Water Res.* 52 (2014) 112–121. doi:10.1016/j.watres.2013.12.044.
- [5] M. Xie, L.D. Nghiem, W.E. Price, M. Elimelech, S. Water, N. Haven, Toward Resource Recovery from Wastewater: Extraction of Phosphorus from Digested Sludge Using a Hybrid Forward Osmosis–Membrane Distillation Process, *Environ. Sci. Technol. Lett.* 1 (2014) 191–195. doi:10.1021/ez400189z.
- [6] T. Husnain, Y. Liu, R. Riffat, B. Mi, Integration of forward osmosis and membrane distillation for sustainable wastewater reuse, *Sep. Purif. Technol.* (2015). doi:10.1016/j.seppur.2015.10.031.
- [7] C.R. Martinetti, A.E. Childress, T.Y. Cath, High recovery of concentrated RO brines using forward osmosis and membrane distillation, *J. Memb. Sci.* 331 (2009) 31–39. doi:10.1016/j.memsci.2009.01.003.
- [8] M. Xie, L.D. Nghiem, W.E. Price, M. Elimelech, A forward osmosis-membrane distillation hybrid process for direct sewer mining: System performance and limitations, *Environ. Sci. Technol.* 47 (2013) 13486–13493. doi:10.1021/es404056e.
- [9] Q. Ge, P. Wang, C. Wan, T.-S. Chung, Polyelectrolyte-Promoted Forward Osmosis–Membrane Distillation (FO–MD) Hybrid Process for Dye Wastewater Treatment, (n.d.). doi:10.1021/es300784h.
- [10] K.Y. Wang, M.M. Teoh, A. Nugroho, T.S. Chung, Integrated forward osmosis-membrane distillation (FO-MD) hybrid system for the concentration of protein solutions, *Chem. Eng. Sci.* 66 (2011) 2421–2430. doi:10.1016/j.ces.2011.03.001.
- [11] R. Robinson, R. Stokes, *Electrolyte solutions*, 2nd ed., Dover, New york, 2002.
- [12] E. Clarke, D. Glew, Evaluation of the thermodynamic functions for aqueous sodium chloride from equilibrium and calorimetric measurements below 154 C, *Phys. Chem. Ref. Data*. 14 (1985) 489–610.
- [13] J. Dean, *Lange’s Handbook of Chemistry.*, New york, 1999. doi:10.1080/10426919008953291.
- [14] K.R. Patil, A.D. Tripathi, G. Pathak, S.S. Katti, Thermodynamic properties of aqueous electrolyte solutions. 2. Vapor pressure of aqueous solutions of sodium bromide, sodium iodide, potassium chloride, potassium bromide, potassium iodide, rubidium chloride, cesium chloride, cesium bromide, cesium iodide, *J. Chem. Eng. Data*. 36 (1991) 225–230. doi:10.1021/je00002a021.
- [15] K.R. Patil, A.D. Tripathi, G. Pathak, S.S. Katti, Thermodynamic properties of aqueous electrolyte solutions. 1. Vapor pressure of aqueous solutions of lithium chloride, lithium bromide, and lithium iodide, *J. Chem. Eng. Data*. 35 (1990) 166–168. doi:10.1021/je00060a020.
- [16] J. Ren, J.R. McCutcheon, A new commercial thin film composite membrane for forward osmosis, *Desalination*. 343 (2014) 187–193. doi:10.1016/j.desal.2013.11.026.
- [17] M. Al-Furaiji, J. Arena, M. Chowdhury, N. Benes, A. Nijmeijer, J. McCutcheon, Use of Forward Osmosis in Treatment of Hyper-Saline Iraqi Produced Water, Unpublished. (2016).
- [18] M.S. Al-Rubaie, M.A. Dixon, T.R. Abbas, Use of flocculated magnetic separation technology to treat Iraqi oilfield co-produced water for injection purpose, *Desalin. Water. Treat.*, 53 (2015) 2086–2091. doi:10.1080/19443994.2013.860400.

- [19] T.Y. Cath, A.E. Childress, M. Elimelech, Forward osmosis: Principles, applications, and recent developments, *J. Memb. Sci.* 281 (2006) 70–87. doi:10.1016/j.memsci.2006.05.048.
- [20] A. Alkhudhiri, N. Darwish, N. Hilal, Membrane distillation: A comprehensive review, *Desalination*. 287 (2012) 2–18. doi:10.1016/j.desal.2011.08.027.
- [21] M. Qtaishat, T. Matsuura, B. Kruczek, M. Khayet, Heat and mass transfer analysis in direct contact membrane distillation, *Desalination*. 219 (2008) 272–292. doi:10.1016/j.desal.2007.05.019.
- [22] W.M. Haynes, *Handbook of Chemistry and Physics*, 96th ed., CRC press, 2015.
- [23] J.R. McCutcheon, R.L. McGinnis, M. Elimelech, Desalination by ammonia-carbon dioxide forward osmosis: Influence of draw and feed solution concentrations on process performance, *J. Memb. Sci.* 278 (2006) 114–123. doi:10.1016/j.memsci.2005.10.048.
- [24] P. Termpiyakul, R. Jiratananon, S. Srisurichan, Heat and mass transfer characteristics of a direct contact membrane distillation process for desalination, *Desalination*. 177 (2005) 133–141. doi:10.1016/j.desal.2004.11.019.
- [25] J. Li, Y. Guan, F. Cheng, Y. Liu, Treatment of high salinity brines by direct contact membrane distillation: Effect of membrane characteristics and salinity, *Chemosphere*. 140 (2015) 143–149. doi:10.1016/j.chemosphere.2014.12.006.
- [26] Y. Guan, J. Li, F. Cheng, J. Zhao, X. Wang, Influence of salt concentration on DCMD performance for treatment of highly concentrated NaCl, KCl, MgCl₂ and MgSO₄ solutions, *Desalination*. 355 (2015) 110–117. doi:10.1016/j.desal.2014.10.005.
- [27] B. Tansel, Significance of thermodynamic and physical characteristics on permeation of ions during membrane separation: Hydrated radius, hydration free energy and viscous effects, *Sep. Purif. Technol.* 86 (2012) 119–126. doi:10.1016/j.seppur.2011.10.033.

7

Reflections & Outlook

7.1 Reflections

7.1.1 Reflections on produced water management

Co-producing water during oil and gas extraction operations is often inevitable. The possible options for produced water management include: inject the produced water into the same formation, discharge produced water to the surface or purify it for beneficial use. All options require some level of treatment. To use produced water for injection purposes, softening treatment¹ is necessary to avoid problems in pumping and piping. Also, discharging produced water to the surface needs treatment to meet the onshore and offshore water disposal regulations. Using produced water for beneficial uses requires more extensive treatment depending on the quality of produced water and the target application. For better management of produced water in a specific area, the spatial distribution of water scarcity in this area and its relation to the locations where produced water is generated should be evaluated. In this thesis, implementation of oilfield produced water as a new water resource in the south of Iraq is studied. In chapter 2, water demand and supply in the southern provinces of Iraq was estimated to quantify water scarcity. In general, water is consumed mainly by domestic use, irrigation, livestock and industry. The results show that irrigation accounts for about 81 % of the total water demand in the southern region. Also, a total water shortage was estimated at 430 Mm³/year in the south of Iraq. At the same time, a huge amount of waste water is generated every day during oil extraction especially if we know that more than 3 million barrels of oil per day are produced in the southern region. Currently, the fresh water used for above described purposes is the surface water in the area represented by the two rivers: the Tigris and the Euphrates. The results showed that two out of the four southern provinces (Dhi Qar and

¹ Softening is the removal of ions (like Ca⁺² and Mg⁺²) that result in water hardness and cause scaling problems.

Maysan) have no water shortage while the other two provinces (Al Basrah and Al Muthanna) have severe water deficit. A proper management of the available water resources and using unconventional water resources (like produced water) can solve the water shortage in the area. Reallocation of the water quotas among the four provinces can ensure fair distribution of the available fresh water. Considering water resources other than the two rivers (e.g. ground water, marsh water and produced water) can also contribute to reducing the water shortage.

7.1.2 Reflections on forward osmosis

Forward osmosis has been studied in the literature for feed solutions with salinities less than 100,000 mg/L. However, FO has the potential to treat solutions with higher concentrations. In this thesis (chapter 3), forward osmosis was tested in the treatment of produced water with an elevated level of salinity of up to 240,000 mg/L. An ammonia-carbon dioxide ($\text{NH}_3\text{-CO}_2$) draw solution showed poor performance compared to magnesium chloride (MgCl_2). In the case of the ammonia-carbon dioxide draw solution, calcium carbonate (CaCO_3) scaling (that is forming from the interaction between the calcium ion that exists in the feed solution with the carbonate ion from the draw solution) leads to a reduction in water flux. Moreover, the pH increase of the feed solution associated with the $\text{NH}_3\text{-CO}_2$ draw solution enhances scaling deposition as it significantly affects the solubility of calcium carbonate. It can be concluded here that the $\text{NH}_3\text{-CO}_2$ draw solution is not suitable for treating any streams that contain a high concentration of calcium ions. A better FO performance with higher water flux and no scaling was observed when using MgCl_2 as a draw solution. In general, inorganic based draw solutions would be more suitable for the treatment of the hyper-saline produced water.

7.1.3 Reflections on membrane distillation

One of the limiting factors that affect the development of forward osmosis is the reclamation of the draw solution. In chapter 4, direct contact membrane distillation (DCMD) is examined

for the separation of the inorganic-based draw solutions (i.e. NaCl, KCl and MgCl_2) of FO using commercial membrane distillation membranes. The results showed that DCMD has the ability to treat highly concentrated solutions with almost complete salt rejection. However, the different solutions showed different performance regarding water flux. The vapor pressure and the viscosity of the solution determine the DCMD water flux when using the same membrane. Also, the membrane structure plays a crucial role in the performance of DCMD for a given draw solution. The thickness of the membrane should be selected carefully to assure good thermal insulation and high mass transfer rate. The pore size difference between the tested commercial MD membranes (within the range of 0.1-0.45 micron) showed minimal effect on the DCMD water flux. A membrane with a higher porosity provides more evaporation surface area for diffusion and will hence show a higher water flux. The highest porosity for a commercial membrane that was available was 85 % for polypropylene (PP) membrane from 3M. However, membranes with a higher porosity of up to 90 % can be prepared by electrospinning [1,2]. In chapter 5, hydrophobic electrospun PVDF nanofibers for DCMD were prepared. The electrospun PVDF nanofibers lack mechanical strength. Hence robust PES commercial nanofibers were used to support the PVDF nanofibers to fabricate a triple-layer membrane. The triple-layer membrane consists of a PES layer in the middle and electrospun PVDF nanofibers on both sides of the PES layer. The fabricated membrane showed better DCMD performance (higher water flux) compared to the commercial PVDF membrane.

7.1.4 Reflections on Produced water treatment

The treatment of produced water using a continuous FO-MD process was studied in chapter 6. The performance of four draw solutions (NaCl, KCl, LiCl, and MgCl_2) was examined in FO-MD. FO is driven by the difference in the osmotic pressure across the membrane while MD is driven by the difference in vapor pressure. This difference in driving forces results in different

behavior of the different draw solutions in the FO-MD operation. Draw solutions with solubility below 6 M which consist of two ions like NaCl and KCl are not suitable for treatment of high salinity streams in FO-MD because they cannot generate the required osmotic pressure for the FO process. At a given concentration, solutions with three ions like MgCl_2 provide higher osmotic pressures and consequently a higher FO water flux. LiCl can be prepared at very high concentrations up to 14 M. However, at high concentrations the vapor pressure decreases and leads to a low MD water flux. MgCl_2 at a concentration of 4.8 M showed the best performance with comparable water fluxes in both FO and MD. The FO-MD process showed 100 % rejection of oil and salts and no change in conductivity of permeate was observed during the 20 hr. of operation, hence showing excellent desalination performance.

7.2 Outlook

The focus of this thesis was on the southern region of Iraq where most of the Iraqi oil is produced. Further research on management of produced water can be broader to include the whole country. The overall oil production in Iraq has started to be increased in the last few years as the average daily production in the northern region of the country (Kurdistan) developed to reach about 600,000 barrels of oil per day in January 2016. Estimation of water demands and supply in the northern region would contribute to better water management practices in the region and then the whole country. Studies on the quantity and quality of produced water in the northern oilfields is necessary as there is not enough information in the literature about it.

Treatment of hyper-saline produced water was investigated experimentally in this thesis using the FO-MD process. Even though the $\text{NH}_3\text{-CO}_2$ draw solution has the advantage of enabling cost-efficient recovery, it was not efficient enough to treat the hyper-saline produced water. However, some steps can be studied to improve the FO process using the $\text{NH}_3\text{-CO}_2$ draw solution. Buffering the feed solution at a pH lower than 6 will increase the solubility of CaCO_3

and reduce its deposition on the membrane surface. Also, a pre-treatment step to reduce the concentration of Ca^{2+} can improve the FO performance by avoiding scale formation.

Efforts can be directed towards testing more draw solutions with different properties in the treatment of hyper-saline produced water. This includes (but is not limited to): switchable polarity solvents (SPS), magnetic nanoparticles (MNPs) draw solution, trimethylamine (TMA) and EDTA sodium salt. SPS draw solutions consist of mixtures of carbon dioxide, water, and tertiary amines. The SPS can be regenerated by the reversible transition from miscibility with water to immiscibility by removing carbon dioxide from the solution at moderate temperature (60 °C) and the existence of nitrogen gas [3]. MNPs have the benefit of being easily collected and separated from water using magnetic field [4]. TMA is a thermolytic draw solution with molecules larger than ammonia, so it is expected to be better retained by the membrane in forward osmosis [5]. This feature could be beneficial for decreasing the scaling of CaCO_3 that is affected by the reverse ammonia flux. EDTA sodium salt has a large size that can be separated by nanofiltration [6]. However, the relatively low solubility (~1 M) of the EDTA sodium salt can be a drawback for using it in the treatment of highly concentrated solutions.

The use of electrospun PVDF nanofiber membranes in membrane distillation was studied in this thesis. A lot of research can still be done on using various hydrophobic polymers (e.g. Polytetrafluoroethylene (PTFE), polypropylene (PP) and ethylene chloro trifluoro ethylene (ECTFE)) to make high porosity nanofiber based membranes. Hydrophilic polymers (e.g. polyacrylonitrile (PAN), polyvinylalcohol (PVA) and Nylon) can also be used in membrane distillation if a proper modification to enhance the hydrophobicity is applied. Some of the proposed modification methods include chemical vapor deposition and plasma deposition using appropriate materials for a coating that can change the surface to hydrophobic like hexyl acrylate [7] and poly divinylbenzene [8]. Also, there are some nanoparticles like carbon

nanotubes (that can be incorporated into the polymer solution before electrospinning) that enhance the hydrophobicity and mechanical strength of the membrane.

The DCMD configuration was studied in this thesis in the FO-MD process and showed good performance. However, studying the other MD configurations (i.e. air gap membrane distillation (AGMD), sweeping gas membrane distillation (SGMD) and vacuum membrane distillation (VMD)) in an FO-MD setup will add more knowledge to the field.

The synthetic produced water with high salinity was treated in a lab-scale FO-MD set up for 20 hr. of operation. Long term studies on using FO-MD in a larger scale (i.e. pilot plant) is highly recommended.

Finally, a comparison between the FO-MD process and the thermal distillation processes for the treatment of hyper-saline produced water is needed. This is can be done by conducting energy and cost (both capital and operational costs) analysis of the FO-MD process on pilot testing and compare them to those of the thermal processes that are available in the literature [9–11]. The FO-MD process works at ambient pressure and relatively low temperatures (compared to the thermal processes) so it is anticipated to be more cost effective than the thermal desalination processes.

7.3 References

- [1] M. Essalhi, M. Khayet, Self-sustained webs of polyvinylidene fluoride electrospun nanofibers at different electrospinning times: 1. Desalination by direct contact membrane distillation, *J. Memb. Sci.* 433 (2013) 167–179. doi:10.1016/j.memsci.2013.01.023.
- [2] M. Essalhi, M. Khayet, Self-sustained webs of polyvinylidene fluoride electrospun nano-fibers: Effects of polymer concentration and desalination by direct contact membrane distillation, *J. Memb. Sci.* 454 (2014) 133–143. doi:10.1016/j.memsci.2013.11.056.
- [3] M.L. Stone, C. Rae, F.F. Stewart, A.D. Wilson, Switchable polarity solvents as draw solutes for forward osmosis, *Desalination*. 312 (2013) 124–129. doi:10.1016/j.desal.2012.07.034.
- [4] M.M. Ling, K.Y. Wang, T. Chung, Highly Water-Soluble Magnetic Nanoparticles as Novel Draw Solutes in Forward Osmosis for Water Reuse, (2010) 5869–5876. doi:10.1021/ie100438x.
- [5] C. Boo, Y.F. Khalil, M. Elimelech, Performance evaluation of trimethylamine-carbon dioxide thermolytic draw solution for engineered osmosis, *J. Memb. Sci.* 473 (2015) 302–309. doi:10.1016/j.memsci.2014.09.026.
- [6] N.T. Hau, S.S. Chen, N.C. Nguyen, K.Z. Huang, H.H. Ngo, W. Guo, Exploration of EDTA sodium salt as novel draw solution in forward osmosis process for dewatering of high nutrient sludge, *J. Memb. Sci.* 455 (2014) 305–311. doi:10.1016/j.memsci.2013.12.068.
- [7] A. Suresh, D. Anastasio, D.D. Burkey, Potential of hexyl acrylate monomer as an initiator in photo-initiated CVD, *Chem. Vap. Depos.* 20 (2014) 5–7. doi:10.1002/cvde.201304322.
- [8] A. Asatekin, K.K. Gleason, Polymeric nanopore membranes for hydrophobicity-based separations by conformal initiated chemical vapor deposition, *Nano Lett.* 11 (2011) 677–686. doi:10.1021/nl103799d.
- [9] H. Ettouney, Design of single-effect mechanical vapor compression, *Desalination*. 190 (2006) 1–15. doi:10.1016/j.desal.2005.08.003.
- [10] M. Al-Shammiri, M. Safar, Multi-effect distillation plants: state of the art, *Desalination*. 126 (1999) 45–59. doi:10.1016/S0011-9164(99)00154-X.
- [11] O.A. Hamed, M.A.K. Al-Sofi, M. Imam, G.M. Mustafa, K. Ba Mardouf, H. Al-Washmi, Thermal performance of multi-stage flash distillation plants in Saudi Arabia, *Desalination*. 128 (2000) 281–292. doi:10.1016/S0011-9164(00)00043-6.

Summary

Summary

The treatment of hyper-saline produced water using a forward osmosis- membrane distillation (FO-MD) process is studied in this thesis.

In **chapter 1**, both thermal and membrane desalination processes were discussed and the pros and cons of these processes for the treatment of high salinity water streams were presented. A special emphasis was given to the forward osmosis and membrane distillation processes as the most suitable solutions for the treatment of hyper-saline produced water.

In **chapter 2**, an estimation of water resources in the south of Iraq and the water demands was made to calculate the water deficit in the region. The results showed that a water shortage of 430 Mm³/year was estimated in the southern four provinces in Iraq. Some water management solutions including the use of produced water were proposed to compensate water shortage in this oil-rich region. The region contains some of the largest oilfields in the world with oil production of more than 3 million barrel per day. Treatment of the water co-produced with oil in the south of Iraq is quite challenging due to its high salinity.

In **chapter3**, forward osmosis (FO) was investigated in the treatment of hyper-saline produced water. Two draw solutions from different categories were tested in this chapter: thermolytic (ammonia (NH₃) -carbon dioxide (CO₂)) based draw solutions and electrolyte (magnesium chloride (MgCl₂)) based draw solutions. Severe scaling effects were observed when using the NH₃-CO₂ draw solution which resulted in a reduction in the forward osmosis water flux. Calcium carbonate (CaCO₃) was the main component that caused the observed scaling and the formation of the calcium carbonate was enhanced by the pH increase of the feed solution. The MgCl₂ draw solution provided a relatively higher water flux (4 L.m⁻².hr⁻¹) compared to the water flux (1 L.m⁻².hr⁻¹) of the NH₃-CO₂ draw solution with no scaling effect. Also, the NH₃-CO₂ draw solution has the disadvantage of a high reverse ammonia flux to the feed solution.

The loss in ammonia needs to be replaced adding more cost to the process. Besides, the transport of ammonia to the feed side of the membrane causes a pH increase at the feed side which enhances CaCO_3 scaling. Therefore, MgCl_2 was chosen as a better candidate for the treatment of hyper-saline produced water using a forward osmosis process. The following step was to study the recovery of the draw solution. Direct contact membrane distillation (DCMD) has the ability to separate highly concentrated inorganic solutions and was therefore chosen as the process to be studied further.

In **chapter 4**, three different commercial membranes (PVDF, PP, and ECTFE) were studied for the treatment of highly concentrated solutions (MgCl_2 , NaCl and KCl) using DCMD. The impact of the membrane properties (pore size, porosity, thickness and material of the membrane) was investigated. The ECTFE membrane showed the highest flux followed by the PP membrane with a slightly lower flux and then the PVDF membrane with much lower flux. This difference in water flux is attributed to the difference in porosity and thickness of the used membrane. Membranes with higher porosity provide higher evaporation surface area and consequently higher mass transfer rate (water flux). A thinner membrane is favorable in terms of water flux as it has lower resistance to the mass transfer. However, in terms of thermal insulation, temperature polarization effects will be more pronounced in thinner membranes. The pore size of the membrane, studied in the range from 0.45 to 0.1 micron, has a minimal effect on water flux. The water flux for the different draw solutions was in the following order: $\text{KCl} > \text{NaCl} > \text{MgCl}_2$. This order is compatible with the order of the vapor pressures of the named solutions. All the tested membranes showed high salt rejections (higher than 99.5%).

In **chapter 5**, triple-layer nanofibrous membranes were prepared and tested in DCMD for treating highly concentrated salt solutions. The fabricated membranes consist of a core PES commercial nanofiber mat and an electrospun PVDF nanofiber layer on both sides of the membrane. The objective of this chapter was to prepare robust hydrophobic membranes with

high porosity for DCMD applications. The here developed triple-layer membrane showed higher performance compared to the commercial PVDF membrane for the treatment of 5 M NaCl. The membrane with a thickness of 115 micron exhibited the best performance. The 85 and 145 micron membranes showed a similar, but lower, water flux due to the conflict between mass transfer and thermal insulation for the membranes with different thicknesses.

In **chapter 6**, synthetic produced water was treated using an integrated FO-MD process. Four draw solutions (NaCl, KCl, MgCl₂, and LiCl) were used in the FO-MD process. The optimum draw solution gives comparable water fluxes in both FO and MD when using membrane modules with an identical membrane area. The NaCl and KCl draw solutions showed poor performance in the FO-MD process as they provided a low or negative FO water flux and a high MD water flux. The MgCl₂ draw solution with a concentration of 4.8 M showed excellent performance with a stable water flux of about 4 (L.m⁻².hr⁻¹). The LiCl draw solution can be prepared at elevated levels of concentrations due to its high solubility. At 4.8 M, the MD water flux was much higher than the FO water flux. However, at a concentration of 10 M, the LiCl draw solution showed a relatively high water flux in FO and a low MD water flux.

Chapter 7 presented the reflections of the knowledge obtained in this thesis on management and treatment of hyper-saline produced water. The results proved the feasibility of treating waste streams with extremely high salinity (240,000 ppm). The treated water can be used in different beneficial applications like irrigation, injection to enhance oil recovery and even as drinking water. Finally, some recommendations and ideas for a future work were given to contribute to the continuity of investigations in produced water management and treatment.

Samenvatting

Samenvatting

Deze thesis gaat over de verwerking van extreem zout water afkomstig uit oliewinning (*hyper-saline produced water*) met een proces waarin voorwaartse osmose en membraandestillatie wordt gecombineerd.

In **Hoofdstuk 1** worden warmte- en membraangebaseerde ontzoutingsprocessen bekeken, en de voor- en nadelen van elk proces tegen elkaar afgewogen. De nadruk ligt op voorwaartse osmose- en membraandestillatieprocessen, die worden gezien als de best beschikbare technieken voor de behandeling van extreem zout water uit oliewinning.

In **Hoofdstuk 2** wordt het watertekort in het zuiden van Irak geschat door de hoeveelheid beschikbaar water af te zetten tegen de waterbehoefte. Het watertekort berekend voor de vier zuidelijke provincies van Irak is 430 miljoen m³ per jaar. Om dit tekort te verminderen worden in dit hoofdstuk een aantal watermanagementoplossingen voorgesteld, waaronder het gebruik van bij oliewinning geproduceerd water. De regio beschikt over enkele van 's werelds grootste olievelden en produceert meer dan drie miljoen vaten olie per dag, en daarbij wordt ook een grote hoeveelheid water geproduceerd. Om dit water geschikt te maken voor gebruik als drinkwater is ontzouting nodig, echter zorgt de hoge zoutconcentratie in het geproduceerde water voor een aantal uitdagingen.

In **Hoofdstuk 3** worden experimenten beschreven waarbij osmose wordt gebruikt om extreem zout geproduceerd water te ontzilten. Twee werkoplossingen van verschillende categorieën worden behandeld in dit hoofdstuk; de eerste op basis van thermolyse, waarbij ammonia (NH₃) en koolstofdioxide (CO₂) met elkaar reageren, en een andere op basis van elektrolyten, in dit geval magnesiumchloride (MgCl₂). Met de MgCl₂-werkoplossing kon een flux van 4 L.m⁻².h⁻¹ worden behaald, terwijl de NH₃-CO₂ werkoplossing een maximale flux van 1 L.m⁻².h⁻¹ liet zien. Tijdens het gebruik van de NH₃-CO₂ werkoplossing in een voorwaarts

osmoseproces bleek veel ammonia vanuit de werkoplossing de zoutwaterstroom in te stromen. De vorming van calciumcarbonaat (CaCO_3 , het hoofdbestanddeel van de kalkaanslag) werd bevorderd door een verhoging van de pH van de zoutwaterstroom, waardoor de flux omlaagging. Het vervangen van de op deze manier verloren ammonia zorgt tevens voor extra kosten. MgCl_2 werd gekozen als de betere kandidaat van de twee voor ontzilting van extreem zout geproduceerd water door middel van voorwaartse osmose.

In **Hoofdstuk 4** worden drie verschillende commercieel verkrijgbare polymeren (PVDF, PP and ECTFE) vergeleken bij toepassing in direct-contact membraandestillatie (DCMD). Deze techniek werd toegepast om sterk geconcentreerde oplossingen van MgCl_2 , NaCl en KCl in water te ontzilten. De impact van drie membraaneigenschappen, te weten poriegrootte, porositeit, en dikte, werd bestudeerd voor ieder van deze materialen. Het ECTFE-membraan had de hoogste flux van deze materialen, kort gevolgd door PP; PVDF had een veel lagere flux. Het gemeten verschil in waterflux wordt toegeschreven aan verschillen in porositeit en dikte van de gebruikte membranen. Zo heeft een poreuzer membraan een grotere oppervlakte voor verdamping, en dus een hogere massaoverdrachtssnelheid. Een dunner membraan is gunstig voor de waterflux vanwege de lagere weerstand tegen massaoverdracht, daarentegen zijn temperatuurpolarisatie-effecten van grotere invloed in dunnere membranen. De poriegrootte van de membranen was in deze studie tussen 0.45 en 0.1 micron en bleek een zeer klein effect op de waterflux te hebben. De waterflux in een membraan bleek evenredig met de dampspanningen van de werkoplossingen: $\text{KCl} > \text{NaCl} > \text{MgCl}_2$. Alle geteste membranen hadden een zoutretentie van meer dan 99.5 %.

In **Hoofdstuk 5** is de productie en analyse van nanofibreuze membranen van drie lagen dik beschreven. Deze membranen bestaan uit een kern van een commercieel verkrijgbare PES nanovezel mat met aan beide zijden daarvan een nanofibreuze PVDF laag gemaakt door middel van elektrospinning. Het doel van dit hoofdstuk was om robuuste hydrofobe membranen met

een hoge porositeit te produceren die geschikt zijn voor toepassing in DMCD-processen. Het in dit hoofdstuk beschreven drielaagsmembraan presteerde beter voor ontzilting van een 5 M NaCl-oplossing dan een commercieel verkrijgbaar PVDF-membraan. Het membraan met een dikte van 115 micron liet iets betere resultaten zien dan de membranen met dikten van 85 en 145 micron. Een dikte van 115 micron bleek het beste compromis tussen een snelle massaoverdracht en een goede thermische isolatie.

Hoofdstuk 6 beschrijft ontzilting van een modeloplossing van geproduceerd water met behulp van een geïntegreerd proces bestaande uit voorwaartse osmose (FO) en membraandestillatie (MD). Vier werkoplossingen (NaCl, KCl, MgCl_2 and LiCl) werden met elkaar vergeleken; een optimale werkoplossing zou een vergelijkbare flux moeten geven in beide processen bij gebruik van membranen met identieke oppervlakte. De NaCl en KCl werkoplossing bleken niet de beste oplossing te bieden: beiden hadden een lage of negatieve FO waterflux en een hoge MD waterflux. De MgCl_2 -werkoplossing met een concentratie van 4.8 M had een hoge en stabiele waterflux van 4 ($\text{L}\cdot\text{m}^{-2}\cdot\text{hr}^{-1}$). De concentratie van LiCl-werkoplossingen kan hoog zijn door de goede oplosbaarheid van LiCl in water. Bij een concentratie van 4.8 M was de MD-waterflux veel hoger dan de FO-waterflux, maar bij een concentratie van 10 M was de waterflux van FO relatief hoog en die van MD relatief laag.

Hoofdstuk 7 reflecteert op de in deze thesis opgedane kennis over management en verwerking van extreem zout geproduceerd water. De resultaten van de experimenten laten zien dat water met een extreem hoge zoutconcentratie van 240.000 ppm ontzilt kan worden. Het ontzilte water kan worden geïnjecteerd om meer olie uit bestaande bronnen te halen, gebruikt worden voor irrigatie, en is zelfs geschikt als drinkwater. Tenslotte worden enkele aanbevelingen gegeven en ideeën aangedragen voor toekomstig werk op het gebied van management en verwerking van geproduceerd water.

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Mustafa Al-Furaiji was born the 8th of April 1979 in Baghdad, Iraq. He obtained his bachelor in chemical engineering from university of Baghdad in June 2002. In 2003, he started working as a process engineer in the ministry of science and technology (MOST) in Iraq. He obtained his Master degree in chemical engineering from university of Baghdad in September 2009 with a graduation project on using forward osmosis in water treatment. From 2009 to 2011, Mustafa worked in MOST in the department of water treatment as a senior engineer. In 2011, he received a scholarship from the higher committee of education development in Iraq HCED to undertake a Ph.D. at the University of Twente under supervision of Prof. Arian Nijmeijer and Prof. Suzanne Hulscher. As a part of his Ph.D., he worked two years as a visiting scholar at the University of Connecticut in Storrs, USA, under supervision of Prof. Jeffrey McCutcheon. His Ph.D. research was focusing on treatment of hyper-saline produced water using forward osmosis-membrane distillation process.

Publications

- [1] **M. Al-Furaiji**, U. Karim, D. Augustijn, B. Waisi, S. Hulscher, *Evaluation of water demand and supply in the south of Iraq*, **Journal of Water Reuse and Desalination**. 6 (2016) 214-226. doi:10.2166/wrd.2015.043.
- [2] B. Waisi, U. Karim, D. Augustijn, **M. Al-Furaiji**, S. Hulscher, *A study on the quantities and potential use of produced water in southern Iraq*, **Water Science and Technology: Water Supply**. 15 (2015) 370-376. doi:10.2166/ws.2014.122.
- [3] **M. Al-Furaiji**, J. Arena, M. Chowdhury, N. Benes, A. Nijmeijer, J. McCutcheon, *Use of Forward Osmosis in Treatment of Hyper-Saline Iraqi Produced Water*, to be submitted.
- [4] **M. Al-Furaiji**, N. Benes, A. Nijmeijer, J. McCutcheon, *Application of direct contact membrane distillation for treating high salinity solutions: Impact of membrane structure and chemistry*, submitted to **Journal of Separation and Purification Technology**.

- [5] **M. Al-Furaiji**, J. Arena, J. Ren, N. Benes, A. Nijmeijer, J. McCutcheon, *Triple layer nanofiber membrane for treating high salinity brines using direct contact membrane distillation*, to be submitted.
- [6] **M. Al-Furaiji**, N. Benes, A. Nijmeijer, J. McCutcheon, *Use of a FO-MD integrated process in the treatment of high salinity produced water*, to be submitted.
- [7] **M. Al-Furaiji**, **M. Worthington**, D. Burkey, J. McCutcheon, A. Suresh, *Using iCVD to Functionalize Hydrophilic Electrospun Nanofibers for Membrane Distillation Applications*, submitted to **Journal of Membrane Science**.
- [8] M. Leitch, **M. Al-Furaiji**, Y. Zhao, , G. Lowry, J. McCutcheon, M. Mauter, *Improved prediction of membrane distillation flux for fibrous membranes using Buckingham-Pi dimensional analysis*, to be submitted.
- [9] A. Ambrosi, **M. Al-Furaiji**, J. McCutcheon, N. Cardozo, I. Tessaro, *Transport of components in the separation of ethanol/water dilute solutions by forward osmosis*, submitted to **AIChE Journal**.

Conferences

- [1] American Institute of Chemical Engineers (AIChE) 2015, Salt Lake City, the United States (2 oral presentations and 1 poster presentation)
- [2] North American Membrane Society (NAMS) 2015, Boston, the United States (poster presentation)
- [3] The Association of Environmental Engineering & Science Professors (AEESP) 2015 Conference, Yale University, Connecticut, the United States (poster presentation)

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