6-1-2016

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Peter Nasr

Recommended Citation

APA Citation

Nasr, P. (2016).*Groundwater desalination using forward Osmosis in Egypt* [Master’s thesis, the American University in Cairo]. AUC Knowledge Fountain.
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MLA Citation

Nasr, Peter. *Groundwater desalination using forward Osmosis in Egypt*. 2016. American University in Cairo, Master's thesis. *AUC Knowledge Fountain*.
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THE AMERICAN UNIVERSITY IN CAIRO

School of Sciences and Engineering

GROUNDWATER DESALINATION USING FORWARD OSMOSIS IN EGYPT

By

PETER FAYEZ NASR

Dissertation submitted in partial fulfillment of the requirements of the degree of
Doctor of Philosophy in Engineering
with a concentration in Environmental Engineering

Under supervision of:

Dr. Hani Sewilam

Professor, Mechanical Engineering Department and Director, Center of Sustainable Development, School of Science and Engineering

April 2016

DEDICATION

I dedicate this work to my son Michael and my daughter Nicole for simply being the love of my life.

PREFACE

I have always been interested in finding engineered solutions to pressing environmental concerns in Egypt. The PhD program at the American University in Cairo gave me a first-class opportunity to pursue this interest. Knowing that Egypt is not only facing a water scarcity problem, but also an inevitable energy crisis, exploring novel sustainable technologies to provide fresh water sources became a necessity. Accordingly, I started researching state-of-the-art desalination technologies until I fell in love with Forward Osmosis.

After collecting relevant significant information, I published my first paper "Forward osmosis: an alternative sustainable technology and potential applications in water industry". This paper mainly highlighted the different applications for this promising technology. Another paper followed, which was "The potential of groundwater desalination using forward osmosis for irrigation in Egypt", which focused on selecting potential locations to apply this capable technology to desalinate groundwater for irrigation purposes in Egypt. A poster was also presented on the same topic during the Youssef Jamil Summer School, which was held in Cardiff, Wales, 2014. I was also honored to co-author a book chapter with my supervisor Dr. Hani Sewilam, entitled "Desalinated Water for Food Production in the Arab Region". This book is a joint collaboration between UNU-INWEH and UNESCO.

To get more exposure in the field, I was keen to attend the "International Forward Osmosis Association World Summit" held in Lisbon, Portugal, 2014. There, I was fortunate to be invited by University of Technology, Sydney, Australia, being a world leader in fertilizer drawn forward osmosis technology, to attend a one-month training. During my one-month stay, I learnt how to run FO lab experiments, study new topics related to FO, investigate different types of membranes and learn relevant thermodynamics principles. The outcome of this training was another published paper "Investigating the performance of ammonium sulphate draw solution in fertilizer drawn forward osmosis process". After that, I travelled to San Francisco, USA, to visit Porifera Company, one of the world flourishing membrane providers. During this mission, I was trained how to operate a bench-scale device to experimentally test FO membranes performance.

After these tasks, I had adequate knowledge and experience to start examining on my own. My objective was to investigate the proposed desalination scheme given the Egyptian setting. I started by collecting a real groundwater sample and started testing it at the AUC premises, investigating process efficiency. I was also interested in selecting the optimum draw solution and membrane for actual application. The outcome of this work was another provisionally accepted paper (currently in press) entitled "Investigating Fertilizer Drawn Forward Osmosis Process for Groundwater Desalination for Irrigation in Egypt". In addition, I was privileged to present a brief summary of my research outcome to a selection of current and former Egyptian ministers, including Former Prime Minister Ibrahim Mahlab, and that was during their visit to AUC premises in January 2016.

I see my endeavor as a contribution in investigating a promising sustainable desalination technique. If this technology is realized, the impact on the agricultural sector would be remarkable, especially for a water-stressed country like Egypt. Thesis outcomes could be used by decision makers in Egypt for implementation purposes.

ACKNOWLEDGEMENTS

I would like to thank God, the most Merciful. Without His guidance this work would not exist. I would like to acknowledge my father and mother for backing me up all along. A very special thank you is for my lovely wife Irene for doing her best to always provide me with a peaceful environment during this research and for the sacrifice she has had to make in supporting my study. I am thankful to my supervisor, Dr. Hani Sewilam, who can never be given the credit he deserves for his support, patience and for being there when I needed him the most. I am also grateful to Dr. Ho Kyong Shon and Dr. Sherub Phuntsho (University of Technology, Sydney) who kindly invited me as a visiting scholar and gave me the great opportunity to have the first forward osmosis experience in my life. During my visit to UTS they were always helpful and ready for my questions. I wish to thank Dr. Jennifer Klare (Porifera Inc.) for teaching me how to use the fluxometer during my training visit to USA and for providing me with numerous helpful remarks. I wish also to thank my advising Committee (Dr. Adham Ramadan and Dr. Walid Fouad) for their constant guidance during my research work. My gratitude is further extended to Dr. Ahmed El Gindy for providing me with useful clarifications. I express special gratitude to Dr. Nabil El Maraghy for his advice, informative discussions and innovative ideas. It is hard to forget Eng. Ahmed Saad, supervisor of the Environmental Engineering lab at the American University in Cairo, for his assistance all along. My gratitude is extended to my friends and colleagues for being very supportive of this endeavor.

Last but not least, I would like to thank Mr. Youssef Jamil for the financial support that I received during my PhD candidature. Also, I would like to thank Center of Sustainable Development for funding my experiments and sponsoring my visits to Australia and USA.

PUBLICATIONS

A number of publications were formulated from this dissertation as the work developed. The list of publications is provided below.

Journal Articles Published

1. Nasr, P., & Sewilam, H. (2015). Forward osmosis: an alternative sustainable technology and potential applications in water industry. *Clean Technologies and Environmental Policy*, *17*(7), 2079–2090. http://doi.org/10.1007/s10098-015-0927-8
2. Nasr, P., & Sewilam, H. (2015). The potential of groundwater desalination using forward osmosis for irrigation in Egypt. *Clean Technologies and Environmental Policy*, *17*(7), 1883–1895. http://doi.org/10.1007/s10098-015-0902-4
3. Nasr, P., & Sewilam, H. (2016). Investigating the performance of ammonium sulphate draw solution in fertilizer drawn forward osmosis process. *Clean Technologies and Environmental Policy*, *18*(3), 717–727. http://doi.org/10.1007/s10098-015-1042-6

Journal Articles in Press (available online)

1. Nasr, P., & Sewilam, H. (2016). Investigating Fertilizer Drawn Forward Osmosis Process for Groundwater Desalination for Irrigation in Egypt. *Desalination and Water Treatment*. http://doi.org/10.1080/19443994.2016.1170639

Book Chapters

1. Sewilam, H., & Nasr, P. (2015). Desalinated Water for Food Production in the Arab Region. In *Water-Energy-Food Security Nexus in the Arab Region*. Springer.

List of Abbreviations

BGW : Brackish groundwater
BW : Brackish water
CP : Concentration polarization
CTA : Cellulose Triacetate
DI : Distilled water
DS : Draw solution
EC : Electric conductivity
ECP : External concentration polarization
ESP : Exchangeable Sodium Percentage
FDFO : Fertilizer drawn forward Osmosis
FO : Forward Osmosis
FS : Feed solution
HTI : Hydration Technology Innovation
ICP : Internal concentration polarization
MED : Multi-effect distillation
MSF : Multistage flashing
MW : Molecular weight
MWRI : Ministry of Water Resources and Irrigation
NF : Nanofiltration
NPK : Nitrogen Phosphorus Potassium
NTU : Nephelometric Turbidity Units
PA : Polyamide
PDA : Polydopamine
RO : Reverse Osmosis
RSC : Residual Sodium Carbonate
RSF : Reverse solute flux
SAR : Sodium Adsorption Ratio
SDI : Silt Density Index
SEM : Scanning Electron Microscope
SRSF : Specific reverse solute flux
SSP : Soluble Sodium Percentage
SWRO : Seawater Reverse Osmosis
TDS : Total dissolved solids
TFC : Thin film composite
WWTP : Wastewater treatment plant

List of Symbols

A : Pure water permeability coefficient ($Lm^{-2}h^{-1}bar^{-1}$)
B : Salt permeability coefficient ($Lm^{-2}h^{-1}$)
C : solute concentration (mg/L or Moles or M)
D : diffusion coefficient (m^2s^{-1})
d_h : Hydraulic diameter (m)
J_s : Solute flux ($g.m^2.h^{-1}$)
J_w : Water flux ($Lm^{-2}h^{-1}$ or LMH)
k_f : Mass transfer coefficient
K : Resistance to solute diffusion within membrane support layer ($s.m^{-1}$)
M : Molar concentration of the solution (M)
M_w : Molecular weight (mol/g)
n : Van’t Hoff factor
P : Applied pressure (bar)
R : Universal gas constant ($0.0821\ L\cdot atm\cdot mol^{-1}\cdot K^{-1}$)
R_s : Salt rejection (%)
S : Structural Parameter (m)
Sh : Sherwood number
T : Absolute temperature (K)
π : Osmotic pressure (atm or bar)
σ : Reflection coefficient

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

Rapid population growth is putting huge stress on limited fresh water sources in Egypt. Agriculture is considered the major consumer of fresh water in Egypt, consuming more than 80% of fresh water available. Creating new freshwater sources for irrigation purposes becomes inevitable to meet the increasing demand. Groundwater desalination could be the solution to this problem. If a low-cost sustainable desalination technology is realized, impact on the agricultural sector would be remarkable for water stressed country like Egypt.

Forward Osmosis (FO) is an innovative membrane separation technology that can be applied to efficiently desalinate groundwater. FO desalination relies on the theory of natural osmotic pressure driven by concentration difference instead of hydraulic pressure in RO (Reverse Osmosis). Thus, desalination can be achieved using significantly low energy. FO desalination process involves the use of a concentrated draw solution (DS), generating elevated osmotic pressure, flowing on one side of a semi-permeable FO membrane, and a feed solution (FS), with a lower osmotic pressure, flowing by the other side. Fresh water leaves the FS and enters the DS by natural diffusion. The diluted DS is then separated from the fresh water and draw solutes are recovered. One application of FO process is Fertilizer Drawn Forward Osmosis (FDFO). This application offers a unique advantage as separation and recovery of draw solute is not essential since the draw solution adds value to the end product.

The convenience of FDFO desalination is that produced water can be directly utilized for fertigation because fertilizers are needed anyway for the plants avoiding the need for separation and recovery of draw solutes. However, FDFO desalination has some limitations that should be considered. Novel draw solutions and capable FO membranes are the main concern of most FO researchers as both greatly affect overall process efficiency. The high nutrient content in product water is another limitation making meeting irrigation water quality standards a challenge.

Applying FDFO technology in Egypt for augmenting irrigation water by desalinating abundant brackish groundwater is investigated in this work. As Egypt is a groundwater-rich country, application of FDFO desalination technology would lead to a revolutionary platform where unutilized brackish groundwater can be efficiently

made use of to generate valuable nutrient-rich irrigation water. Egyptian irrigation schemes and mapping of groundwater aquifers in Egypt have been carefully investigated. Based on a carefully studied selection criteria, two proposed locations are suggested for this application in Egypt: 1) Nile Valley and Delta region and 2) Red Sea coast in Eastern Desert and Sinai region.

In Nile valley and Delta region, it is suggested to apply FDFO technology coupled with localized irrigation instead of flood irrigation. The suggested technique could possibly cultivate 1 million feddan using renewable groudnwater. Proposed scheme will lead to a healthier Nile River and is expected to eventually minimize further soil salinization being a reported problem in the area which negatively affects crop yield

In Red Sea coast in Eastern Desert and Sinai region, FDFO desalination is a promising technology to help alleviate the severe water scarcity problem inhibiting the area’s development. Already existing RO facilities could be easily integrated to the suggested FDFO technology. In this study it is suggested to have decentralized small-scale farms, instead of hundreds of thousands of feddan as is common in Delta and Nile valley regions. This will minimize water losses and keep the desalinated water at a competitive price.

FDFO desalination success is greatly affected by the choice of a suitable draw solution. This study focused only on nitrogenous-based fertilizers being by far the most dominant class of fertilizers used in Egypt. Four nitrogenous Egyptian fertilizers have been closely evaluated with respect to their availability, economics and performance. The three factors played a major role in the fertilizer selection. Ammonium Sulpahte was selected to be the most suitable fertilizer draw solution exhibiting high osmotic pressure, being non-expensive, non hygroscopic, resistant to valorization, highly soluble in water and containing sulphur which is needed by the plant.

Performance of ammonium sulphate DS was then tested experimentally. The FO membrane used was thin film composite (TFC) membrane supplied by Woongjin, Korea and fhe FS was synthetic salty water prepared using different concentrations of NaCl. A bench-scale FO setup was used to run the experiments. The performance was assessed based on water flux, reverse permeation and feed ions rejection at different

DS concentration. It is concluded that there is a logarithmic correlation between flux and ammonium sulphate concentration where any additional increase in ammonium sulphate concentration inhibits water flux due to dilutive internal concentration polarization (DICP) effects. Increasing FS concentration leads to flux decline due to the drop in the differential bulk osmotic pressures between DS and FS. Specific Reverse Solute Flux (SRSF) values at flux less than 10 $Lm^{-2}h^{-1}$ is significantly higher than that for flux more than 10 $Lm^{-2}h^{-1}$. As a result, it is recommended to operate the process at a flux exceeding 10 $Lm^{-2}h^{-1}$ to avoid undesired loss of draw solute by reverse permeation. SRSF is almost constant irrespective of ammonium sulphate DS concentration. For the same DS concentration, flux and SRSF are inversely proportional. Except when operated at low ammonium sulphate concentration and high FS concentration, the TFC membrane used in this study exhibited high rejection of FS ions for almost all DS concentrations (more than 90%).

To sensibly test the efficiency of the ammonium sulphate draw solution, a real brackish Egyptian groundwater sample was collected, analyzed and used as FS. Being available, three FO membrane samples were assessed in this part of the study and the best membrane was selected for further investigations. In comparison to HTI's Cellulose Triacetate (CTA) and Woongjin TFC membranes, Porifera's commercial membrane proved to be best membrane with respect to baseline flux, where DS was NaCl and FS was DI water. Having the smallest structural parameter (S), internal concentration polarization (ICP) is minimized yielding highest flux. Different concentrations of ammonium sulphate were used as DS using the BGW sample. Like previously, the performance was assessed based on water flux, reverse permeation and feed ions rejection. A logarithmic relation was drawn between water flux and ammonium sulphate concentration. Same relation existed between ammonium sulphate concentration and water flux due to DICP effects. However, in this study, SRSF values did not exceed 0.18 g/l for both NH_4^+ and SO_4^{2-} ions, indicating high membrane selectivity. At flux exceeding 20 $Lm^{-2}h^{-1}$, NH_4^+ ion reported higher SRSF values than that of SO_4^{2-} ion.. Again, SRSF came out to be almost constant irrespective of ammonium sulphate concentration. While increasing draw solution concentration lead to increasing Na^+ ion rejection, it caused a significant decline in Cl^- ion rejection. This phenomenon could be probably associated to an ion exchange mechanism and reversal of membrane surface charge.

In conclusion, FDFO is a promising technology that could possibly alleviate the water scarcity problem in Egypt. Not only is FDFO a sustainable desalination technology, but also it has numerous advantages over conventional desalination technologies. Abundant brackish groundwater could be efficiently exploited to produce valuable nutrient-rich irrigation water, being the major fresh water consumer in Egypt. The scheme studied demonstrated that ammonium sulphate is an efficient DS for FDFO process, especially using Porifera's commercial FO membrane, exhibiting high osmotic pressure, low reverse solute permeation and remarkable rejection of feed solute. The proposed scheme could lead to a technology platform that would supply supplementary irrigation water, reduce soil salinity, manage fertilizer application and close the irrigation – brackish water – drainage vicious loop.

CHAPTER 1 – INTRODUCTION

1.1 Introduction

Evolving the science of water purification became imperative for the development of sustainable new technologies to help solve global water scarcity problem. Egypt is becoming a water stressed country and there is a clear mismatch between demand and available supply. This gap can only be met by creating new water sources. Accordingly, desalination could supplement fresh water using abundant unused saline water resources (El-Sadek, 2010).

Although the costs of most desalination technologies have decreased in the recent decades due to innovation, the process remains energy intensive (like in the case of RO). Thus, research directed to novel technologies for producing high quality water with lower energy consumption than the current available processes still interests the research community.

1.2 Research Motivation and Objective

1.2.1 Research Motivation

Irrigation by far is the most significant consumption which is about 85% of the total consumption in Egypt (ESCWA, 2009; FAO, 2005b; UNESCO, 2012b). Any minor irrigation water savings will significantly increase water availability for other users, such as social or environmental. This puts agriculture under pressure to develop water management and explore available opportunities to match supply and demand. Desalination is a technical option to increase the availability of freshwater both in coastal areas with limited resources and in areas where brackish waters, such as brackish groundwater, is available (Beltrán & Koo-Oshima, 2004).

The production of fresh water from saline water is one of the most significant challenges facing Egypt nowadays, as Egypt does not only face a water scarcity problem but also an inevitable energy crisis. Water and energy have always been related, since energy is needed to treat and transport water and water is needed to grow crops. Both energy and water are required to enable an acceptable human life quality and to maintain sustainable population levels. In the meantime, saving water saves energy and vice versa (US EPA, 2012).

It will be inevitably required to decrease the cost of irrigation water using state-of-the-art desalination technologies (El-Sadek, 2010). Emphasis should be placed on improving production efficiency by increasing the quantity of water produced per unit of energy consumed, and reducing capital and energy costs. Since desalination as now practiced cannot sustainably augment water supplies, the ideal solution is to find an energy-efficient type of desalination that can use the product water for irrigation, being the largest consumer of fresh water.

1.3 Objective

The main objective of this study is to inspect the potential application of Fertilizer Drawn Forward Osmosis (FDFO) scheme using commonly available fertilizers to desalinate Brackish Groundwater in Egypt to be used as a supplementary source of irrigation water. Some specific objectives of this study include:

- Explain the FDFO concept as a sustainable desalination-for-irrigation-water option and discuss its limitations and advantages
- Set a selection criteria for potential areas in Egypt to apply FDFO scheme and suggest the most suitable areas based on this criteria
- Experiment a number of available FO membranes samples using a bench scale setup in the laboratory
- Investigate different chemical fertilizers available in Egypt using a thermodynamic modeling software
- Investigate the performance of the selected fertilizer draw solution with respect to flux, reverse permeation and rejection
- Test a real brackish groundwater sample using the selected membrane and draw solution. Performance is assessed based on flux, reverse permeation and rejection.

1.4 Tasks and activities

1.4.1 Data Collection and Analysis

- Investigate Egypt’s groundwater with respect to quality, quantity and sustainability
- Inspect water quality for irrigation and its limitations

- Review local and global desalination technologies with emphasis on the energy requirements
- Elaborate the Forward Osmosis (FO) concept as a low-energy desalination option and discuss different applications in water industry as well as advantages and limitations
- Analyze FDFO concept as a potential application for FO desalination and assess its applicability in the Egyptian context
- Study FDFO advantages and challenges
- Set a selection criteria for highlighting potential locations in Egypt to apply FDFO scheme
- Suggest most promising locations based on the above mentioned criteria and discuss advantages and limitations
- Survey and compare nitrogenous-based fertilizers used in Egypt

1.4.2 Experimental Investigations

- Set-up a bench scale FO unit
- Experiment a number of available FO membranes samples using NaCl and DI as DS and FS, respectively
- Compare baseline flux of the different membrane samples using different concentrations on NaCl and select one membrane for further investigations
- Investigate different chemical fertilizers available in the Egyptian market using thermodynamic modeling software and choose one for experimental testing
- Investigate the performance of the selected fertilizer draw solution with respect to flux, reverse permeation and rejection
- Collect a real brackish groundwater sample from a suitable location for FDFO application
- Test the brackish groundwater sample using the selected membrane and draw solution. Performance is assessed based on flux, reverse permeation and rejection

1.5 Structure of the Study

The thesis is divided into eight chapters.

Chapter 1 covers a general introduction of the subject, research motivation, objectives and related tasks and activities.

Chapter 2 presents a comprehensive literature review discussing water scarcity, desalination technologies, sustainability and link between desalination and energy, desalination in Egypt, groundwater system and irrigation water.

Chapter 3 focuses on forward osmosis process, fertilizer types and fertilizer drawn forward osmosis technology.

Chapter 4 discusses the selection of potential locations for FDFO application in Egypt by investigating Egypt's irrigation and groundwater, setting a selection criteria and suggesting two potential areas of application in Egypt.

Chapter 5 addresses the selection of a potential fertilizer draw solution for FDFO application in Egypt by setting a selection criteria and screening Egyptian fertilizers based on this criteria.

Chapter 6 investigates the performance of the selected fertilizer draw solution for FDFO application experimentally. Assessment is based on water flux, reverse permeation and feed ions rejection.

Chapter 7 builds on chapter 6, where a real Egyptian brackish groundwater sample is experimentally tested using the selected fertilizer draw solution and performance is assessed based on water flux, reverse permeation and feed ions rejection.

Chapter 8 summarizes conclusions and recommendations.

CHAPTER 2 - LITERATURE REVIEW

2.1 Water Scarcity

2.1.1 Global Water Scarcity

The age of water scarcity is upon us. Nowadays, the world is facing increasing demands on supplies of fresh water due to increased population, domestic and agricultural consumption and extraction for power production and industrial uses (Mayer, Brady, & Cygan, 2010). Wachman (2007) argues that “water becomes the new oil as world runs dry”. The United Nations has reported that “0.35 billion people in 25 different countries, particularly in the Middle East and Africa, are currently suffering from water shortage, and this is expected to grow to 3.9 billion people (two-thirds of the world population) in 52 countries by the year 2025” (S. J. Kim, Ko, Kang, & Han, 2010). Of the whole world’s water, 94% is ocean salty water and only 6% is fresh water. Of the latter, almost one quarter is represented in mountain ice caps and three quarters is underground (Buros, 1990).

The world’s current population of 7 billion is expected to be 9 billion by the year 2050 (UNESCO, 2012a). Most of the projected population increase will be taking place in developing and/or under-developed countries (Figure 2.1). While 1.4 billion people worldwide lack proper potable water supplies, 2.6 billion do not have access to suitable sanitation (Amarasinghe & Smakhtin, 2014), leading to millions of people dying every year from diseases transmitted through unsafe water. Therefore, lack of adequate access to clean water is one of the most significant and challenging issues that the world is facing.

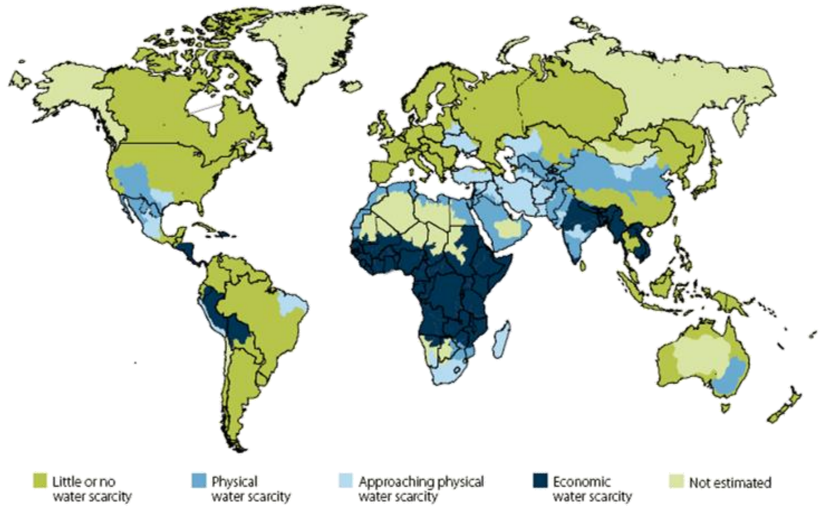


Figure 2.1 - Global Water Scarcity (UN Water, 2014)

Agriculture consumes almost 70% of fresh water available worldwide (FAO, 2013). Food availability will eventually be directly connected to water availability. Prudent management of world water resources is an important challenge.

2.1.2 Water Scarcity in Egypt

Egypt is one of the countries facing water scarcity; not only due to its limited water resources, but also due to its dryness (Figure 2.2). Egypt’s main water resource is the Nile River through the Nile agreement with Sudan assigning 55.5 billion m^3/y to Egypt, which was adequate for Egypt's 1959 population of 24 million. Egypt is currently facing an annual water deficit of around 7 billion m^3 (Dakkak, 2013). As of year 2004 Egypt’s total renewable water resources of 86.8 billion m^3/year results in an average per capita share of about 800 m^3/cap/year (Abo Soliman & Halim, 2012). Given a constant supply of water and a rapidly growing population, by 2030 Egypt is projected to have only about half the per capita water availability that it had in 1990 (Figure 2.3) (UNESCO, 2012a). It has been reported by Nashed, Sproul, & Leslie (2014) that the construction of the 170-m tall Grand Ethiopian Renaissance Dam would most probably result in approximately 18.7% decrease in Egypt’s annual Nilewater share. United Nations is warning that Egypt will most probably run out of water by the year 2030 (UNESCO, 2012b), as by then forecasts expect a share of water around 500 m^3/cap/year, indicating a serious case of 'water scarcity' given a constant supply and a rapidly growing population (Figure 2.2 and Figure 2.3).

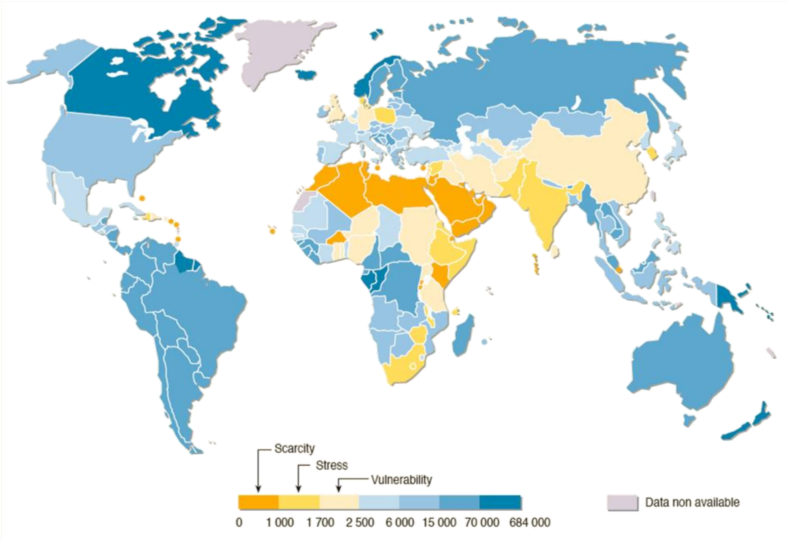


Figure 2.2 - Freshwater availability for year 2007 - m^3/capita/y) (UNESCO, 2012a)

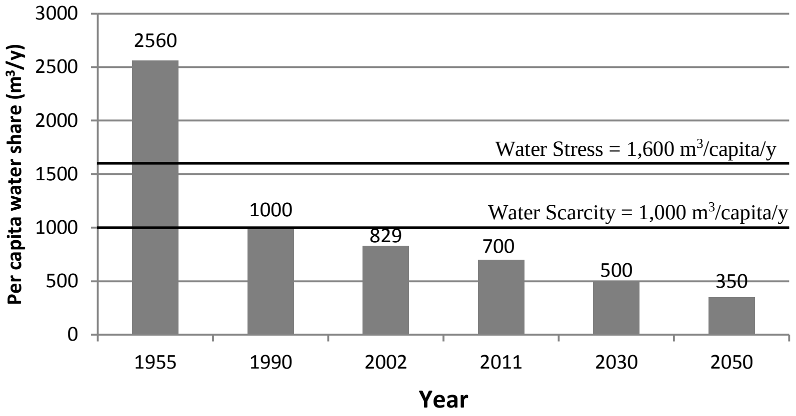


Figure 2.3 - Water scarcity indicated in terms of per capita water share in Egypt over time (ICARDA, 2011; Nashed et al., 2014)

Agriculture is the major water user in Egypt having a share greater than 80% of the total water requirement (El-Sadek, 2010). Fast deterioration in surface and groundwater quality causes shortage of water accessible for different uses. Water quality degradation also has a variety of other effects such as potential human health problems, loss of biodiversity and the irrevocable groundwater pollution (George, 1983).

That being said, it becomes clear that Egypt suffers from water scarcity and mismatch between demand and available supply. This gap can only be met by creating new water sources. Accordingly, desalination could be utilized to create additional water sources from abundant saline and/or brackish water sources (El-Sadek, 2010).

2.2 Desalination Technologies

2.2.1 History of Desalination

Desalination has long been used by water-scarce countries to generate potable water supplies (Krishna, 2004). Back in the first century A.D., not only were siphons used to pass salt water through wool threads trapping the salt, but also the Romans filtered seawater through clayey soil (Popkin, 1968). Saint Basil, a Greek leader, wrote that the “sailors boiled seawater, collecting the vapor in sponges to quench their thirst”. In 1869, the first complete distillation process was built at Aden in England to provide fresh water to vessels stopping at the port (Popkin, 1968).

Nowadays, desalination plants globally have the capacity to generate more than 41 billion liter a day, enough water to provide over 130 liter a day for every citizen in the United States (AMTA, 2007).

2.2.2 Desalination Types

According to Wetterau (2011), there are two major categories of desalination technologies (Figure 2.4): 1) Thermal Evaporation and 2) Membrane Separation. While thermal desalination processes employs heat energy to evaporate the water from the salt solution, membrane desalination uses semi-permeable membranes to selectively permit the passage of certain ions.

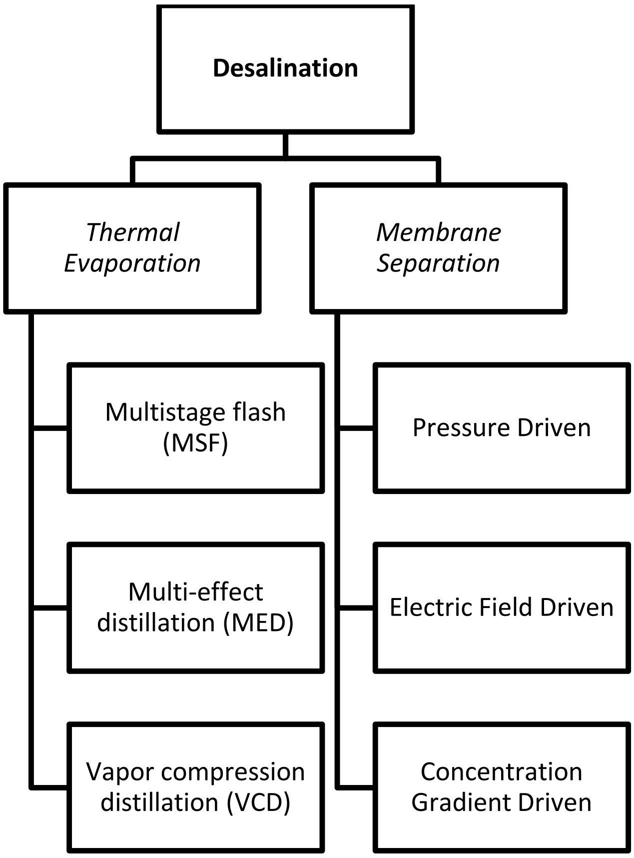


Figure 2.4 - Desalination technologies

2.2.3 Thermal Evaporation Desalination

Thermal desalting mimics the natural water cycle, where seawater evaporates mainly from the oceans accumulating in clouds as vapor, and then condensing and falling to the Earth as rain (ESCWA, 2009). More than half of the world's desalination is generated by thermal evaporation (AMTA, 2007). Thermal energy is usually the major desalting cost. According to plant design, produced water usually has salt concentrations ranging between 5-50 ppm of Total Dissolved Solids (TDS) and between 25-50 % of the source water is recovered. (AMTA, 2007).

There are 3 types of thermal desalination (Figure 2.4): 1) Multistage flash evaporation (MSF), 2) Multi-effect distillation (MED) and 3) Vapor compression distillation (VCD).

2.2.3.1 Multistage flash evaporation (MSF)

MSF (Figure 2.5) distills salty water through flashing a part of the water into steam in multiple stages (UKAEA and BIS, 1967). Heated brine is introduced in open channel flow into a chamber under reduced pressure (Buros, 1990). Some of the water evaporated immediately and is condensed on tubes cooled by the feed seawater flowing toward the steam-heated heat input section. A series of such chambers (or stages) at progressively reduced pressure forms the plant.

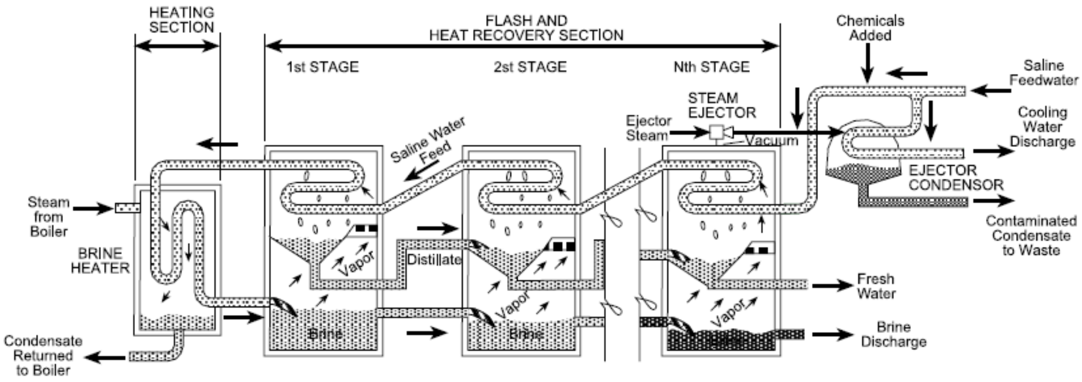


Figure 2.5 – Multistage Flashing (Buros, 1990)

2.2.3.2 Multi-effect distillation (MED)

MED (Figure 2.6) happens in a succession of vessels. This technology utilizes the idea of minimizing the surrounding pressure in the various vessels (Krishna, 2004), allowing seawater to go through multiple boiling without providing supplementary heat after the first effect (UKAEA and BIS, 1967). MSF and MED require thermal input in addition to electric power (AMTA, 2007).

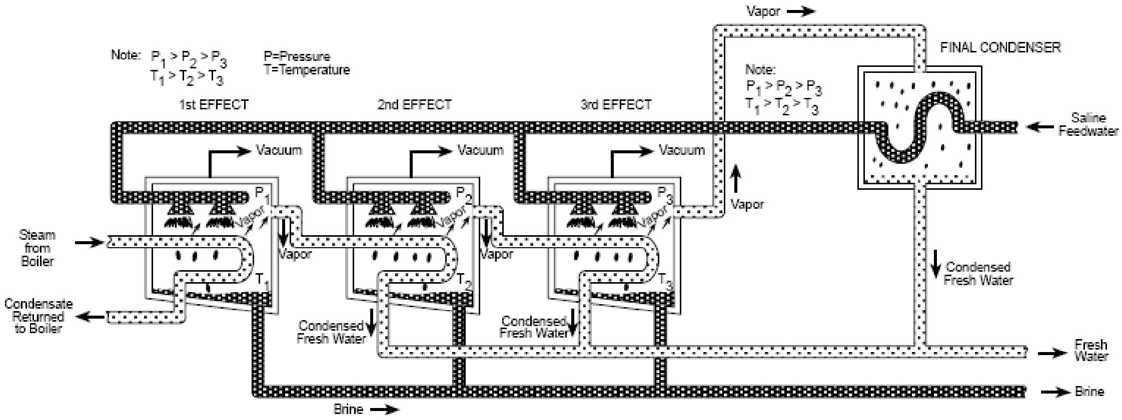


Figure 2.6 – Multi-effect Distillation (Buros, 1990)

2.2.3.3 *Vapor Compression distillation (VCD)*

In VCD (Figure 2.7), compressed vapor is utilized to change the boiling point of water (UKAEA and BIS, 1967). This technology consumes solely electric energy. Typically, it is the most inexpensive evaporative process, yet the fan compressors used usually reduce the output capacity of the equipment (Krishna, 2004).

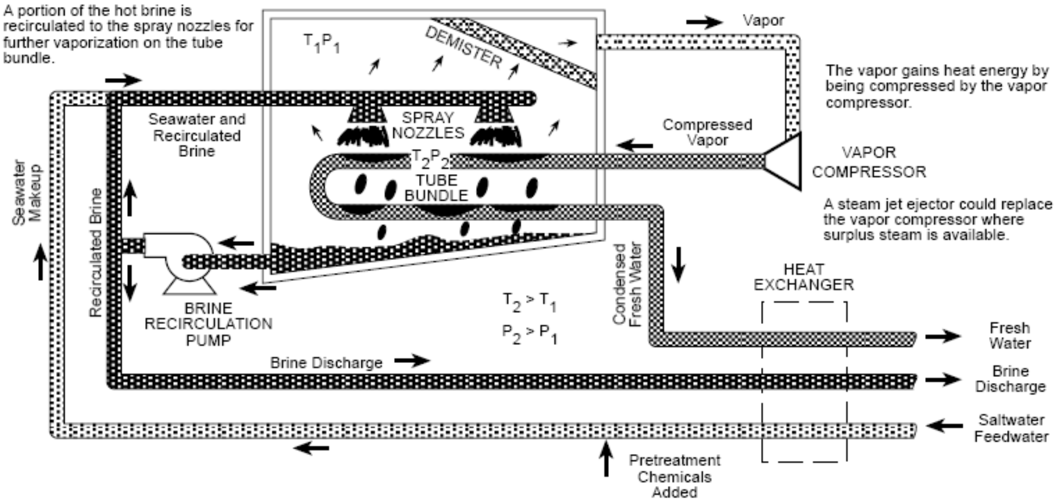


Figure 2.7 – VCD (Buros, 1990)

2.2.4 Membrane Separation Desalination

Membrane separation entails a membrane which separates fresh water from salty water. There are three kinds of membrane desalination: 1) Pressure driven membrane desalting, 2) Electric field driven membrane desalting and 3) Concentration gradient membrane desalting, as per Figure 2.4.

2.2.4.1 Pressure Driven Membrane Desalting

Pressure driven membrane desalting is a type of desalination that produces fresh water by forcing salt water through a selective semi-permeable membrane (Figure 2.8). To overcome the natural osmotic pressure gradient, which would tend to drag water from the fresh to the saline side of a membrane, an external pressure is applied (Mayer et al., 2010). Not only is the energy consumption dictated by the applied pressure to rise above the osmotic pressure, but also by the water and salt transport characteristics of the membrane (ESCWA, 2009). The most famous example of this type of desalination is Reverse Osmosis (RO), which occurs when pure water flows across a membrane, from low to higher concentration. RO is usually used to remove Sodium and Chloride from feed water and it is efficient in desalinating brackish and seawater (Krishna, 2004).

RO plants usually recover 50-80% of feed brackish water and 30-60% of feed seawater (AMTA, 2007). Energy consumption for membrane seawater desalting typically ranges between 2.6 to 5.3 kWh/m^3, while that for thermal desalination can range from 2.6 to 10.6 kWh/m^3 (Wetterau, 2011). Typical feed pressure operation for RO is between 5.5 and 10 MPa (Wetterau, 2011).

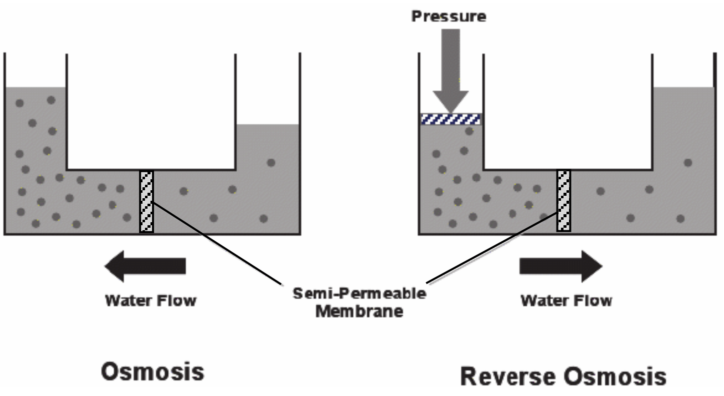


Figure 2.8 - Reverse Osmosis Process (Wetterau, 2011)

Nanofiltration (NF) is another example of pressure driven membrane desalting that removes specific ions (Krishna, 2004). While NF membranes are able to remove 90 to 98% of divalent ions such as Ca and Mg, they are able to remove only 60 to 85% of monovalent ions, such as sodium and chloride (Wetterau, 2011). As more monovalent ions can pass through the nano-membrane, the osmotic pressure required is less than that of RO, which reduces the hydraulic pressure requirements to 3.4 to 4.8 MPa for seawater desalination (Wetterau, 2011)

2.2.4.2 Electric Field Driven Membrane Desalting

Electric field driven membrane process (Figure 2.9), usually known as ‘electrodialysis’, is an electromechanical process, which uses an electric field to attract positive and negative ions from salty water through ion selective membranes, consuming the salt in the source water (AMTA, 2007). Energy is usually used in the form of resistive losses and as electrochemical reactions at the electrodes (Mayer et al., 2010). Recovery rates for this type of desalination range between 75-95%.

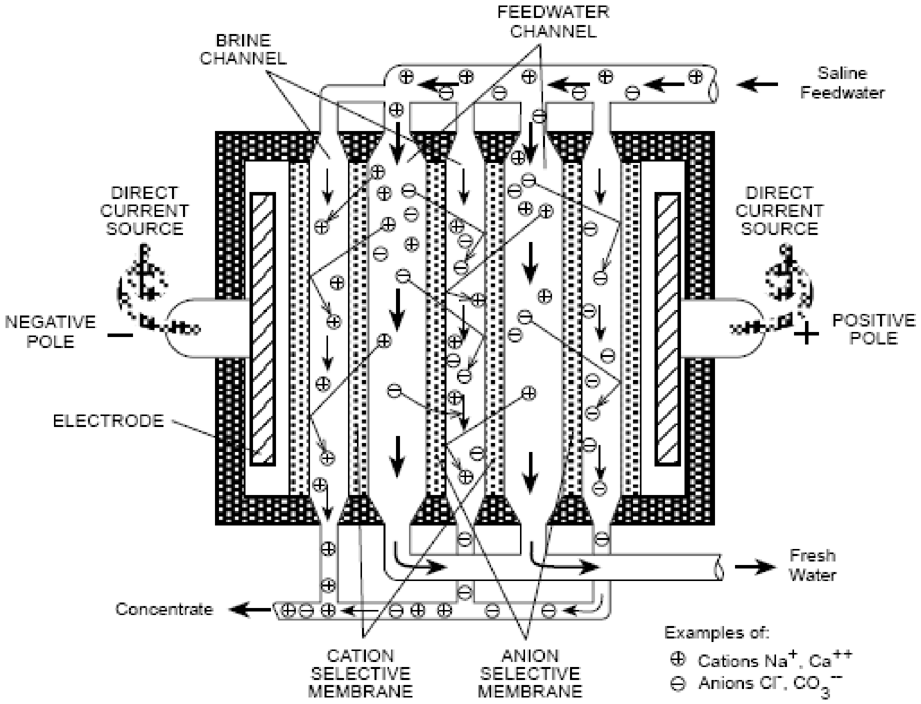


Figure 2.9 – Electrodialysis (Buros, 1990)

2.2.4.3 Concentration Gradient Driven Membrane Desalting

Concentration gradient driven membrane desalting is best represented by Forward Osmosis (FO), employing a selective membrane to separate pure water from a saline solution (Figure 2.10). Yet, as an alternative of using external pressure to force pure water to pass through the membrane, FO employs a natural pressure gradient provided by a “draw solution” (such as ammonium carbonate) (McCutcheon, McGinnis, & Elimelech, 2006). The elevated osmotic pressure of the draw solution attracts water towards it through the membrane. Afterwards, freshwater is separated from the draw solution using an additional separation process, which can differ according to nature of the draw solute and target use of final product. The separated draw solutes are either recovered and reused in the FO process or discharged (Elimelech, 2007). This type of desalination will be discussed in more details in Chapter 3.

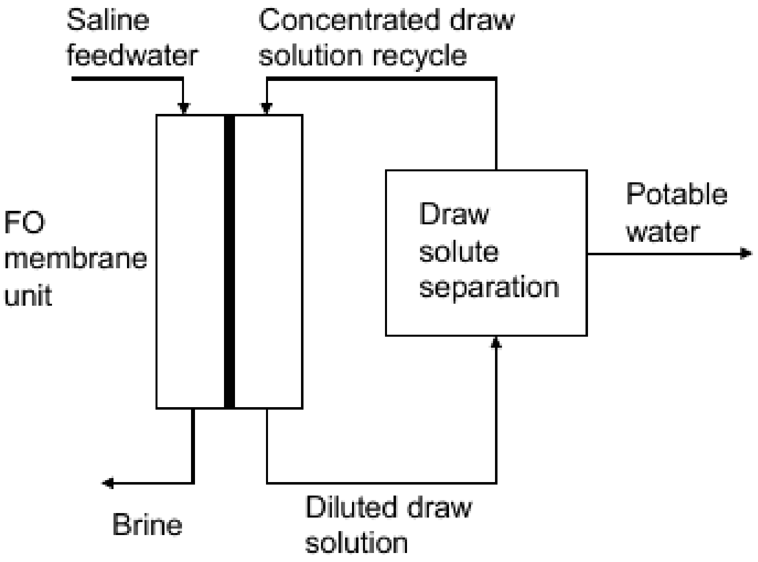


Figure 2.10 - Typical Forward Osmosis Desalination Process (Wetterau, 2011)

2.2.5 Advantages and Disadvantages of Selected Desalination Technologies

A survey of the installed desalination technologies indicates that the most installed technologies are multi-stage flash distillation and RO processes (Figure 2.11). Buros (1990) argues that these two technologies represent more than 85% of the total capacity worldwide while the remaining 15% is made up of the MSF, electrodialysis, and vapor compression processes, and other minor processes.

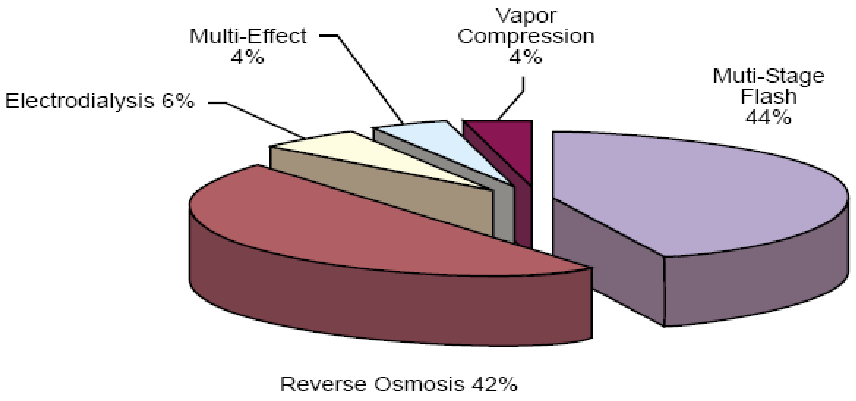


Figure 2.11 - Pie chart of installed desalination technologies worldwide (Buros, 1990)

Table 2.1 reviews the advantages and disadvantages of selected desalination techniques.

Table 2.1 - Advantages and Disadvantages of selected desalination technologies (ESCWA, 2009; British Information Services by the Central Office Information, 1967)

Desalination technology	Advantage	Disadvantage
MSF	• Simple • Produces high quality water • Cost drops at large capacity • Can be semi-operational so limiting down time • Does not generate waste from backwash	• High energy consumption • Air pollution • Slow response to water demand fluctuations • Scaling in tubes
MED	• Wide selection of feed water • Produces high quality water • Less energy consumption than MSF • Requires lower temperature operation; this reducing scaling and energy costs	• Higher energy requirements than RO • Slow response to water demand fluctuations • Lower capacity than MSF
VCD	• Low energy consumption	• Expensive form of energy (electricity) is required • High capital cost (compressors)
RO	• Less energy consumption compared to MSF and MED • Low thermal impact of discharges • Less problem with corrosion • High recovery rates (about 45% of seawater) • Removal of unwanted contaminants such as trihalomethane precursors, pesticides and bacteria • Small plant footprint • Flexible to meet fluctuations in water demand	• Sensitive to feed water quality • Membrane fouling requiring for chemical cleaning thus loss of productivity • Complex to operate • Lower product water purity

2.3 Sustainability and Link between Desalination and Energy

Desalination as currently implemented fails to sustainably supplement fresh water to meet future enormous demand (Danasamy, 2009). Reverse osmosis (RO) cannot generate water in a sustainable fashion as long as the energy needed is produced from fossil fuels. More emissions would cause more water scarcity, demanding even more energy consumption, causing an unstoppable downward spiral. Researchers have been trying hard to avoid this problem by using novel energy sources for desalinating by thermal techniques. These technologies may make use of the reject thermal energy from other processes (such as industrial and geothermal) and generate fresh water from saline. Yet, the heat temperature required by such technologies for feasible operation is too high so significant amount of energy in the form of fossil fuels is inevitable (Danasamy, 2009). A significant amount of electrical energy is needed as well in addition to the high-quality heat requirement (ESCWA, 2009).

The ultimate way out of this problem would be a technology that uses low quality heat and uses little or no electrical energy. Such technology would have the capability to produce fresh water in a sustainable fashion from salty water.

2.4 Desalination in Egypt

Desalination could be a sustainable water resource for domestic as well as agricultural use in many regions in Egypt, being gifted by almost 2,400 km of coastline on two major seas (Mabrouk, Jonoski, Solomatine, & Uhlenbrook, 2013). Since the current cost of desalinated water is relatively high, desalination is mainly practiced to provide water in Red Sea touristic areas (Figure 2.12), where is it feasible (El-Sadek, 2010).

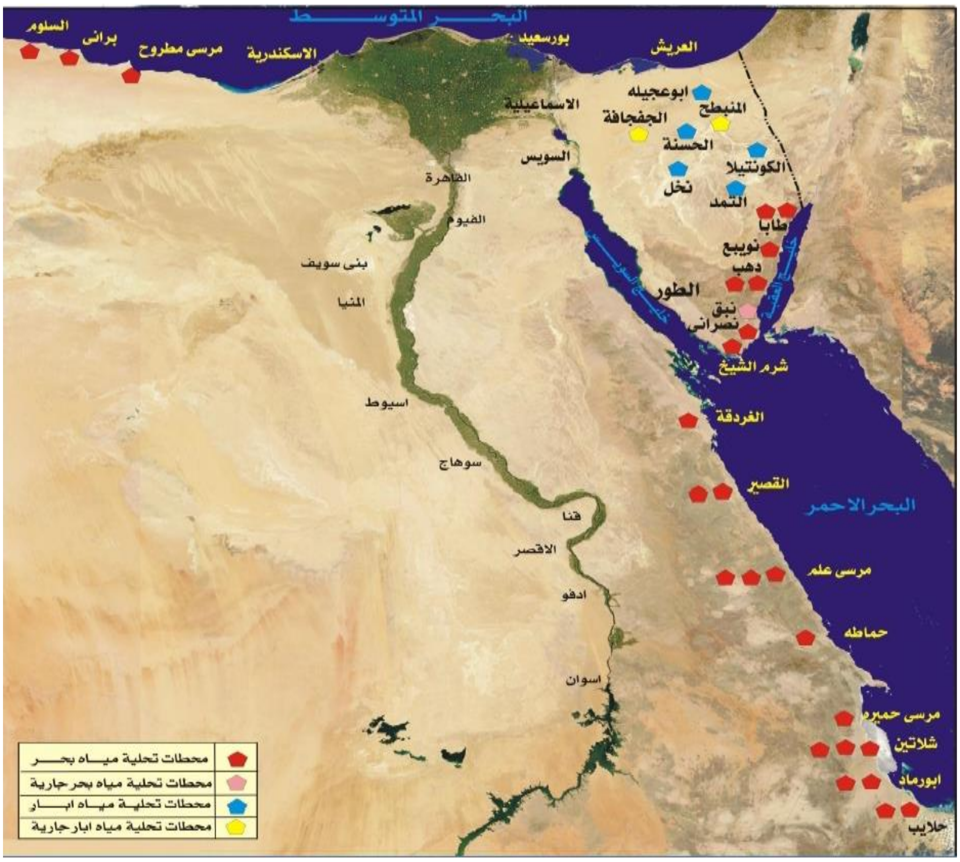


Figure 2.12 – Desalination plants in Egypt (Moawad, 2007)

2.4.1 Advancement of Desalination in Egypt

Currently, Egypt is promoting both the public and the private sector to invest in desalination. Egypt's desalination experience began with distillation, Electrodialysis and ended with Reverse Osmosis (Moawad, 2007). The outstanding accomplishments in desalination technologies globally have decreased the costs considerably. Expensive water transportation costs and high possibility of water pollution are challenges to be addressed for meeting water needs of remote areas through the public water network (MWRI, 2009). Desalination is adopted mostly for augmenting fresh water to shoreline areas as well as petroleum and energy industries. Figure 2.13 demonstrates the installed capacities in Egypt.

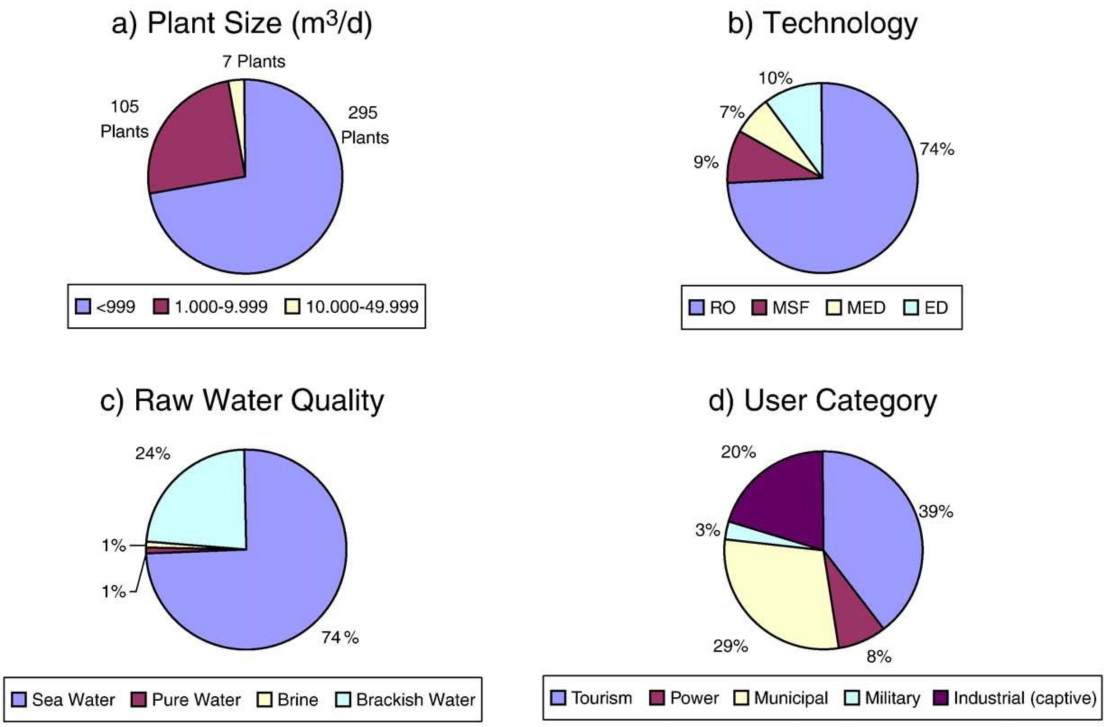


Figure 2.13 – Desalination installation capacities in Egypt (El-Sadek, 2010)

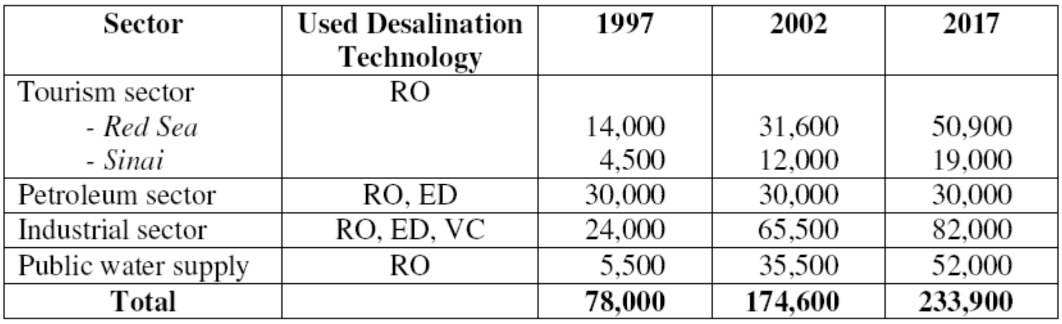
Egypt's actual experience in desalination started in the mid nineteen seventies. By then, water treatment started to be more preferred than water transportation for extended kilometers (Yousef, Sakr, & Shakweer, 2007). This is due to more than one reason: urban growth along the coastal regions, the growth in distant areas reducing the pressure in the valley and delta, creation of new opportunities in oil fields and resorts (A. R. Allam, Saaf, & Dawoud, 2003). The public in Egypt believe in the notion that desalting costs are not competitive and are expensive, which has inhibited the awareness and utilization of this potential water source (El-Sadek, 2010).

2.4.2 Future Prospective of Desalination in Egypt

Unfortunately, desalination has been looked upon lightly as a potential supply of fresh water in Egypt. However, in some instances it is more economic to employ desalination in distant areas as the cost of transporting Nile water is quite high (Talaat, Sorour, Abulnour, & Shaalan, 2003). Thus, desalination is possibly a sustainable water source for fresh water supply in numerous areas. The prospect use of desalination for different uses will rely mainly on the rate of technology advancement and the energy cost. Energy experts anticipate that the solar and wind energy prices will drop in the future (U.S. Department of Energy, 2014; World Bank, 2012). Thus, if powered by solar or wind energy, desalination can be a competitive technology and can be widely used (Buros, 1990). In case the need for water goes beyond available resources, it will be imperative to use desalination in the future. As brackish water desalination costs significantly less than seawater desalination, the former may be desalinized at a sensible price offering a feasible option for desalinated water for irrigation. The volume of desalinated water nationwide nowadays is about 50 million m^3 annually (El-Sadek, 2010). Small communities in dry areas still use primitive techniques for treating water.

Table 2.2 illustrates the different economic sectors and the most common desalination technology and the capacities expected up to the year 2017.

Table 2.2 - Desalination technologies and produced and expected desalinated water at different sectors in Egypt (Rayan, Djebedjian, & Khaled, 2004)



Sector	Used Desalination Technology	1997	2002	2017
Tourism sector	RO			
- *Red Sea*		14,000	31,600	50,900
- *Sinai*		4,500	12,000	19,000
Petroleum sector	RO, ED	30,000	30,000	30,000
Industrial sector	RO, ED, VC	24,000	65,500	82,000
Public water supply	RO	5,500	35,500	52,000
Total		**78,000**	**174,600**	**233,900**

2.4.3 Cost of Desalinated Water in Egypt

Desalination cost can be divided into two main categories: 1) direct and indirect capital costs and 2) annual operating costs. The direct capital costs account for the procurement of machinery, land and construction of the facility (Yousef et al., 2007). Indirect capital costs comprise the shipping, construction overhead and contingency expenses (Wetterau, 2011). Annual operating costs include manual labor, power, chemicals, spare parts and miscellaneous items (Salim, 2012).

Estimating the actual cost of desalinated water is not an easy task, as the price is affected by numerous factors, such as labor, technology, plant capacity, contract type, feed and product water quality and local energy costs. However, the price is especially sensitive to the capacity of the plant due to economy of scale. Desalinated water cost is the key factor affecting the utilization of desalination technology. Hafez & El-Manharawy (2003) claim that RO energy requirement ranges between 8 to 11 kWh/m^3, depending on the facility size. Yet, nowadays, due to technological advancement in energy savings, Moawad (2007) reports that energy consumption of an RO plant is close to 3.5 kWh/m^3. According to El-Sadek (2010), the average cost of one m^3 of desalinated seawater is about $0.7 to $0.9, depending on the desalination technology adopted and the plant construction date[1]. However, the selling price varies according to the consumer such as public water supply or tourism. For example, in many of the tourists resorts of Sharm El-Sheikh, the drinking water is supplied to the hotels and restaurants at a price of 1.15 to 1.75 \$/m^3 (Rayan et al., 2004). It is worth noting that such prices are not feasible to produce water for irrigation as it is reported that the cost of desalinated water is almost 3.5 times higher than the cost of the natural fresh water and it is the main obstacle on the application of desalination for irrigation purposes (Phuntsho, 2012).

2.5 The Groundwater System

The water table is the defined as “the surface below which all the voids in soil are saturated with water” (Freeze & Cherry, 1979). The “unsaturated zone” sits on top of the water table. In this zone the soil voids are incompletely full of water.

Leakage is the water descending beyond the plant root zone, where leakage that enters the saturated zone is identified as “groundwater recharge” and groundwater that escapes the saturated zone is recognized as “groundwater discharge” (Freeze & Cherry, 1979).

2.5.1 Saline Groundwater

The dissolved solids concentration is an easy parameter for characterization of groundwater quality (Weert, Gun, & Reckman, 2009). Usually, it is expressed in Total Dissolved Solids (TDS). Yet, the use of alternatives such as the Chloride Content (mg/l) or the Electrical Conductivity (EC) is common too (Y. Wang & Jiao, 2012).

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[1] The author did not consider the subsidized energy price in Egypt.

Practically, salty water is divided according to salinity level. Title of category, parameters to which category limits are linked (TDS, chloride content, EC) and values of category limits vary in literature. In this work, a basic classification is followed which is based on TDS level (Freeze & Cherry, 1979). Figure 2.14 shows the four categories.

Fresh water	• 0 - 1,000 mg/l
Brackish water	• 1,000 - 10,000 mg/l
Saline water	• 10,000 - 100,000 mg/l
Brine	• > 100,000 mg/l

Figure 2.14 - Water salinity classification (Weert et al., 2009 after Freeze & Cherry, 1979)

2.5.2 Causes of Groundwater Salinity

According to Domenico & Schwartz (1998), there are two main causes of the problem of groundwater salinity. The first is due to natural causes and the second is due to anthropogenic causes.

2.5.2.1 Natural Causes of Groundwater Salinity

2.5.2.1.1 Groundwater Rich in Minerals due to Evaporation

This source of groundwater is related to shallow water table condition, and progresses as evaporation takes place, while washing out of built- up salts is weak (Yechieli & Wood, 2002). Usually, highly saline lakes spread the salt in the close by groundwater to a few meters. A salt crust is developed at the bottom of the lake when dry.

2.5.2.1.2 Groundwater Rich in Minerals Content due to Dissolution

Groundwater may also be saline due to dissolution of soluble minerals from existing ground carbonate layers. Provided that time and other conditions favor dissolution of salts, groundwater may turn into brackish (GRA, 2009).

2.5.2.1.3 Saline Groundwater due to Membrane Effects

Compressed formations of clay or shale in deep sedimentary basins may turn into salt membranes (Domenico & Schwartz, 1998). Although ground water is permeating through these layers, yet the bigger dissolved ions are not allowed to percolate, which leads to groundwater salinity. The process is usually named “salt filtering”, “ultra-filtration” or “hyper-filtration” (Weert et al., 2009).

2.5.2.1.4 Saline Groundwater due to Geothermal Origin

In some cases, mineralized water may be produced as a by-product of igneous and volcanic activities. It is usually called “juvenile water” as it has not been part of the hydrological cycle. This process rarely happens, yet, may be noticed in regions of significant igneous activity. High temperature and groundwater under pressure in regions with high igneous activity exhibit a high dissolving ability (Weert et al., 2009). Hydrothermal groundwater systems may convey this saline groundwater to other locations creating contained hot and saline springs near the surface (Domenico & Schwartz, 1998).

2.5.2.2 Anthropogenic Causes of Groundwater Salinity

2.5.2.2.1 Saline Groundwater due to Irrigation

Irrigation supplements water needed for vegetation evapotranspiration. The water vapor leaving the plant is free from dissolved solids, so much less in minerals than the original provided water (Y. Wang & Jiao, 2012). Irrigation may also cause water-logging and harmful evaporation from the water table occurs. Therefore, a significant amount of residue of relatively mineralized water is accumulated in the soil. From there it may be absorbed by the soil (causing soil salinization), reach the surface water or infiltrate underneath the root zone (GRA, 2009). It may also reach an aquifer and lead to a gradual increase in salinity of its water. In addition, irrigation by brackish water from some source (such as wastewater) may contribute to salinization of the groundwater system (Weert et al., 2009).

2.5.2.2.2 Saline Groundwater due to Anthropogenic Pollution

Anthropogenic pollution is the pollution affecting the environment due to human intervention and activity. Anthropogenic pollutants might reach the groundwater and add to groundwater salinity (van Weert, 2012). Familiar example of anthropogenic pollutants is road salt (used in winter season to raise melting point of snow). Groundwater salinization effects of such processes are expected to be geographically confined.

2.5.3 Natural Drivers Affecting Groundwater Salinity

2.5.3.1 Deposition of Marine Sediments

Seawater fills the voids of the sediments due to deposition of marine sediments and it usually remains inside the sediment formation for an extended period of time causing groundwater salinity (Weert et al., 2009).

2.5.3.2 Sea Level Variation

High sea level might lead to flooding of shoreline areas and it tends to promote seawater intrusion into coastal groundwater (GRA, 2009). On the other hand, low sea levels create conditions for aggravated flushing of saline groundwater (van Weert, 2012).

2.5.3.3 Meteorological Processes and the Hydrological Cycle

While evaporation continuously leads to the development of brackish and saline groundwater, rainfall has an opposite effect by flushing and refreshing saline formations (Domenico & Schwartz, 1998; Freeze & Cherry, 1979).

2.5.3.4 Climate Change

Climate change not only reshapes meteorological variables, but also indirectly changes sea level. Anticipated climate change would lead to a higher temperature and higher sea levels, increasing the risks associated with seawater intrusion especially in areas where rain is rare. Thus, it will be expected that salinity of groundwater would increase due to enhanced mineralization of recharge water, less naturally occurring flushing and stronger human interventions activities, such as irrigation and groundwater extraction (GRA, 2009).

2.5.4 Anthropogenic Drivers Affecting Groundwater Salinity

2.5.4.1 Coastal Protection, Land Reclamation and Drainage

Coastal protection, land reclamation and drainage strongly influence local and regional settings as they help reduce the intrusion of seawater into the aquifers (Y. Wang & Jiao, 2012). Yet, if drainage causes drop of groundwater levels, this may modify the groundwater regimes leading to migration of native saline groundwater to fresh aquifers and thus seawater intrusion becomes more serious (Weert et al., 2009).

2.5.4.2 Groundwater Abstraction

Groundwater abstraction disrupts the subsurface hydrodynamic pressure field (van Weert, 2012). If saline groundwater exists in the subsurface system, it is mobilized due to pumping and move to relatively fresh zones (Freeze & Cherry, 1979).

2.5.4.3 Irrigation

Irrigation promotes the increase in salinity of soil and groundwater because the plants use only pure water. Thus, the irrigation leaves behind a residue of dissolved minerals. Salinity due to irrigation is obvious in dry conditions (Domenico & Schwartz, 1998).

2.5.4.4 Intentional and Unintentional Disposal of Waste or Wastewater

Subsurface injection of saline water is an example of intentional disposal of water or wastewater. This operation is common in the oil industry and waste disposal related activities. Doing this, fresh groundwater may change to saline (Domenico & Schwartz, 1998). Non-intentional disposal of waste or waste water may also promote groundwater salinity like in the case of use of salt in winter season for de-icing the roads (Weert et al., 2009).

2.5.5 Causes of Irrigation Salinity

Irrigation salinity occurs in irrigated landscapes (Figure 2.15). It occurs due to significant leakage and groundwater recharge leading to rise of water table, which brings salts into the root zone. This phenomenon impacts plant growth rate and the soil structure (Grattan, 2002). Leakage from rainfall and irrigation increase the recharge rates in irrigation areas. This causes possibly high salinity rates. Water tables a couple of meters from the soil surface signify the possibility for salt accumulation at the soil surface (Podmore, 2009).

High salinity risk and water logging in green areas is mainly due to inefficient irrigation and drainage systems. Unequal water distribution leads to the existence of under-irrigated areas where salt accumulates and other over-irrigated areas which are waterlogged (Fipps, 2003). Groundwater accumulation can develop below cultivated plots due to leakage from inefficient irrigation schemes (flood irrigation), pushing saline groundwater into watercourses (Y. Wang & Jiao, 2012). Irrigating using saline water causes soil salinization and requires applying more fresh water to flush salts away from the root zone (D. Armstrong, 2009).

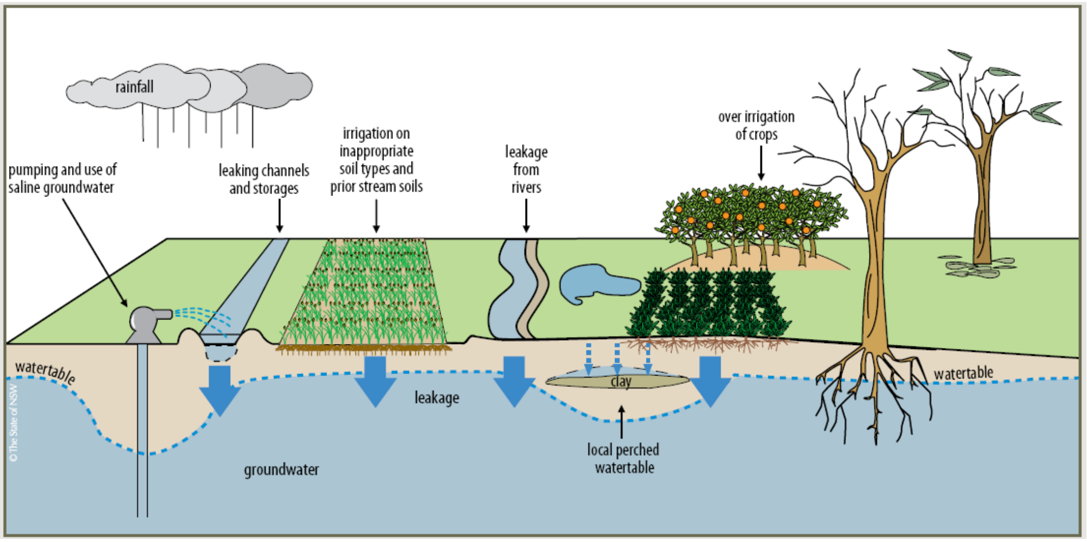


Figure 2.15 –Causes of irrigation salinity (D. Armstrong, 2009)

In addition, under-irrigation increases soil salinity levels as salts in the irrigation water need to be washed away frequently to prevent their accumulating to levels limiting productivity (Podmore, 2009). Improper coordination of crop, soil type and irrigation method can also lead to unwanted leakage. Irrigating water-intensive crops using unsuitable irrigation techniques should be avoided in case of permeable soils with a high sand content (D. Armstrong, 2009). Soil type (Figure 2.16), climate and the amount of deep-rooted vegetation are some the factors that influence leakage rates (Podmore, 2009). Substituting deep-rooted plants with irrigated annual crops is a favorable practice as this lessens the intensity of evapotranspiration. Thus, more water will percolate to the soil and will recharge the water table (Grattan, 2002).

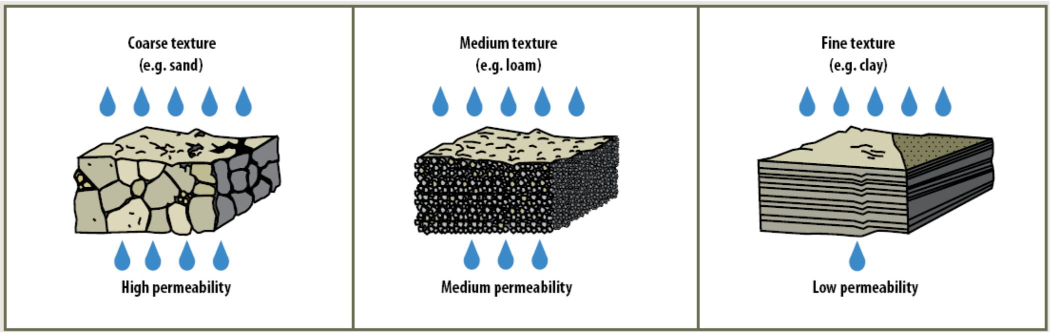


Figure 2.16 - The permeability of different soil types (D. Armstrong, 2009)

2.5.6 Impacts of Irrigation Salinity

Impacts of irrigation salinity could be divided into agricultural, environmental and socio-economic impacts (Podmore, 2009).

2.5.6.1 Agricultural Impact

According to Podmore (2009), costs associated with high irrigation water salinity include:

- less farm yield
- water-logging
- less water quality for livestock, household and irrigation utilization
- damage of farmhouse buildings
- livestock health issues
- corrosion of machinery
- deterioration of soil due to erosion
- loss of useful flora and fauna
- less land value

2.5.6.2 Environmental Impact

According to Podmore (2009), environmental impacts due to land and water bodies salinity comprise:

- deterioration of green areas
- erosion of soil
- limited wetland habitation and deterioration of aquatic life
- less biodiversity of stream fauna
- flourishing of weeds and unwanted alteration in plant populations
- damage of parks and wildlife shelters

2.5.6.3 Socio-economic Impact

Podmore (2009) argues that impacts on the framework and structure of the society from increasing salinity include:

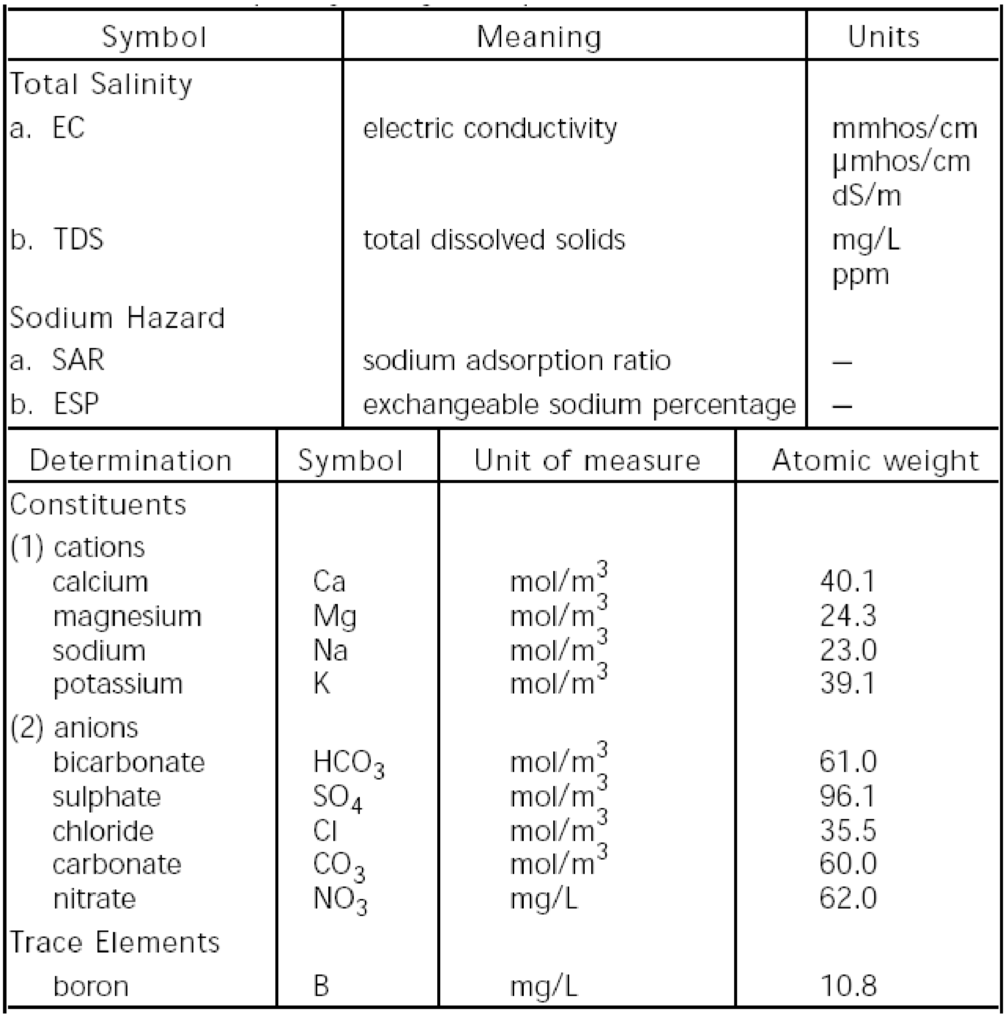
- Loss of land value
- Unfavorable impact on recreation and tourism values
- less incomes due to decline in yield
- Unfavorable impact on employment
- less regional rural and urban population

2.6 Irrigation Water

2.6.1 Quality Requirements and Limitations

Irrigation water quality is defined by a number of parameters which are used to evaluate salinity hazards and find out suitable management techniques. Important parameters investigated in any groundwater quality analysis includes: 1) the content of soluble salts, 2) the ratio of sodium to positive ions, 3) the bicarbonate content in relation to the calcium and magnesium content, and 4) the concentration of certain elements. These four factors mainly identify the fitness of water for irrigation. Table 2.3 illustrates different parameters used to investigate the fitness of water for irrigation (Fipps, 2003).

Table 2.3 – Terms and units commonly used for understanding water quality analysis reports (Fipps, 2003)



Symbol	Meaning	Units
Total Salinity		
a. EC	electric conductivity	mmhos/cm µmhos/cm dS/m
b. TDS	total dissolved solids	mg/L ppm
Sodium Hazard		
a. SAR	sodium adsorption ratio	–
b. ESP	exchangeable sodium percentage	–

Determination	Symbol	Unit of measure	Atomic weight
Constituents			
(1) cations			
calcium	Ca	mol/m^3	40.1
magnesium	Mg	mol/m^3	24.3
sodium	Na	mol/m^3	23.0
potassium	K	mol/m^3	39.1
(2) anions			
bicarbonate	HCO_3	mol/m^3	61.0
sulphate	SO_4	mol/m^3	96.1
chloride	Cl	mol/m^3	35.5
carbonate	CO_3	mol/m^3	60.0
nitrate	NO_3	mg/L	62.0
Trace Elements			
boron	B	mg/L	10.8

2.6.1.1 Salinity Problem

There are two types of salinity problems: 1) total salinity and 2) sodium salinity (Grattan, 2002).

2.6.1.1.1 Salinity Hazard

Highly saline water is deadly to vegetation and leads to salinity hazard. Saline soils are soils having alarming concentrations of total salinity. Elevated levels of salt in the soil may lead to a drought state (George, 1983). Due to the fact that the roots of the plants are unable to absorb water, the plants dry, even though the fields appear to be wet (Fipps, 2003).

Water salinity is typically evaluated by TDS (total dissolved solids) or EC (electric conductivity). Usually, TDS assess soil's total salinity in ppm or mg/L. On the other hand, EC measures the capacity of the water to pass electricity and is usually expressed in: mmhos/cm or µmhos/cm or dS/m, as given in Table 2.3 (Fipps, 2003).

The source of the sample is identified by subscripts with the symbol EC:

- EC_{iw} : electric conductivity of the irrigation water
- EC_{e} : electric conductivity of the soil
- EC_{d} : soil salinity of the saturated extract taken from underneath the roots

2.6.1.1.2 Sodium Hazard

If irrigation water contains significant levels of sodium, it will be critical to plants due to the negative impact of sodium on the soil. This type of water causes sodium hazard (George, 1983). Sodium hazard is commonly articulated in SAR or Sodium Adsorption Ratio. SAR is the proportion of Na^+ ion to Ca^{++} and Mg^{++} ions (George, 1983):

$$\mathrm{SAR} = \frac{\mathrm{Na}^+}{\sqrt{\frac{\mathrm{Ca}^{++} + \mathrm{Mg}^{++}}{2}}}$$

Equation 2.1

SAR evaluates the affinity of the water to replace Ca^{++} and Mg^{++} ions in the soil with Na^+ ion. As Na^+ clays have poor structure, they tend to experience permeability issues. Ca^{++} and Mg^{++} ions are significant as they tend to counteract the effect of Na^+ (Fipps, 2003).

Soil's structure-breakdown is a natural outcome of continuous irrigation using water with high SAR level. Sodium attaches to the soil so the soil turns to be firm, consolidated and impermeable to water (Fipps, 2003). Special modifications are essential to preserve soils experiencing high SARs. Calcium and magnesium have the ability to counteract the effect of sodium hazard and assist in sustaining desired soil characteristics (George, 1983).

Soluble sodium percent (SSP) is sometimes utilized to estimate sodium hazard. The SSP is the ratio of Na^+ ions to the total cations present (Fipps, 2003). It is calculated according to the following equation.

$$\mathrm{SSP} = \frac{\mathrm{Na}^+}{\sum \mathrm{Cations}} * 100 \qquad \textbf{Equation 2.2}$$

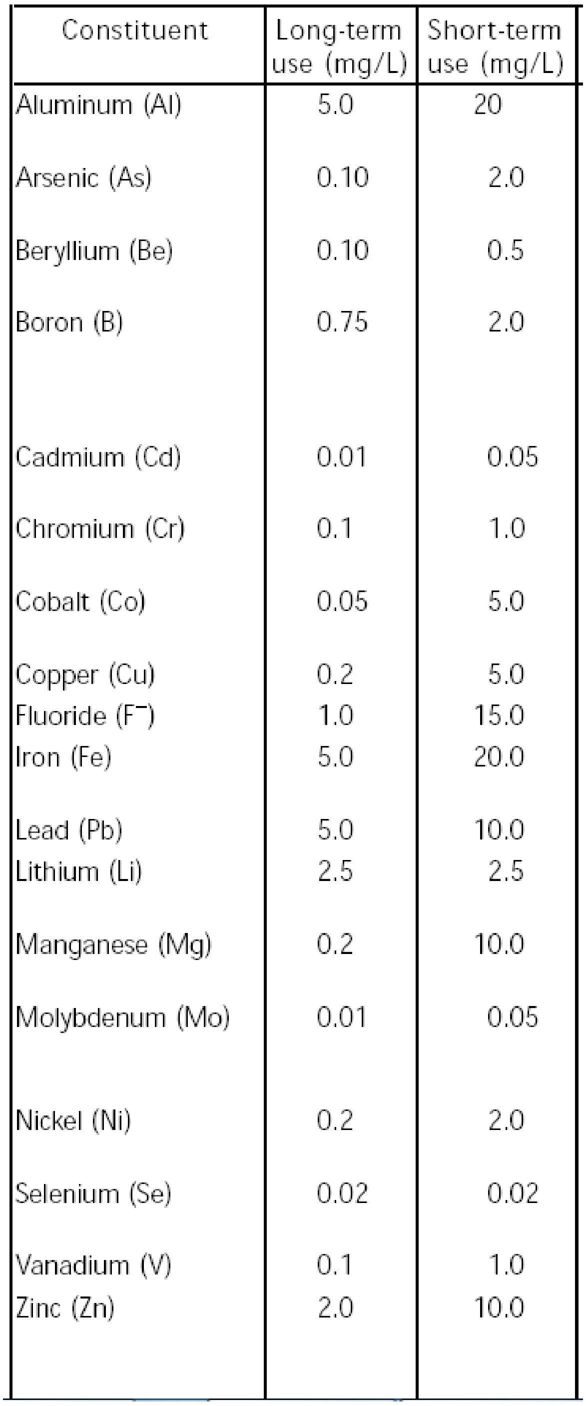
If SSP exceeds 60%, sodium buildup starts to occur causing disintegration in the soil structure (Fipps, 2003).

2.6.1.2 Ions, Trace Elements and Other Hazards

According to Fipps (2003), there are other elements existing in irrigation water which can lead to toxicity of vegetation. Recommended limits for different constituents in irrigation water are presented in Table 2.4.

Following Sodium and Chloride, Boron is the most important constituent of concern. Although essential to plant growth, Boron may be toxic to sensitive plants, such as citrus, if its concentration exceeded 1 mg/l. In addition, Boron can also accumulate in the soil. Moreover, excess concentration of K ion might cause Mg deficiency and Fe chlorosis. A disproportion of Mg and K may cause plant toxicity but this effect can be mitigated by increasing calcium levels (Fipps, 2003).

Table 2.4 - Recommended limits for constituents in irrigation water (Fipps, 2003)



Constituent	Long-term use (mg/L)	Short-term use (mg/L)
Aluminum (Al)	5.0	20
Arsenic (As)	0.10	2.0
Beryllium (Be)	0.10	0.5
Boron (B)	0.75	2.0
Cadmium (Cd)	0.01	0.05
Chromium (Cr)	0.1	1.0
Cobalt (Co)	0.05	5.0
Copper (Cu)	0.2	5.0
Fluoride (F^-)	1.0	15.0
Iron (Fe)	5.0	20.0
Lead (Pb)	5.0	10.0
Lithium (Li)	2.5	2.5
Manganese (Mg)	0.2	10.0
Molybdenum (Mo)	0.01	0.05
Nickel (Ni)	0.2	2.0
Selenium (Se)	0.02	0.02
Vanadium (V)	0.1	1.0
Zinc (Zn)	2.0	10.0

2.6.2 Effects of Poor Quality of Irrigation Water

Poor irrigation water quality negatively impacts both plant and soil.

2.6.2.1 Effect on Plant

Generally speaking, saline soil reduces the available soil water and stimulates drought state. The extent of this osmotic effect may vary with the plants growth stage and sometimes may be unobserved due to drop in crop yield. Different symptoms such as tip or marginal burn, necrosis, and defoliation (Figure 2.17) may or may not take place (George, 1983).

Figure 2.17 – Burnt leaves signifying high salinity (WateReuse Foundation, 2007)

Certain ions may build up in the plant and affect yield. Concentration by evaporation may cause specific ion toxicities, which are common in woody perennials, such as citrus. High levels of iron and carbonate may discolor plants to cause cosmetic problems (Grattan, 2002).

2.6.2.1.1 Crop Yield

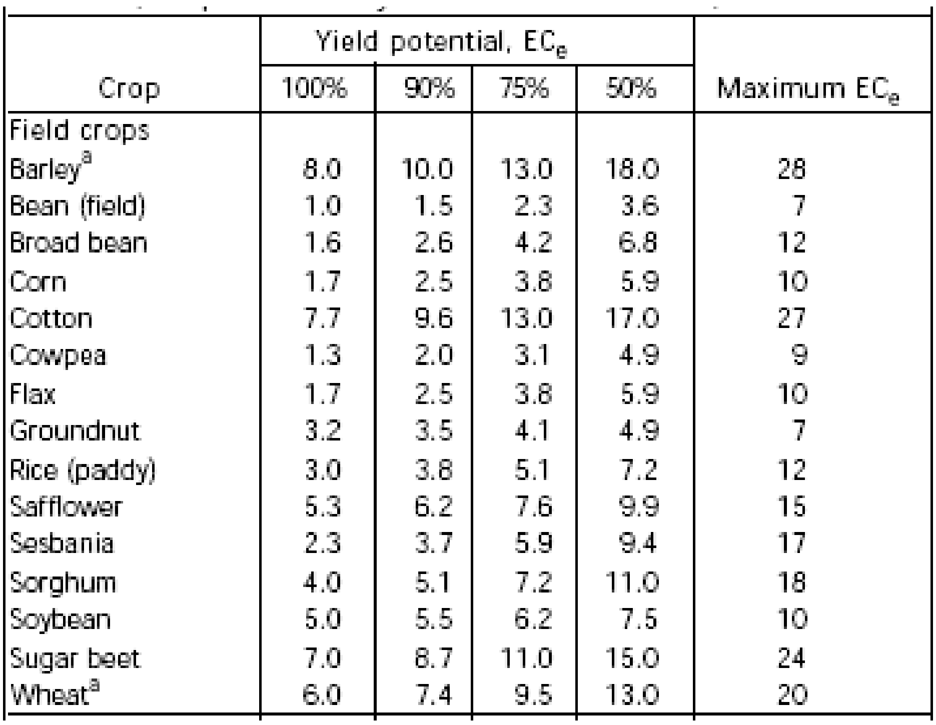
Table 2.5 shows the expected yield decrease for different soil salinity levels (Fipps, 2003). Table 2.6 shows yield decrease due to various water salinities (Fipps, 2003).

Table 2.7 illustrates the chloride tolerance of different crops. It is worth noting that, Boron is of special importance as elevated boron levels lead to plant toxicity. Its concentration should not go above the values given in Table 2.8 (Fipps, 2003). The resilience of vegetation to sodium measured in Exchangeable Sodium Percentage (ESP) is provided in Table 2.9. ESP is calculated using the following equation (UNSW, 2007):

$$\mathrm{ESP} = \mathrm{Exchangeable}\left[\frac{\mathrm{Na}}{\sum(\mathrm{Ca}+\mathrm{Mg}+\mathrm{K}+\mathrm{Na})}\right] * 100$$

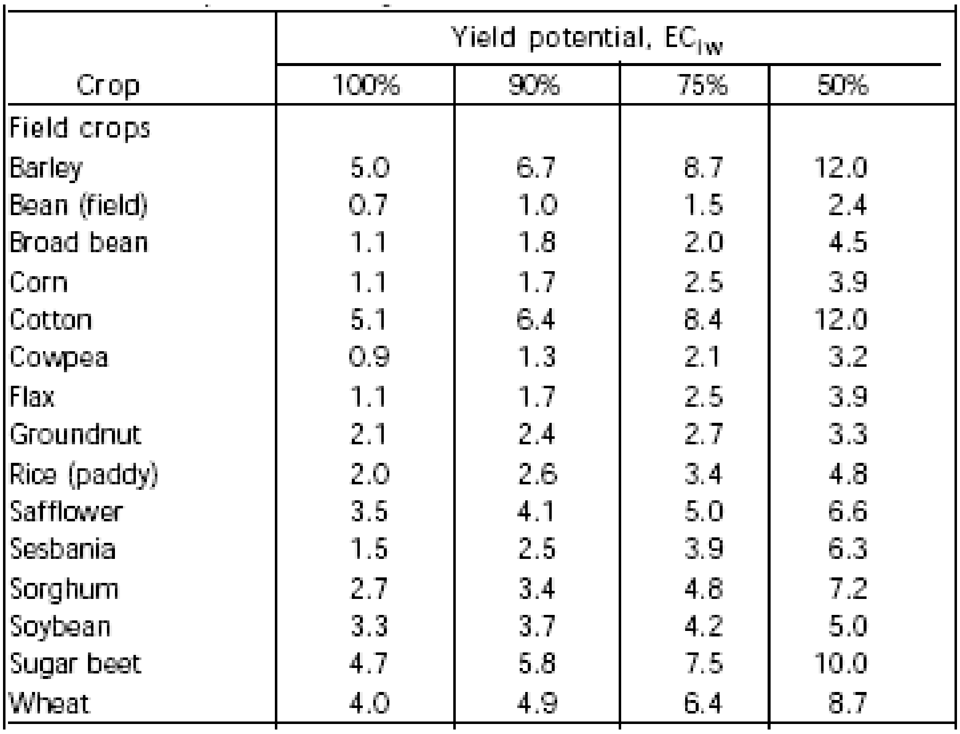
Equation 2.3

Table 2.5 - Soil salinity tolerance levels for different crops (Fipps, 2003)



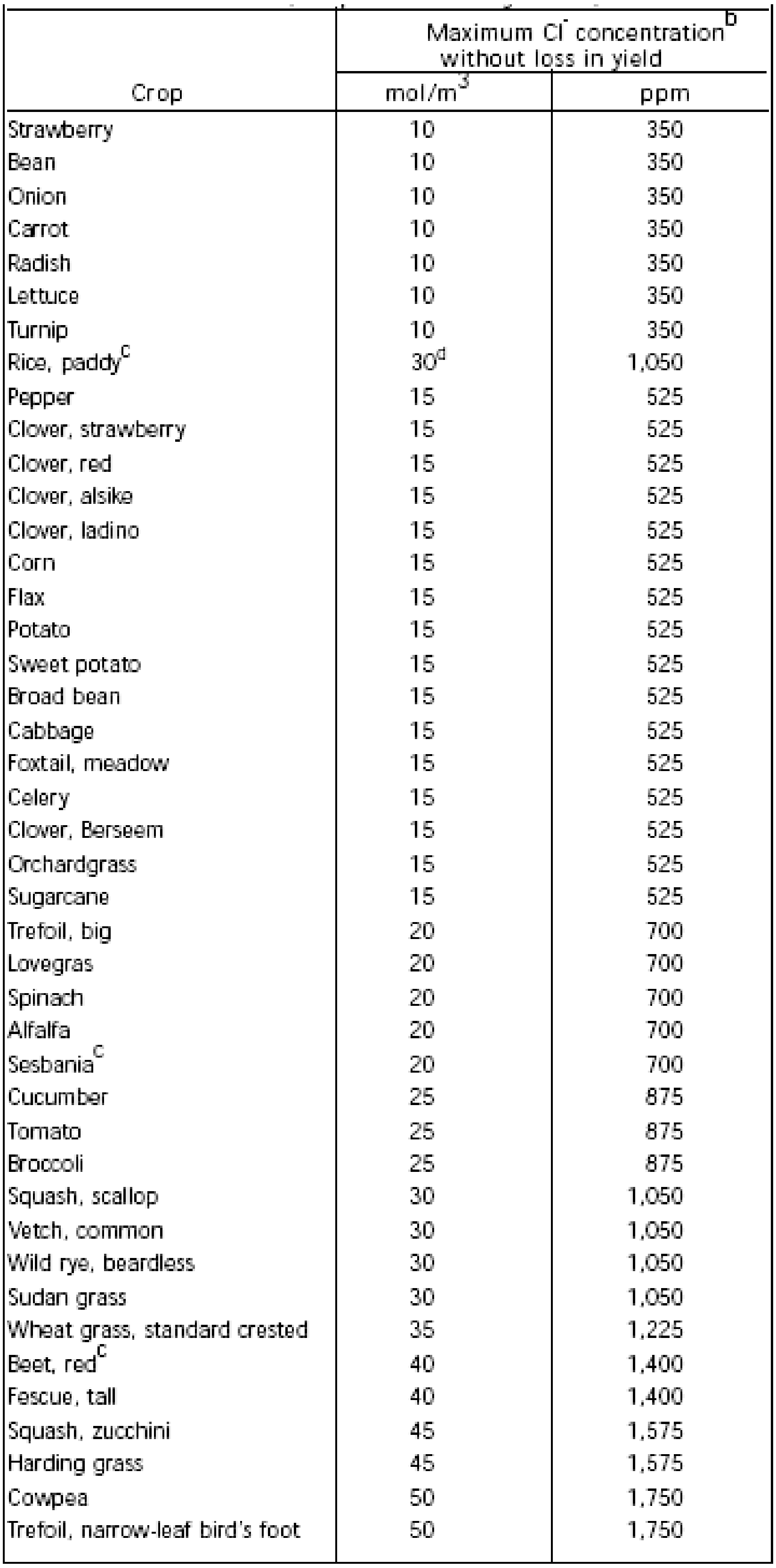
Crop	Yield potential, EC_e				Maximum EC_e
	100%	90%	75%	50%	
Field crops					
Barley[a]	8.0	10.0	13.0	18.0	28
Bean (field)	1.0	1.5	2.3	3.6	7
Broad bean	1.6	2.6	4.2	6.8	12
Corn	1.7	2.5	3.8	5.9	10
Cotton	7.7	9.6	13.0	17.0	27
Cowpea	1.3	2.0	3.1	4.9	9
Flax	1.7	2.5	3.8	5.9	10
Groundnut	3.2	3.5	4.1	4.9	7
Rice (paddy)	3.0	3.8	5.1	7.2	12
Safflower	5.3	6.2	7.6	9.9	15
Sesbania	2.3	3.7	5.9	9.4	17
Sorghum	4.0	5.1	7.2	11.0	18
Soybean	5.0	5.5	6.2	7.5	10
Sugar beet	7.0	8.7	11.0	15.0	24
Wheat[a]	6.0	7.4	9.5	13.0	20

Table 2.6 - Irrigation water salinity tolerances for some crops (Fipps, 2003)



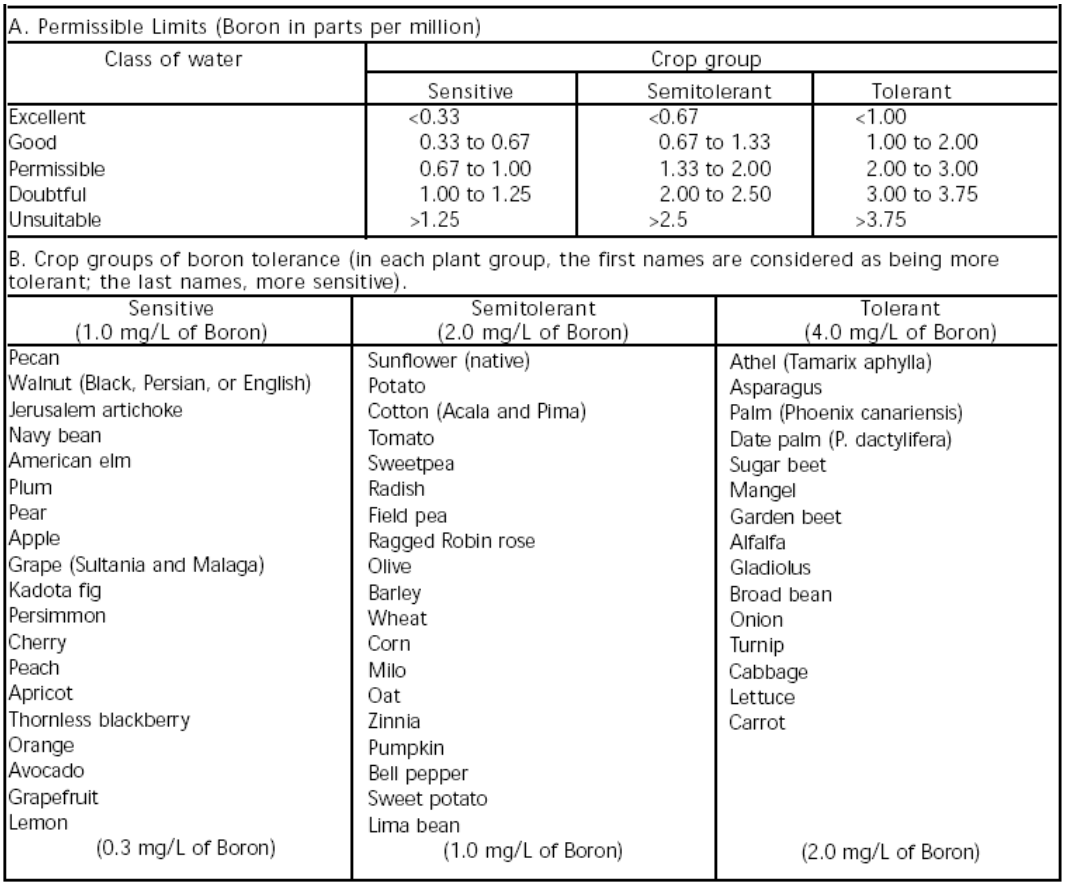
Crop	Yield potential, EC_{iw}			
	100%	90%	75%	50%
Field crops				
Barley	5.0	6.7	8.7	12.0
Bean (field)	0.7	1.0	1.5	2.4
Broad bean	1.1	1.8	2.0	4.5
Corn	1.1	1.7	2.5	3.9
Cotton	5.1	6.4	8.4	12.0
Cowpea	0.9	1.3	2.1	3.2
Flax	1.1	1.7	2.5	3.9
Groundnut	2.1	2.4	2.7	3.3
Rice (paddy)	2.0	2.6	3.4	4.8
Safflower	3.5	4.1	5.0	6.6
Sesbania	1.5	2.5	3.9	6.3
Sorghum	2.7	3.4	4.8	7.2
Soybean	3.3	3.7	4.2	5.0
Sugar beet	4.7	5.8	7.5	10.0
Wheat	4.0	4.9	6.4	8.7

Table 2.7 - Chloride tolerance of agricultural crops (Fipps, 2003)



Crop	Maximum Cl^- concentration[b] without loss in yield	
	mol/m^3	ppm
Strawberry	10	350
Bean	10	350
Onion	10	350
Carrot	10	350
Radish	10	350
Lettuce	10	350
Turnip	10	350
Rice, paddy[c]	30[d]	1,050
Pepper	15	525
Clover, strawberry	15	525
Clover, red	15	525
Clover, alsike	15	525
Clover, ladino	15	525
Corn	15	525
Flax	15	525
Potato	15	525
Sweet potato	15	525
Broad bean	15	525
Cabbage	15	525
Foxtail, meadow	15	525
Celery	15	525
Clover, Berseem	15	525
Orchardgrass	15	525
Sugarcane	15	525
Trefoil, big	20	700
Lovegras	20	700
Spinach	20	700
Alfalfa	20	700
Sesbania[c]	20	700
Cucumber	25	875
Tomato	25	875
Broccoli	25	875
Squash, scallop	30	1,050
Vetch, common	30	1,050
Wild rye, beardless	30	1,050
Sudan grass	30	1,050
Wheat grass, standard crested	35	1,225
Beet, red[c]	40	1,400
Fescue, tall	40	1,400
Squash, zucchini	45	1,575
Harding grass	45	1,575
Cowpea	50	1,750
Trefoil, narrow-leaf bird's foot	50	1,750

Table 2.8 - Limits of boron in irrigation water (Fipps, 2003)



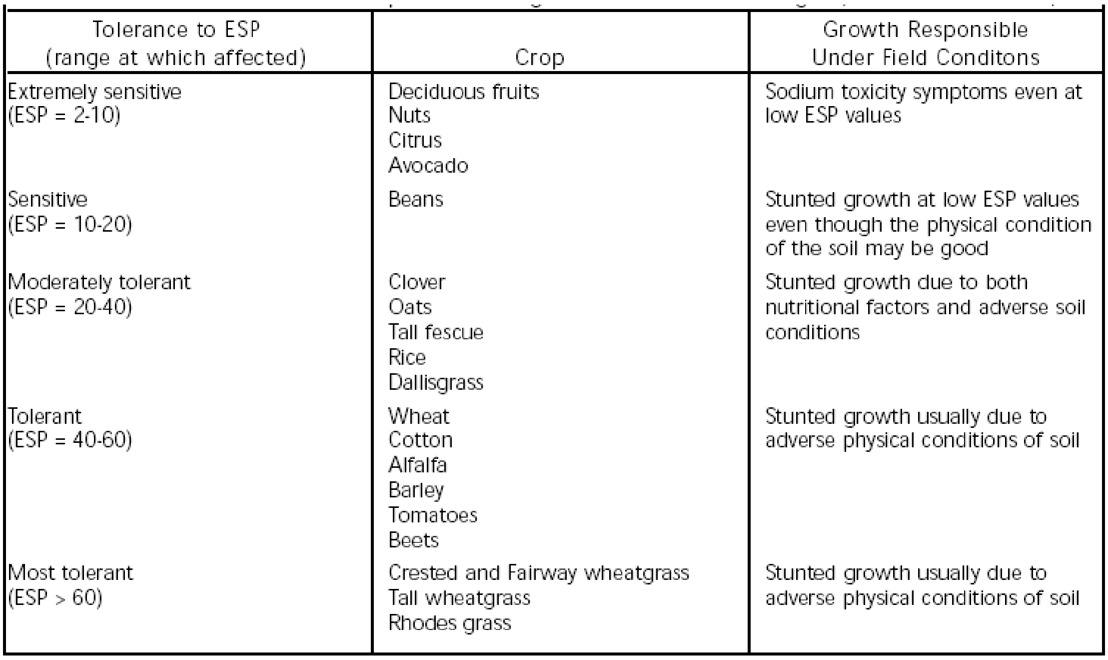
A. Permissible Limits (Boron in parts per million)

Class of water	Crop group		
	Sensitive	Semitolerant	Tolerant
Excellent	<0.33	<0.67	<1.00
Good	0.33 to 0.67	0.67 to 1.33	1.00 to 2.00
Permissible	0.67 to 1.00	1.33 to 2.00	2.00 to 3.00
Doubtful	1.00 to 1.25	2.00 to 2.50	3.00 to 3.75
Unsuitable	>1.25	>2.5	>3.75

B. Crop groups of boron tolerance (in each plant group, the first names are considered as being more tolerant; the last names, more sensitive).

Sensitive (1.0 mg/L of Boron)	Semitolerant (2.0 mg/L of Boron)	Tolerant (4.0 mg/L of Boron)
Pecan	Sunflower (native)	Athel (Tamarix aphylla)
Walnut (Black, Persian, or English)	Potato	Asparagus
Jerusalem artichoke	Cotton (Acala and Pima)	Palm (Phoenix canariensis)
Navy bean	Tomato	Date palm (P. dactylifera)
American elm	Sweetpea	Sugar beet
Plum	Radish	Mangel
Pear	Field pea	Garden beet
Apple	Ragged Robin rose	Alfalfa
Grape (Sultania and Malaga)	Olive	Gladiolus
Kadota fig	Barley	Broad bean
Persimmon	Wheat	Onion
Cherry	Corn	Turnip
Peach	Milo	Cabbage
Apricot	Oat	Lettuce
Thornless blackberry	Zinnia	Carrot
Orange	Pumpkin	
Avocado	Bell pepper	
Grapefruit	Sweet potato	
Lemon	Lima bean	
(0.3 mg/L of Boron)	(1.0 mg/L of Boron)	(2.0 mg/L of Boron)

Table 2.9 - Tolerance of different crops to Exchangeable-Sodium Percentage (ESP) (Fipps, 2003)



Tolerance to ESP (range at which affected)	Crop	Growth Responsible Under Field Conditons
Extremely sensitive (ESP = 2-10)	Deciduous fruits Nuts Citrus Avocado	Sodium toxicity symptoms even at low ESP values
Sensitive (ESP = 10-20)	Beans	Stunted growth at low ESP values even though the physical condition of the soil may be good
Moderately tolerant (ESP = 20-40)	Clover Oats Tall fescue Rice Dallisgrass	Stunted growth due to both nutritional factors and adverse soil conditions
Tolerant (ESP = 40-60)	Wheat Cotton Alfalfa Barley Tomatoes Beets	Stunted growth usually due to adverse physical conditions of soil
Most tolerant (ESP > 60)	Crested and Fairway wheatgrass Tall wheatgrass Rhodes grass	Stunted growth usually due to adverse physical conditions of soil

2.6.2.1.2 Growth Stage

During seed germination, many crops have limited tolerance for salinity. However, plants’ tolerance increases during growth stages (Grattan, 2002). Crops, such as wheat and corn, are vulnerable during the early growth stage. Sugar beet is critical during germination, while the sensitivity of soybeans varies during different growth stages (Fipps, 2003).

2.6.2.2 Effect on Soil

EC_e and SAR, discussed previously, classify soils that are affected by salt to different classes (Fipps, 2003), as per Figure 2.18.

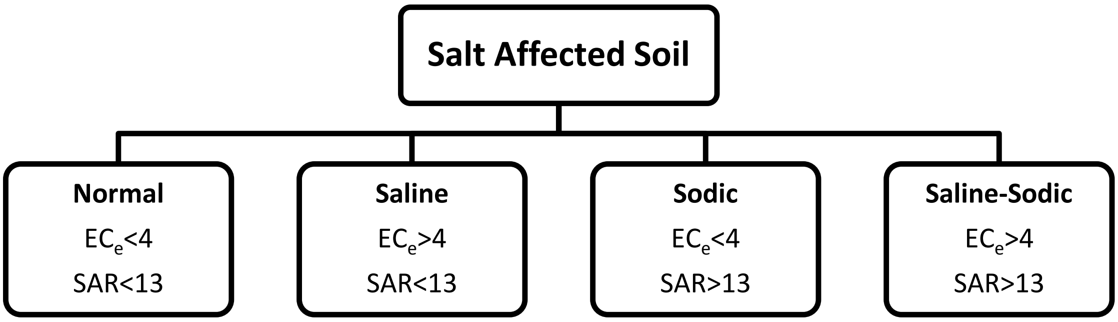


Figure 2.18 - Salt-affected soils classes (Fipps, 2003)

Saline soils usually have a pH less than 8.5. Such soils contain mainly Na^+, Ca^{++} and Mg^{++} ions, which cause the famous whitish layer that builds up on the soil surface (Fipps, 2003). Leaching is effective in recovering these soils since the compounds which cause saline soils are water soluble (Podmore, 2009). In such soils, sodium damages the enduring formation which helps render the soil impermeable. So, leaching solely would be insufficient unless elevated salt levels are reduced (Fipps, 2003). When low salinity water is used to irrigate soils with high ESP levels, the soil segregates and becomes impervious (George, 1983). So, the plant does not get enough water.

2.6.3 Irrigation Water Classification

EC_{iw}, the TDS, and SAR parameters are used to classify the fitness of irrigation water. Allowable limits of different classes of water used for irrigation are illustrated in Figure 2.19. In Figure 2.20, classification of water sodium hazard is shown starting from low to very high according to SAR rating (Fipps, 2003).

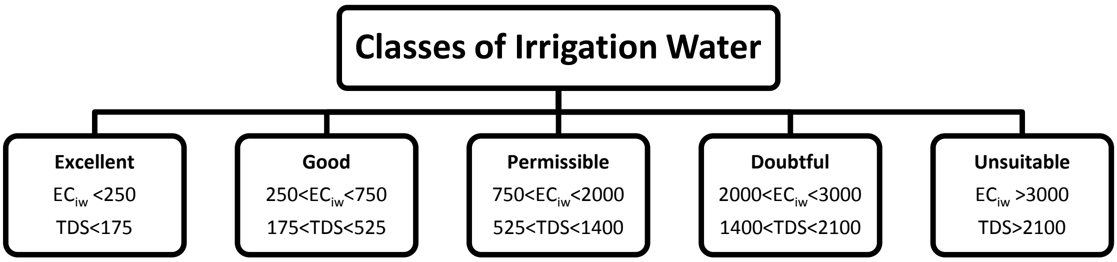


Figure 2.19 – EC and TDS limits for irrigation water (EC_{iw} in Micromhos/cm at 25°C and TDS in Gravimetric ppm)(Fipps, 2003)

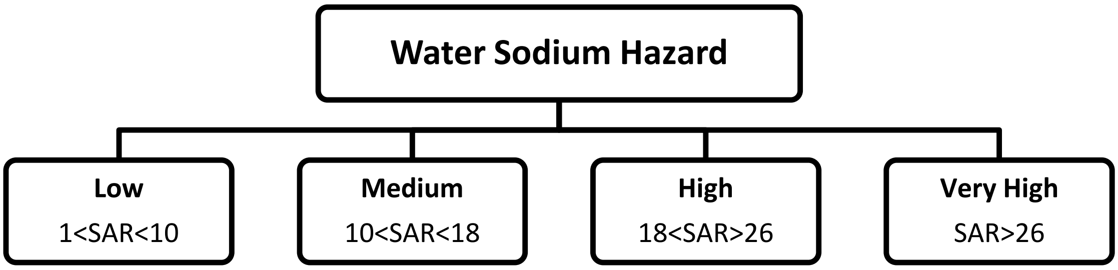


Figure 2.20 – Classification of sodium hazard water according to SAR Values (Fipps, 2003)

CHAPTER 3 – FORWARD OSMOSIS PROCESS AND FERTILIZER DRAWN FORAWD OSMOSIS TECHNOLOGY

3.1 Introduction

This chapter describes the Forward Osmosis concept as a low-energy desalination option and discusses different FO applications in water industry as well as its advantages and limitations. Fertilities Drawn Forward Osmosis scheme is analyzed being a potential application for FO desalination by assessing the different advantages and challenges. Parts of this chapter were formulated the published paper "Forward osmosis: an alternative sustainable technology and potential applications in water industry".

3.2 Forward Osmosis

3.2.1 Osmosis

Osmosis is defined as "the natural diffusion of solvents or water through a semipermeable membrane while preventing the passage of solutes" (T. Cath, Childress, & Elimelech, 2006). If a solution and a solvent are segregated by a semipermeable membrane, the solution starts to be diluted via attracting the solvent through the membrane. In case an external force is applied on the solution preventing the passage of solvent through the membrane and sustaining an equilibrium, this force is termed "osmotic pressure" (Phuntsho, Hong, Elimelech, & Shon, 2014). Thus, osmosis can be defined as "the natural diffusion of water through a semi-permeable membrane from a solution containing lower salt concentration to a solution containing higher salt concentration" (T. Cath et al., 2006). The osmotic pressure (π) is given by Van't Hoff's relation:

$$\pi = nMRT \qquad \textbf{Equation 3.1}$$

where, n = the Van't Hoff factor (the number of particles of compounds dissolved in the solution, for example n=2 for NaCl),

M = molar concentration of the solution,

R = the universal gas constant (0.0821 $\mathrm{L \cdot atm \cdot mol^{-1} \cdot K^{-1}}$)

T = absolute temperature (in K) of the solution.

It is worth noting that the Van't Hoff relation is only relevant to dilute and ideal solutions in which ions are independent. However, at higher ionic concentrations the solution becomes non-ideal as the electrostatic interactions between the ions increase, decreasing the activity coefficient of ions and the osmotic pressure of the solution (Phuntsho et al., 2014).

3.2.2 Forward Osmosis Process

In FO process, the driving force is naturally created due to the differential concentration between a saline solution and a concentrated draw solution across a semi-permeable membrane (T. Cath et al., 2006). FO makes use of osmotic differential ($\Delta\pi$) across the membrane (Figure 3.1), and not the hydraulic pressure differential (as in the case of RO), to transfer pure water across the selective membrane (McCutcheon, McGinnis, & Elimelech, 2005). Being a semi-permeable membrane, the FO membrane permits the permeation of just water molecules, and rejects most solute ions (T. Cath et al., 2006). Fresh water diffuses from feed water towards the draw solution, resulting in concentration of feed solution (producing highly saline solution or brine) and dilution of draw solution, as presented in Figure 3.1 (Elimelech, 2007).

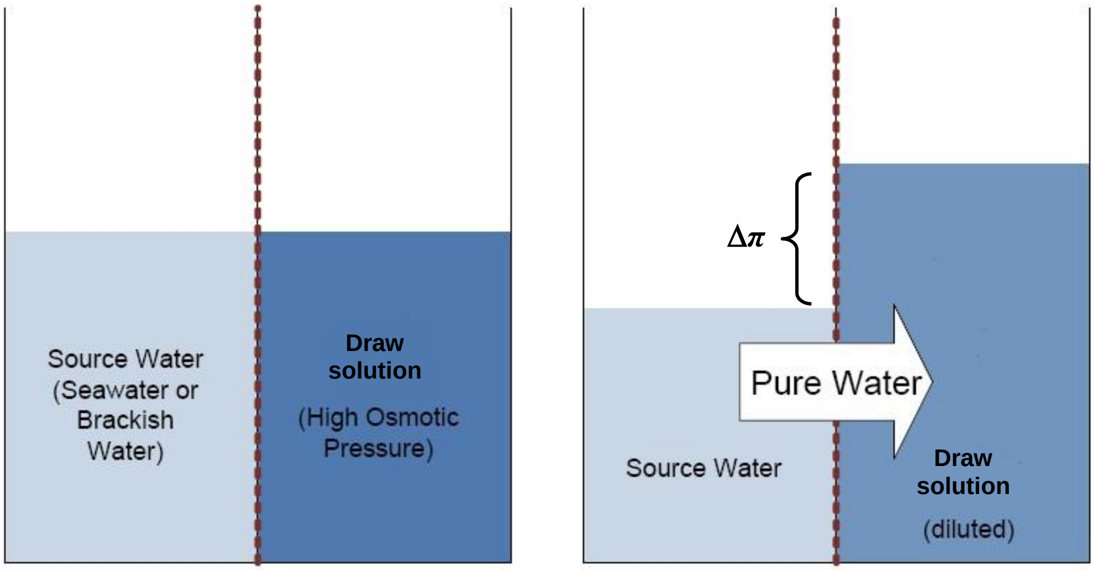


Figure 3.1 - Osmotic pressure differential (Δπ) in FO process (T. Cath et al., 2006; Thompson, & Nicoll, 2011)

According to Cath et al. (2006), the relation describing water transport in FO is:

$$J_w = A(\sigma\Delta\pi - \Delta P) \quad \text{Equation 3.2}$$

where: J_w = the water flux (negative values indicates reverse osmotic flow)

A = water permeability constant of the membrane

σ = reflection coefficient

$\Delta\pi$ = the differential osmotic pressures through the membrane (between the draw and feed solution) (Figure 3.1)

ΔP = applied pressure (for FO: ΔP is zero, for RO: $\Delta P > \Delta\pi$)

Since for FO process ΔP is zero, and σ is assumed unity, Equation 3.2 can be rewritten as follows:

$$J_w = A\,\Delta\pi = A[\pi_{DS} - \pi_{FS}] \qquad \textbf{Equation 3.3}$$

Where π_{DS} = bulk osmotic pressure of the DS

π_{FS} = bulk osmotic pressure of the FS

3.2.3 Draw Solution

The key factor of any successful FO process is the choice of an appropriate draw solution. There are different words used in publications to identify this solution, such as “draw solution”, “osmotic agent”, “osmotic media”, “driving solution”, “osmotic engine”, “sample solution” or “brine” (T. Cath et al., 2006). For clarity purposes, the term “draw solution” or “DS” will be used entirely in this work. A draw solution could be any aqueous solution reporting high osmotic pressure. It should provide sufficient driving force to cause a forward permeation of water across the membrane and therefore it is an essential part of the FO process. The osmotic pressure is a function of concentration, number of species in the solution, the MW of the solute and temperature. Osmotic pressure is independent of the types of species created in the solution (colligative property). A solute with small MW and highly soluble is expected to generate higher osmotic pressure and thus can result in better water flux (McCutcheon et al., 2005). Many types of DS have been studied in the past and they can be generally classified as inorganic-based DS, organic-based DS and other compounds such as magnetic nano-particles, RO brine, ionic polymer hydrogels and dendrimes (Achilli, Cath, & Childress, 2010). The focus of this work will be on inorganic draw solutions.

Over the past few years, many draw solutions were considered. A review of different draw solutions and their recovery techniques is shown in Table 3.1.

Table 3.1 - Summary of the draw solutions tested in FO investigations and their recovery techniques (adapted from Ge, Fu, & Chung, 2014; Ge, Ling, & Chung, 2013; Zhao, Zou, Tang, & Mulcahy, 2012)

Year	Draw solute / solution	Recovery method	Reference
1964	Ammonia and carbon dioxide	Heating	(Neff, 1964)
1965	Volatile solutes (e.g. SO_2)	Heating or air stripping	(Batchelder, 1965)
1965	Mixture of H_2O and another gas (SO_2) or liquid (aliphatic alcohols)	Distillation	(Glew, 1965)
1972	Al_2SO_4	Precipitation by doping $Ca(OH)_2$	(Frank, 1972)
1975	Glucose	None	(Kravath & Davis, 1975)
1976	Glucose–Fructose	None	(Kessler & Moody, 1976)
1989	Fructose	None	(Stache, 1989)
1992	Glucose	Low pressure RO	(Yaeli, 1992)
1997	$MgCl_2$	None	(Loeb, Titelman, Korngold, & Freiman, 1997)
2002	KNO_3 & SO_2	SO_2 was recycled through standard means	(R. L. McGinnis, 2002)
2005–2007	NH_3 & CO_2 (NH_4HCO_3) or NH_4OH–NH_4HCO_3	Moderate heating (~60 °C)	(McCutcheon et al., 2005, 2006)
2007	Magnetic nanoparticles	Captured by a canister separator	(Adham, Oppenheimer, Liu, & Kumar, 2007)
2007	Dendrimers	Adjusting pH or UF	(Adham et al., 2007)
2007	Albumin	Denatured and solidified	(Adham et al., 2007)
2008	Salt, ethanol	Pervaporation-based separations	(McCormick, Pellegrino, Mantovani, & Sarti, 2008)
2010	2-Methylimidazole based solutes	Membrane Distillation	(Yen, N, Su, Wang, & Chung, 2010)
2010	Magnetic nanoparticles	Recycled by external magnetic field	(Ge, Su, Chung, & Amy, 2011; Ling, Wang, & Chung, 2010)
2011	Stimuli-responsive polymer hydrogels	Deswelling of the polymer hydrogels	(Li, Zhang, Yao, Zeng, et al., 2011; Li, Zhang, Yao, Simon, & Wang, 2011)
2011	Hydrophilic nanoparticles	UF	(Ling & Chung, 2011)
2011	Fertilizers	None	(Phuntsho, Shon, Hong, Lee, & Vigneswaran, 2011)
2011	fatty acid-polyethylene glycol	Thermal method	(Linda & Iyer, 2011)
2012	Sucrose	NF	(Su, Chung, Helmer, & Wit, 2012)
2012	Polyelectrolytes	UF	(Ge, Su, Amy, & Chung, 2012)
2012	Thermo-sensitive solute (Derivatives of Acyl-TAEA)	Not studied	(Noh et al., 2012)
2012	urea, ethylene glycol, and glucose	Not studied	(Yong, Phillip, & Elimelech, 2012)
2012	Organic salts	RO	(Bowden, Achilli, & Childress, 2012)
2012	hexavalent phosphazene salts	Not studied	(Stone, Wilson, Harrup, & Stewart, 2013)
2014	Hydro Acid Complexes	Recycled	(Ge et al., 2014)

3.2.3.1 Draw Solution Selection Criteria

According to McCutcheon et al. (2005) and Zhao et al. (2012), an effective DS solute must have the following distinctive properties:

1. High osmotic driving force, which leads to high water flux and recovery rates (Zero Liquid Discharge or "ZLD").
2. Soluble in water
3. Small molecular weight to produce a high osmotic pressure
4. Non-toxic, since limited amounts might exist in produced water after separation. Sometimes, the solute is for eating or drinking, such as sucrose or fructose.
5. Chemically well-matched with the membrane, since the DS can react and deteriorate the membrane.
6. Easily and economically separated from FS and recycled

3.2.3.2 Ammonium Bicarbonate Draw Solution

Utilizing a DS made up of ammonia gas (NH_3) and carbon dioxide gas (CO_2), proved to meet the desired DS characteristics elaborated above (McCutcheon et al., 2005). Not only is the Ammonium bicarbonate highly soluble in water, but also it has a relatively small molecular weight, which leads to high osmotic pressure. Using this type of draw solution, osmotic pressures more than that of seawater can be achieved (Figure 3.2). This FO draw solution exhibits an osmotic pressures more than 200 atm., allowing significant recovery rates and significant decrease in brine discharges from the process, leading to ZLD (McCutcheon et al., 2006).

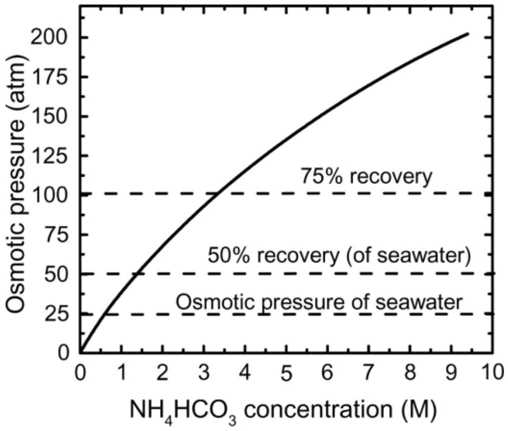


Figure 3.2 - Osmotic pressure produced by ammonium bicarbonate solution at 50°C (McCutcheon et al., 2005).

Another advantage of the ammonium bicarbonate draw solution is that when moderately heated (60 °C), the solutes decompose into NH_3 and CO_2, which can be easily separated and recycled by standard methods (i.e. low-temperature distillation consuming low amounts of energy) (McCutcheon et al., 2005, 2006). The decomposed gases can be recycled to rejuvenate the DS (Figure 3.3).

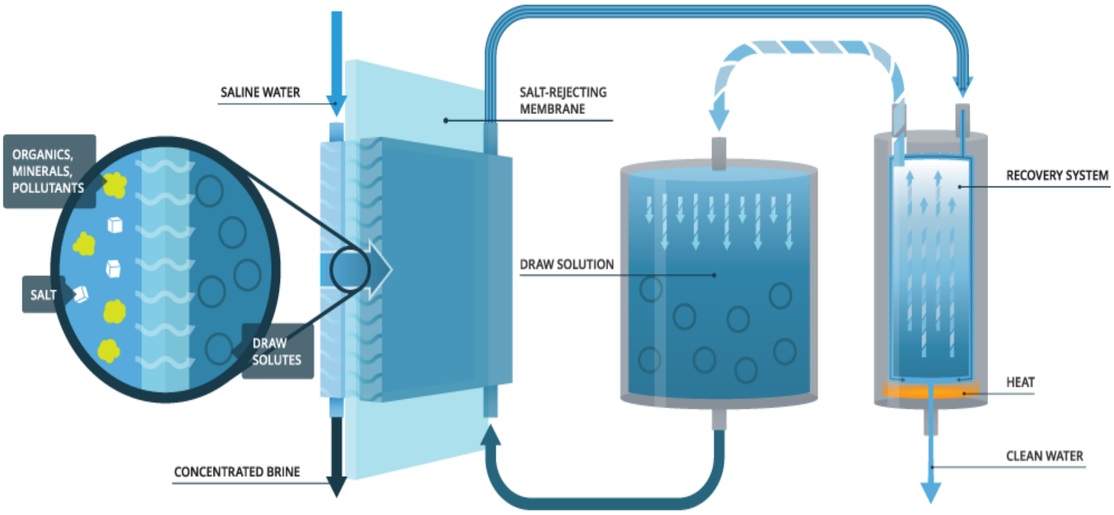


Figure 3.3 - FO process showing draw solution recovery system (Oasys Water, 2013)

3.2.4 Advantages of Forward Osmosis

The FO desalination process requires much less electrical energy than RO or any other conventional thermal desalination processes practiced worldwide (Robert L. McGinnis & Elimelech, 2007). Furthermore, the FO process does not entail the multiple stages, large heat transfer areas, and large pumping volumes needed for MSF and MED (Robert L. McGinnis & Elimelech, 2008).

A lot of research has been directed to FO worldwide, signifying how promising this technology is. Figure 3.4 highlights the increasing attention directed to FO research by displaying the FO associated publications since 2005 until 2015. Since 2005, more than 600 journal papers have been published discussing FO.

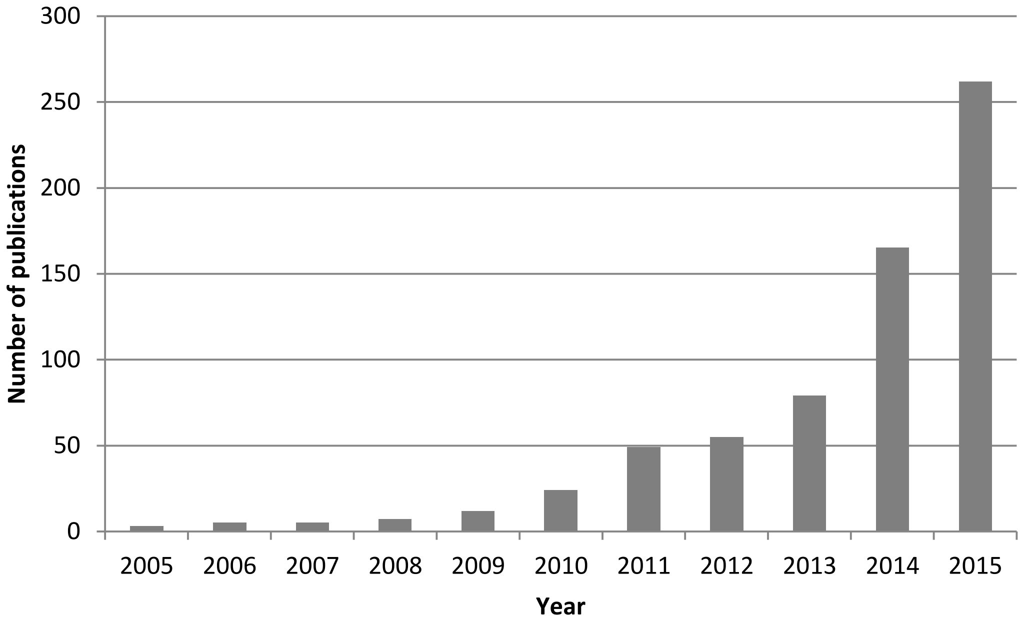


Figure 3.4 - FO Publications between 2005 and 2015, (based on the American University in Cairo Library One Search Engine)

Compared to RO, FO technology is believed to have the edge due to the following reasons:

- FO does not entail high energy requirements like in RO process (Robert L. McGinnis & Elimelech, 2007; C.H. Tan & Ng, 2010; Thompson, & Nicoll, 2011). As per Figure 3.5, it is reported that FO requires almost less than quarter the energy required for RO.
- The FO process does not require the multiple stages, large heat transfer areas, and large pumping volumes required by MSF and MED (Robert L. McGinnis & Elimelech, 2008).
- Recent studies indicate that membrane fouling is not a significant issue in FO process as it is in RO, as fouling in case of FO is physically reversible, so pretreatment and chemical cleaning are no longer essential for FO process as it is in the RO process (Lay et al., 2010).
- FO proved to have a considerably high rejection to a wide range of contaminants other than salt (McCutcheon et al., 2005).
- The equipment used is simple and membrane support is less of a problem (Zhao, Zou, Tang, et al., 2012).
- FO membranes manufacturing is developing rapidly which makes the FO technology even more promising (Lee, Boo, Elimelech, & Hong, 2010).

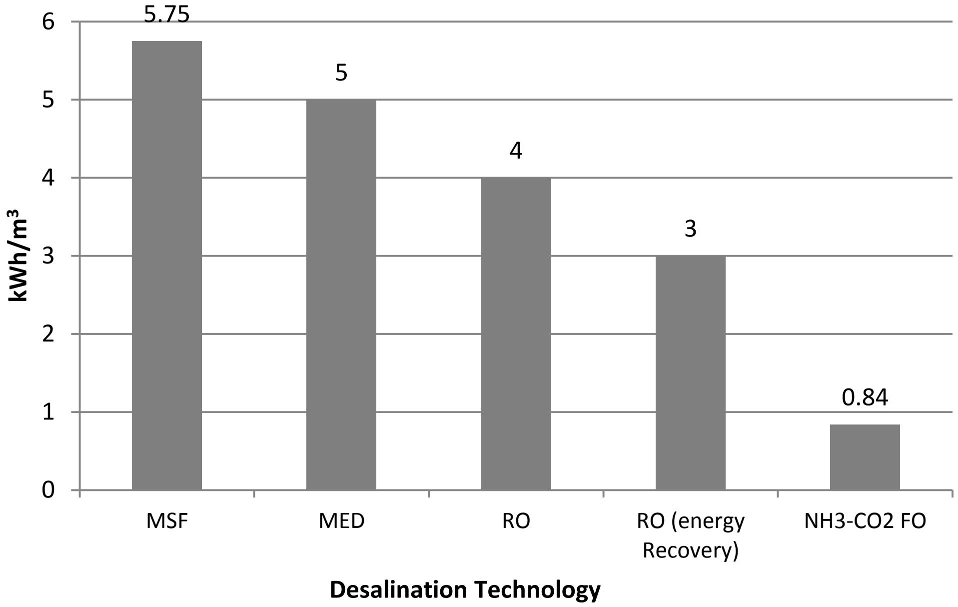


Figure 3.5 - Energy requirements for different desalination processes (Phuntsho, 2012)

3.2.5 Forward Osmosis Membrane

The development of improved semi-permeable membranes for FO is critical for advancing the field of FO (McCutcheon et al., 2005). Not only will this lead to improved performance in current applications, but also will develop new ones. Cath et al. (2006) and Zhao et al. (2012) argue that the preferred properties of FO membranes are the following:

- dense active layer
- minimum thickness with minimum porosity, minimizing ICP and increasing water flux
- hydrophilic to increase flux and control fouling

According to Zhao, Zou, Tang, et al., (2012), membrane development is shown in Table 3.2.

Table 3.2 - FO membrane developments (Zhao, Zou, Tang, et al., 2012)

Year	Membranes	Materials	Preparation methods
2005	Capsule wall membrane	Cellulose acetate or ethyl cellulose	Dip-coating, phase inversion
2007	Hollow fiber NF	Polybenzimidazole (PBI)	Dry-jet wet phase inversion
2008	Flat sheet cellulose acetate membrane	Cellulose acetate	Phase inversion and then annealing at 80–95 °C
2009	Dual-layer hollow fiber NF	PBI–PES/PVP	Dry-jet wet phase inversion (i.e. coextrusion technology)
2010	Hollow fiber	PES substrates, polyamide active layer	Dry-jet wet spinning and interfacial polymerization (IP)
2010	Hollow fiber NF	Cellulose acetate	Dry-jet wet spinning
2010	Flat sheet double-skinned	Cellulose acetate	Phase inversion, and then annealing at 85 °C
2010	Flat sheet TFC membrane	Polysulfone (PSf) support, Polyamide active layer	Phase inversion and IP
2010	Double dense-layer membrane	Cellulose acetate	Phase inversion
2011	Modified RO	PSf support modified by polydopamine	Chemical coating
2011	Flat sheet composite	Cellulose acetate cast on a nylon fabric	Phase inversion
2011	Flat sheet composite	PAN substrate, multiple PAH/PSS polyelectrolyte layers	Layer-by-layer assembly
2011	Positively charged hollow fiber	PAI substrate treated by PEI	Chemical modification
2011	Positively charged flat sheet	PAI substrate treated by PEI	Chemical modification
2011	Flat sheet TFC polyamide	PES/SPSf substrate, Polyamide active layer	Phase inversion and IP
2011	Flat sheet TFC polyamide	PES/sulfonated polymer substrate, Polyamide active layer	Phase inversion and IP
2011	Flat sheet TFC	PSf support, polyamide active layer	Phase inversion and IP
2011	Nanoporous PES	PES cast on PET fabric	Phase inversion
2011	Cellulose ester membrane	Cellulose ester	Phase inversion
2011	Flat sheet TFC polyamide	PES nanofiber support, polyamide active layer	Electrospinning and IP
2011	Flat sheet TFC polyamide	PSf nanofiber support, polyamide active layer	Electrospinning and IP

FO membranes can be categorized according to their manufacturing method: 1) Phase Inversion-formed Cellulose membranes, 2) Thin Film Composite (TFC) membranes and, 3) Chemically Modified membranes (Zhao, Zou, Tang, et al., 2012).

3.2.5.1 Phase Inversion-Formed Cellulosic Membranes

This type of membrane is prepared by phase inversion by cellulose acetate as the coating polymer. In phase inversion, the polymer is precipitated using a range of techniques, such as cooling, saturation using a non-solvent coagulant, evaporation and vapor adsorption (Figure 3.6) (L. K. Wang, Shammas, Hung, & Chen, 2008).

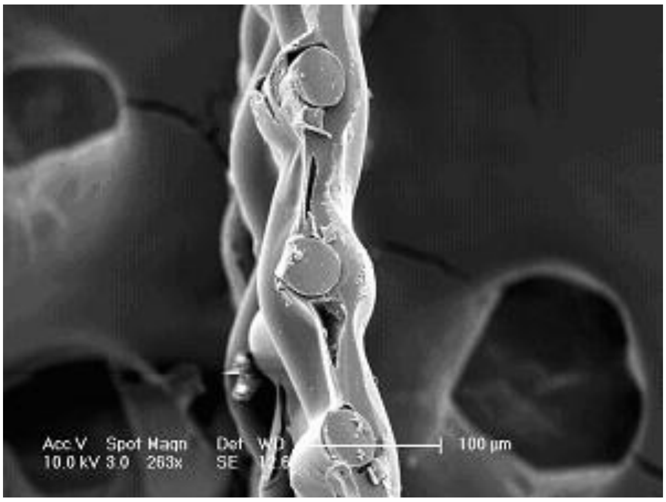


Figure 3.6 - SEM images of cross sections of FO Cellulose Triacetate membrane (McCutcheon et al., 2005)

Cellulose acetate is the most famous type of phase-inversion formed membranes. This type inherits many beneficial properties such as: hydrophilicity, low fouling probability, moderate water flux, mechanical strength, availability and chlorine tolerance (Zhao, Zou, Tang, et al., 2012). However, the problems of CTA membranes ought to be totally understood prior to its use for the development of new FO membranes. Cellulose acetate membranes poorly resist hydrolysis and biological attach (L. K. Wang et al., 2008).

3.2.5.2 Thin Film Composite Membranes

Thin Film Composite (TFC) membranes are most famous for being used in reverse osmosis applications. They are manufactured of polyamide accumulated over a polysulfone layer placed over a non-woven fabric support (Figure 3.7) (Yip, Tiraferri, Phillip, Schiffman, & Elimelech, 2010). Such a configuration insures the preferred properties of rejection of feed salts, high flux, and mechanical strength (Zhao, Zou, Tang, et al., 2012). The polyamide (PA) layer is in charge of the rejection and is selected mainly due to its pure-water permeation and its high rejection of other soluble ions in the feed side including salt ions.

The majority of the methods adopted for preparing TFC-FO membranes are close enough to the common methods for the manufacturing of RO membranes (Zhao, Zou, Tang, et al., 2012). The TFC membranes prepared using interfacial polymerization are expected to exhibit significant salt rejection. Thus, it is the FO membrane support layer that merely dictates overall membrane performance.

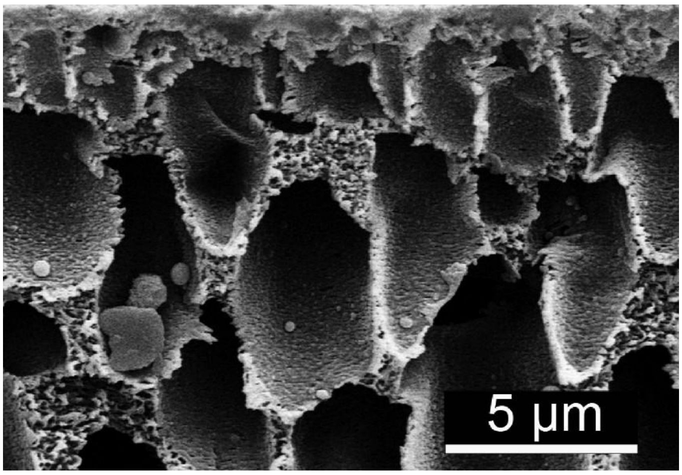


Figure 3.7 - SEM image of a cross-section of a TFC-FO membrane (Yip et al., 2010)

3.2.5.3 Chemically Modified Membranes

Lately, chemical adjustment methods have also been used to manufacture novel FO membranes. As an example, Arena, McCloskey, Freeman, & McCutcheon (2011) used polydopamine (PDA) to change the support layer of common TFC-RO membrane for FO purpose. This modification decreased ICP effects and enhanced water flux. Following that, there has been a development of a kind of hollow fiber FO membrane, where the active layer carries a positive charge on its surface (Setiawan, Wang, Li, & Fane, 2011).

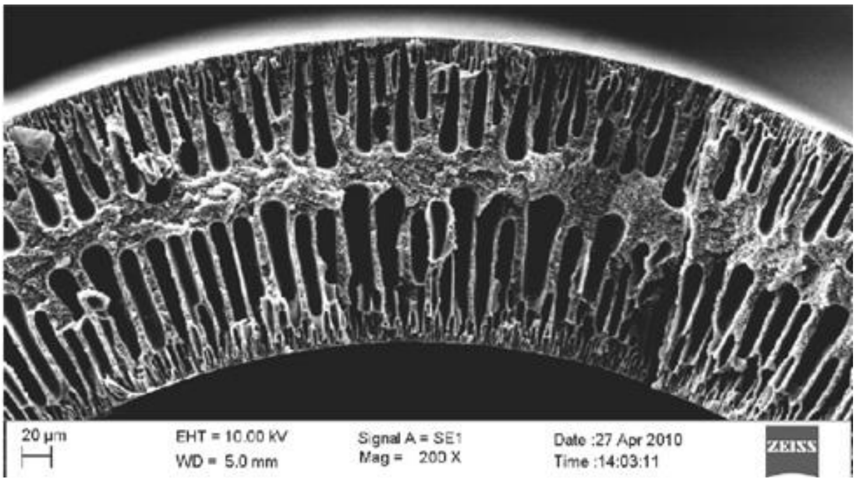


Figure 3.8 -- SEM image of a cross-section of a chemically modified hollow fiber FO membrane (Setiawan et al., 2011)

The need for improvement of novel FO membranes is still huge. Thus, utilizing previous techniques of designing RO or NF membranes is a rational means to progress. Figure 3.8 illustrates a SEM image of a chemically modified follow fiber FO membrane.

3.2.6 Reverse Solute Diffusion

Reverse permeation or reverse diffusion of the solute from the DS to the FS is expected due to the difference in concentrations. Cath et al. (2006) noticed that the reverse permeation of the DS is critical as it may endanger the process efficiency. Reverse permeation adversely aggravates fouling (Lee et al., 2010). Multivalent ions introduce severe Internal Concentration Polarization due to their relatively large hydrated diameter size and low diffusion coefficients (Zhao & Zou, 2011b). The Specific Reverse Solute Flux (SRSF), which is defined as “the ratio of the reverse solute flux to the forward water flux”, is used to indicate of membrane selectivity (Phuntsho, Shon, Hong, et al., 2012). This factor is an important one for the assessment of FO process efficiency, where a high value denotes a decline in membrane selectivity and a low FO efficiency and vice versa (Zhao, Zou, Tang, et al., 2012). A study by Phillip, Yong, & Elimelech (2010) has shown that SRSF is a function of the membrane's active layer selectivity and is not a function of the DS concentration. Moreover, utilizing a multivalent draw solution reduces the reverse permeation but causes significantly high ICP and a considerably high tendency of fouling (Zhao, Zou, Tang, et al., 2012).

It is worth noting that the reverse solute diffusion is closely connected to "concentration polarization" phenomenon, which will be discussed in details in the next section.

3.2.7 Concentration Polarization

Equation 3.3 predicts flux only if the flux is considerably low and if the solution is dilute. However, this is not the usual case. In FO process, the difference in osmotic potential through the active layer is usually less than the difference in bulk osmotic pressures, causing lower-than-expected flux (McCutcheon et al., 2005). Such low flux is usually explained by membrane-related transport process, which is Concentration Polarization (CP). There are two forms of concentration polarization: External CP and Internal CP, as shown in Figure 3.9 (T. Cath et al., 2006).

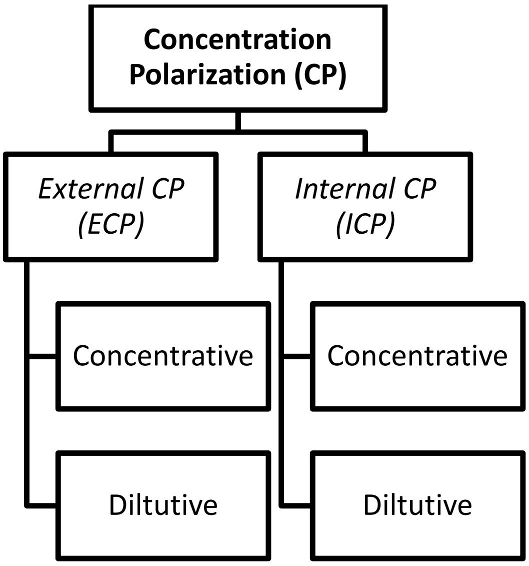


Figure 3.9 - Concentration Polarization types

3.2.7.1 External Concentration Polarization

External Concentration Polarization (ECP) happens outside the membrane formation. It usually takes place at the active rejection layer. There are two kinds of ECP: Concentrative and Dilutive.

When active layer is facing FS, solutes start to deposit on the active layer side of the membrane, causing “concentrative” ECP. Concurrently, the DS contacting the other side of the membrane is dissolving by the permeating water, causing “dilutive” ECP. According to Yip & Elimelech (2011), both concentrative and dilutive ECP decrease the net driving force. The undesirable effect of ECP can be mitigated by a number of corrective measures, such as using higher flowrate and initiating turbulence near the membrane surface (Lay et al., 2010). It has been proven that ECP has an insignificant role in FO (McCutcheon et al., 2006). A modified flux model considering ECP effect for a symmetric membrane is given as follows (Phuntsho, 2012):

$$J_w = A\left[\pi_{DS}\exp\left(-\frac{J_w}{k_F}\right) - \pi_{FS}\exp\left(-\frac{J_w}{k_F}\right)\right] \qquad \textbf{Equation 3.4}$$

where: J_w = the water flux

A = water permeability constant of the membrane

π_{DS} = bulk osmotic pressure of the DS

π_{FS} = bulk osmotic pressure of the FS

k_F = mass transfer coefficient and it equals $\frac{Sh*D}{D_h}$,

where Sh is Sherwood number, D is the diffusion coefficient of FS and D_h is the hydraulic diameter

3.2.7.2 Internal Concentration Polarization

Internal Concentration polarization (ICP) is similar to ECP, except that the former takes place inside the membrane porous support layer (T. Cath et al., 2006). Two phenomena can take place according to FO membrane orientation. That is why, there are two types of ICP: Concentrative and Dilutive.

When the DS is placed facing the active layer and FS faces the support layer, internal concentration polarization (ICP) occurs (Gray, McCutcheon, & Elimelech, 2006). The water flux passing from the support layer across the active layer concentrates solutes on the inner side of the active layer. However, this phenomenon is opposed by back permeation away from the active layer, as shown in Figure

3.10(b). This is called "concentrative” ICP, which received the most attention in literature (T. Cath et al., 2006).

By changing the membrane orientation described above, internal concentration polarization (ICP) becomes significant. As Gray et al. (2006) explains, the solute in the DS must permeate across the support layer reaching the inner plane of the active layer for flux to happen. As pure water passes from the active to the support layer, the solute concentration decreases by convection effects. Although equilibrium condition is rapidly accomplished, the concentration on the inner plane of the active layer is usually less compared to bulk DS concentration. A schematic of the described internal concentration polarization is shown in Figure 3.10(a). This is called "dilutive ICP".

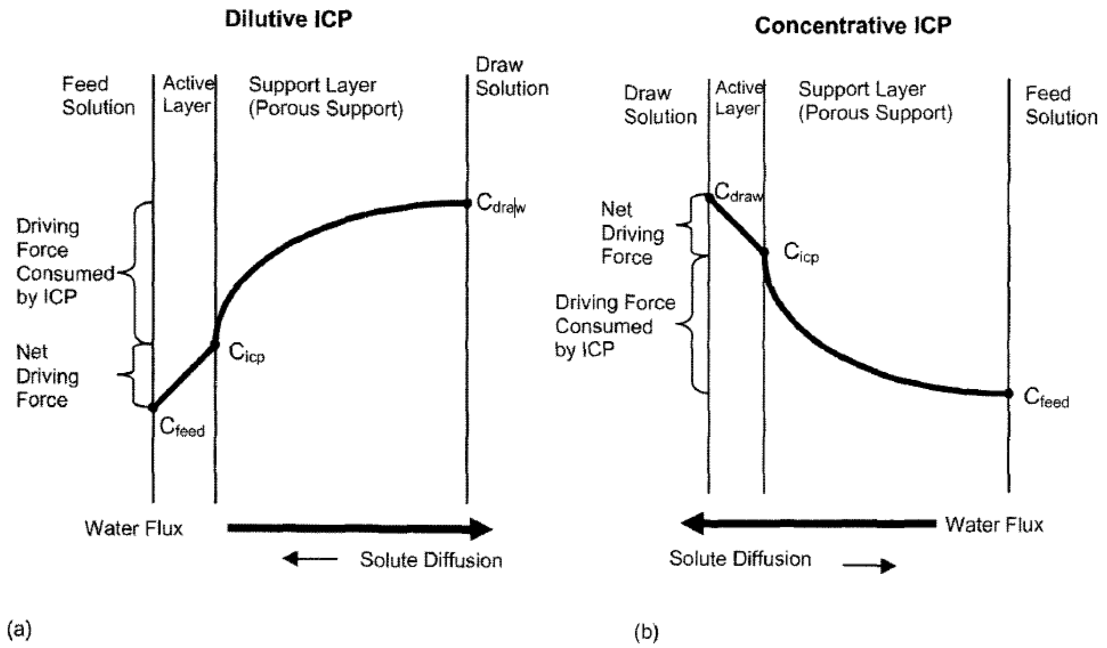


Figure 3.10 – (a) Dilutive ICP, (b) concentrative ICP (Gray et al., 2006)

CICP is modeled by Zhao, Zou, Tang, et al. (2012) as:

$$J_w = A\left[\pi_{DS,m} - \pi_{FS}\exp(-J_w K_D)\right] \qquad \textbf{Equation 3.5}$$

where: J_w = the water flux

A = water permeability constant of the membrane

$\pi_{DS,m}$ = membrane surface osmotic pressure on the permeate side

π_{FS} = bulk osmotic pressure of the FS

K_D = solute resistivity for diffusion within support layer and it equals $\frac{t\tau}{D\varepsilon}$, where D is the solute diffusion coefficient and t, τ and ε are the thickness, tortuosity and porosity of the support layer, respectively.

DICP is given by Chien Hsiang Tan & Ng (2008) as:

$$J_w = A[\pi_{DS}\exp(-J_w K_D) - \pi_{FS,m}]$$ **Equation 3.6**

where: π_{DS} = bulk osmotic pressure of the DS

$\pi_{FS,m}$ = membrane surface osmotic pressure on the FS

3.2.7.3 Dilutive Internal Concentration Polarization Coupled with Concentrative External Concentration Polarization

In FO mode, where active layer faces the FS and the support layer faces the DS, “Dilutive” ICP coupled with “Concentrative” ECP occurs (Figure 3.11). The coupled effect on the process performance is significant resulting in reduction of water flux. Thus, prediction of the permeate flux using FO process modeling has been investigated and developed in order to achieve better performance of the FO membrane. Recent studies have reported the negative impact of coupled ECP and ICP on the effective driving force across the membrane. Studies have concluded that the cause of the substantial flux decline is mainly contributed by the dominated ICP effect through the membrane (Gray et al., 2006; McCutcheon et al., 2005; Chien Hsiang Tan & Ng, 2008; Zhao & Zou, 2011b). A modified model considering coupled effect of DICP and CECP on water flux is given by McCutcheon & Elimelech (2006) as follows:

$$J_w = A\left[\pi_{DS}\exp(-J_w K_D) - \pi_{FS}\exp\left(-\frac{J_w}{k_f}\right)\right]$$ **Equation 3.7**

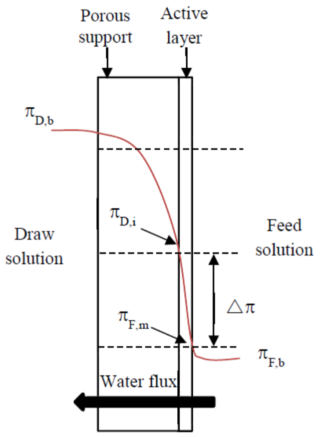


Figure 3.11 – Coupled effect of DICP and CECP in FO mode. ($\pi_{D,b}$ and $\pi_{F,b}$ is the bulk draw osmotic pressure of the draw and feed, respectively, $\pi_{F,m}$ is membrane surface osmotic pressure on the feed side, $\pi_{D,i}$ is the effective osmotic pressure of draw solution, and $\Delta\pi$ is the effective osmotic driving force) (McCutcheon & Elimelech, 2006).

3.2.8 Potential Applications of Forward Osmosis in Water Industry

FO use in water industry has been investigated in a wide range of applications, including desalination, wastewater treatment and food processing. All of these applications can be summarized under two general fields: Desalination and Water Reuse, as illustrated in Figure 3.12, where each field can be further divided into a more specific type of application. Although there are many other useful FO applications, next section will highlight only some of them.

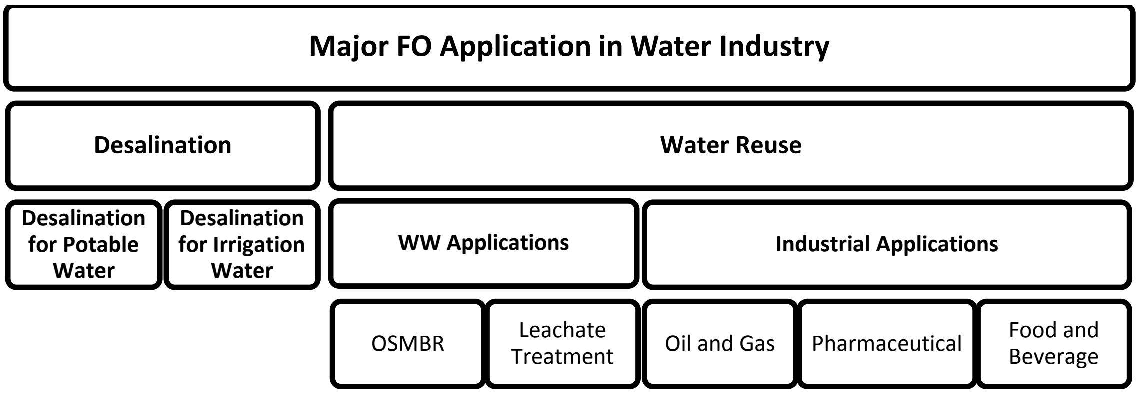


Figure 3.12 - Major FO Applications in Water Industry (Nasr & Sewilam, 2015a)

3.2.8.1 Forward Osmosis Desalination for Potable Water

This type of desalination, which is sometimes called “direct FO desalination”, involves two main steps: (i) osmotic desalination and (ii) separation of draw solutes and fresh water from the draw solution (DS). Although theoretically any solution that generate osmotic pressure more than the osmotic pressure of the feed water can be used as a DS, the DS for Potable water production must have special properties. Besides meeting the general selection criteria mentioned in the previous section, the DS for potable water should be easy to separate, recover and regenerate for reuse with minimum effort. In addition, any trace concentration of the draw solutes in the final desalted water should meet the WHO Guidelines for drinking-water quality (Duranceau, 2012). That is why, one of the main challenges in the application of FO desalination for potable water is the post separation of draw solutes from the fresh water and regeneration for further reuse (McCutcheon et al., 2005). This post-treatment process requires energy, and the success of the FO process will ultimately depend on the post-treatment process (T. Cath et al., 2006). The concept of desalination by the FO process for potable water is shown by the schematic diagram in Figure 3.13.

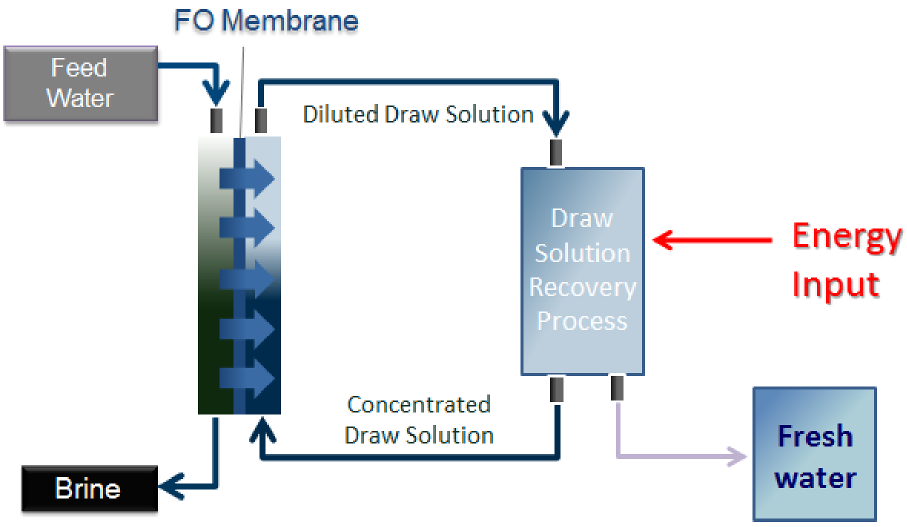


Figure 3.13 - FO desalination for potable water using NH_3-CO_2 solution as DS (McCutcheon et al., 2005)

Table 3.3 summarizes the most recent studies/patents on direct FO desalination for potable water production.

Table 3.3 - Overview of FO desalination reported in the last two decades (Valladares Linares et al., 2014)

Year	Feed solution	Draw solution	Post-treatment	Status
1992	Saline water	Sugar cane	Reverse osmosis	Patent
2002	Seawater	KNO_3, SO_2, and NH_4NO_3	Precipitation (cooling) and separation through thermal waste heat	Patent
2005–2011	NaCl (0.05–2 M)	Ammonia–carbon dioxide solution (ammonium bicarbonate and ammonium hydroxide)	Thermal decomposition	Bench, pilot, and patent
2006	N.D.	Magnetoferritin particles	Magnetic field	Patent
2010	Contaminated water	Cross-linked superabsorbent polymer	Microfiltration	Patent
2011–2013	NaCl (0.034 M)	Ionic polymer hydrogels	Dewatering hydrogels via external pressure	Bench
2011	Synthetic seawater	Hydrophilic nano-particles	Ultrafiltration	Bench
2012	Brackish water	Divalent salts (i.e. Na_2SO_4or $MgSO_4$)	Nanofiltration	Bench
2012	Seawater and brackish water	Cloud point solutes (i.e. polyethylene glycols)	Cloud point extraction (thermal process)	Patent
2012	Seawater, brackish water and contaminated water	Retrograde soluble solutes (i.e. polyoxy random copolymer)	Coalescer (thermal process) and nanofiltration	Pilot and patent
2013	NaCl (0.034 M)	Thermally responsive hydrogels with a semi-interpenetrating network	Dewatering hydrogels via thermal process	Bench
2013	NaCl (0.086 M)	$CuSO_4$	Metathesis precipitation	Bench
2013	Saline water and synthetic seawater	Thermo-responsive magnetic nano-particles	Magnetic field	Bench
2013	Synthetic brackish water	NaCl 0.2–1 M	Solar-powered electrodialysis	Bench

The most famous draw solution used for this application is Ammonium Bicarbonate (CO_2-NH_3), formed by mixing ammonium carbonate and ammonium hydroxide in specific proportions to form three different salt species: ammonium bicarbonate, ammonium carbonate and ammonium carbamate (McCutcheon et al., 2005, 2006; Robert L. McGinnis & Elimelech, 2007). The CO_2-NH_3 solution is capable of generating an osmotic pressure reaching 238 bar, which is sufficient to generate water flux by the FO process (Phuntsho, 2012). Once the DS is diluted, the CO_2-NH_3 mixture can be separated by moderate heating (near 60 °C) which decomposes to CO_2 and NH_3 (McCutcheon et al., 2005). Separation of the fresh product water from the diluted draw solution can be achieved by several separation methods, such as the multi-stage distillation process or membrane distillation (MD) methods (McCutcheon et al., 2005). The degasified solution left behind in the column consists of pure product water and the distillate is a re-concentrated draw solution to be reused in the FO desalination process (Robert L. McGinnis & Elimelech, 2007). However, some researchers claim that residual NH_3 in the product water and difficulty to re-dissolve NH_3-CO_2 back to water may limit the use of CO_2-NH_3 as a draw solution for this application (Ge et al., 2013).

Other studies suggested using a hybrid FO–NF system for desalination where DS containing inorganic multivalent ions were used as the DS for the FO process (C.H. Tan & Ng, 2010; Zhao, Zou, & Mulcahy, 2012). NF was used as the post-treatment to remove the draw solutes because it is capable of rejecting multivalent ions and for having a small energy footprint, unlike the RO process (Figure 3.14). Sometimes RO is applied as a post-treatment process for the separation and recovery of draw solutes from the diluted DS (T. Y. Cath, Hancock, Lundin, Hoppe-Jones, & Drewes, 2010; Yangali-Quintanilla, Li, Valladares, Li, & Amy, 2011), as per Figure 3.15. In these combined FO–NF or FO–RO processes, FO offers has major advantages (T. Y. Cath et al., 2010; C.H. Tan & Ng, 2010):

- high quality drinking water due to the multi-barrier protection approach,
- reduced RO fouling due to pre-treatment by FO,
- recovery of the osmotic energy of RO brine,
- low overall energy input,
- no need for chemical pre-treatment

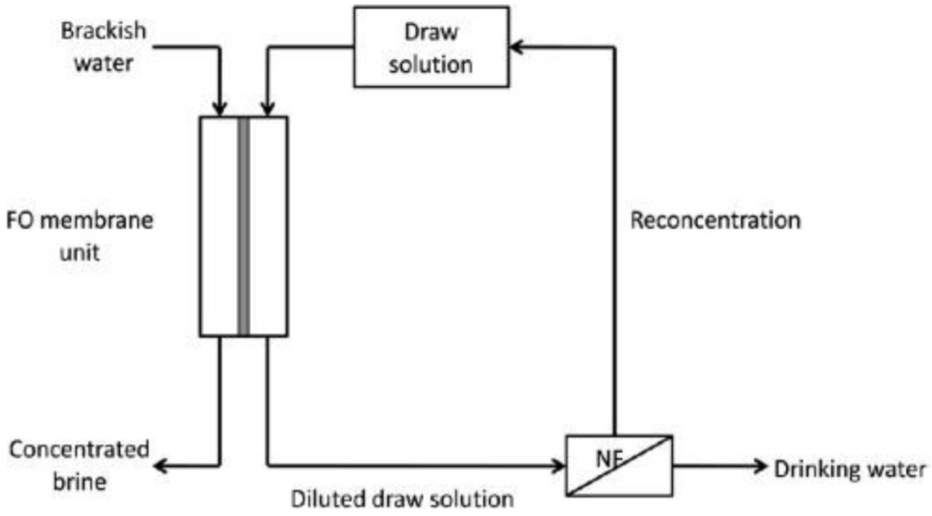


Figure 3.14 - Schematic diagram of the hybrid FO–NF system configuration (Zhao, Zou, & Mulcahy, 2012)

The first commercial FO desalination plant was commissioned in 2012 by Modern Water Company in Al Najdah, Oman, treating 200 m^3/day of seawater. The setup is typically similar to Figure 3.15, where FO process is followed by an RO for recovery and separation of the DS (Moore, Nicoll, Beford, & Harvey, 2014). This plant is considered a milestone in FO development due the outstanding performance in terms of low fouling and scaling potential.

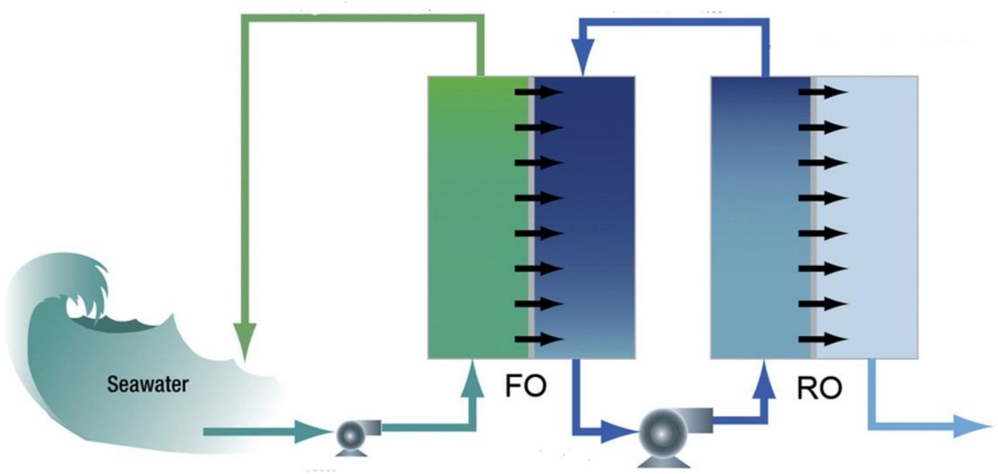


Figure 3.15 - RO being applied as a post-treatment process for FO (T. Y. Cath et al., 2010)

3.2.8.2 Forward Osmosis Desalination for Irrigation Water

FO can be used to produce water for irrigation. This type of FO application is Fertilizer Drawn Forward Osmosis (FDFO), as per Figure 3.16. As Phuntsho (2012) clarifies, two different solutions are used in the FDFO process: saline water (as the feed water) on one side of the membrane, and highly concentrated fertilizer solution (as the Draw Solution) on the other side of the membrane. The two solutions are always kept in contact with the membrane through a countercurrent flow system, where fresh water flows from the saline feed solution towards the highly concentrated fertilizer draw solution. After extracting the water by the FO process, the fertilizer draw solution becomes diluted thus can be used directly for fertigation provided it meets the water quality standards for irrigation in terms of salinity and nutrient concentration avoiding the need for separation and recovery of the draw solution (Phuntsho, Shon, Hong, et al., 2012). However, if the final fertilizer concentration exceeds the nutrient limit, then further dilution may be necessary before applying it for fertigation (Phuntsho, Shon, Majeed, et al., 2012). Although the potential for such idea is very promising, research on this model did not receive enough consideration until recently due to the lack of suitable membranes.

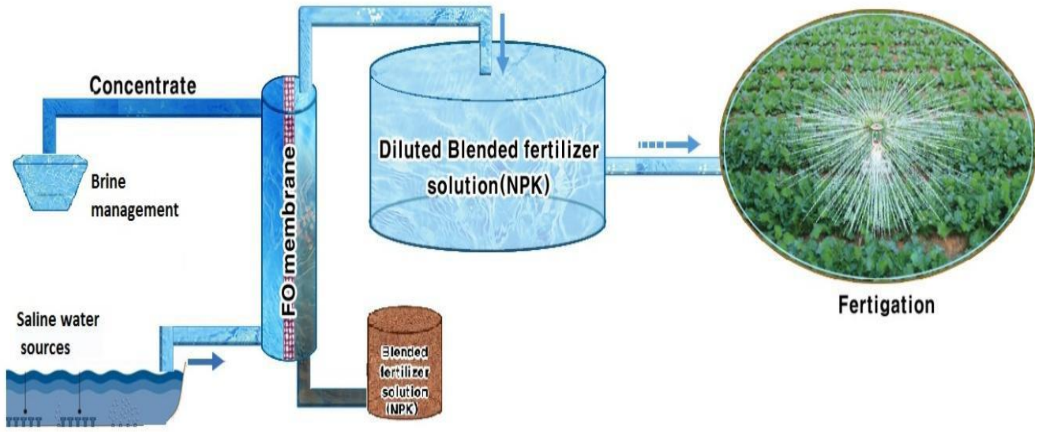


Figure 3.16 - Typical FDFO setup (Phuntsho, Shon, Hong, et al., 2012)

In addition to FO advantages outlined previously, FDFO is a remarkably low energy desalination process. The only energy required in the FDFO process is for sustaining the cross-flow of the feed and draw solutions in contact with the membrane surface and providing sufficient shear force to minimize the Concentration Polarization (CP) effects (Phuntsho, Shon, Majeed, et al., 2012; Phuntsho et al., 2011). This type of FO application will be discussed in more details in Section 3.4.

3.2.8.3 Forward Osmosis for Wastewater Applications

FO holds the potential to treat wastewater efficiently, producing high quality water. Out of the FO literature published in the last decade, approximately 7% addressed complex waters (Lutchmiah, Verliefde, Roest, Rietveld, & Cornelissen, 2014). Enthusiasm surrounding FO for the treatment of complex feeds is because of its advantages over current technologies, as mentioned previously. According to Coday, Xu, et al. (2014), FO can be adapted to treat many complex feed types, such as: complex industrial streams, i.e. from textile industries, oil and gas well fracturing, landfill leachate, nutrient-rich liquid streams, activated sludge, wastewater effluent from municipal sources and even nuclear wastewaters. This section will focus on two major wastewater applications: Osmotic Membrane Bioreactor (OSMBR) and Landfill Leachate Treatment.

3.2.8.3.1 Osmotic Membrane Bioreactor

Integrating FO within a membrane bioreactor (MBR), known as the osmotic membrane bioreactor (OSMBR) is a promising water reclamation application. The system utilizes a submerged forward osmosis (FO) membrane module inside a bioreactor (Figure 3.17). This setup offers the advantage of having higher pollutant rejection with lower hydraulic pressure compared to a conventional MBR system (Lay et al., 2012). In addition, TOC and NH^{4+}-N removals are much higher than those obtained with conventional MBRs, with removals greater than 99% compared to 95% with traditional processes (Achilli, Cath, Marchand, & Childress, 2009). Salt concentration in the bioreactor stabilizes after certain period of operation, in spite of initial flux decline due to reverse salt diffusion of the DS (Phuntsho, 2012).

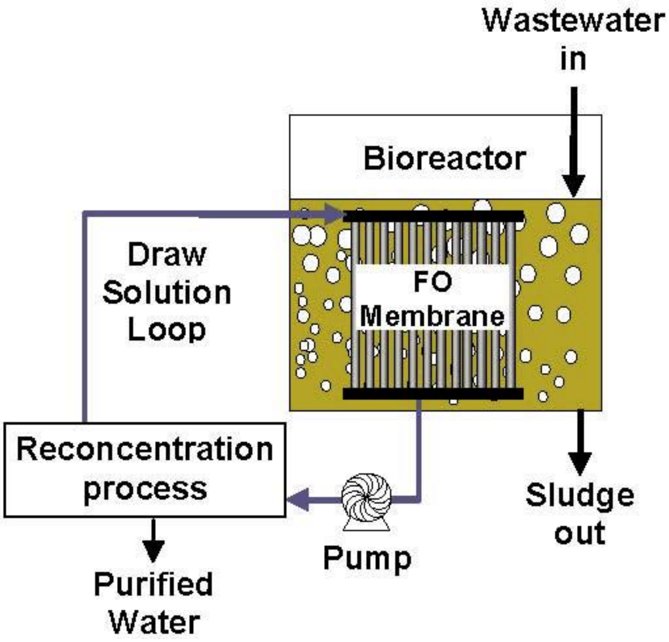


Figure 3.17 - Concept of Osmotic Membrane Bioreactor (OSMBR) (Achilli et al., 2009)

3.2.8.3.2 Landfill Leachate Treatment

The most common treatment for landfill leachate is to process it in a wastewater treatment plant. Yet, wastewater treatment plants normally treat organics, heavy metals, and nitrogen. They often have no treatment for TDS, and in some cases, treatment plants increase TDS (Lutchmiah et al., 2014). Treating landfill leachate is a challenge due to the presence of hard-to-treat constituents in its waste including: high concentrations of solid food waste (organic compounds), high levels of scaling salts, dissolved heavy metals, fouling organics, total dissolved solids (TDS) and a wide variety of other contaminants (T. Cath et al., 2006).

Landfill leachate, being one of the most difficult to treat waste streams, can be successfully processed by a hybrid FO/RO system (Nasr & Sewilam, 2015a). This hybrid system is not only economical, but also capable of generating high quality permeates. The final leachate concentration is between 10 to 20% of the feed concentration (Lampi & Shethji, 2014). The diagram shown in Figure 3.18 shows a system in which hybrid FO/RO system is used to treat leachate.

As per Lampi & Shethji (2014), the system consists of multistage FO and high pressure seawater reverse osmosis (SWRO). The SWRO generates 8% brine (osmotic draw solution) that drives the forward osmosis process and a clean permeate that meets industrial reuse standards or discharged to local water ways. The FO concentrate can be solidified by mixing it with Portland cement and returned to the landfill. The clean permeate from the RO system is discharged to a nearby water stream such as a wetland. The combined FO/RO process proved to be more efficient than the standalone RO process, because RO is less resistant to fouling than the FO process (Lutchmiah et al., 2014). Water recoveries over 90% are achieved generating water quality of total dissolved solids (TDS) less than 100 mg/L. Although FO is inherently low fouling, suspended solids will build decreasing flux. When this occurs, FO modules can be cleaned by a simple osmotic backwashing technique to recover permeation rates (Lampi & Shethji, 2014).

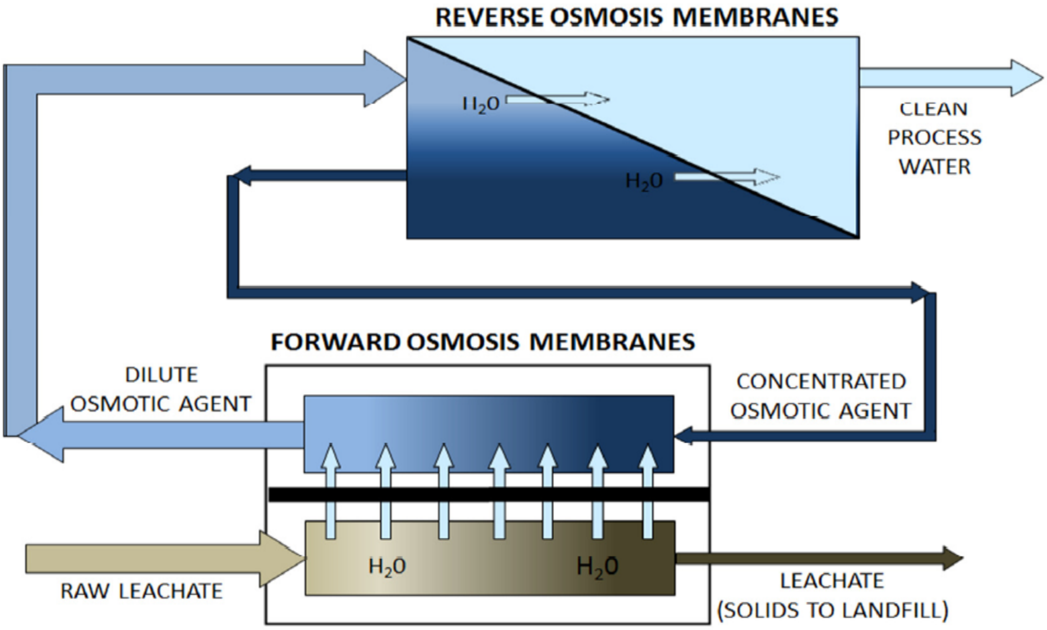


Figure 3.18 - Schematic of hybrid FO/RO system to treat landfill leachate (Lampi & Shethji, 2014)

3.2.8.4 Forward Osmosis for Industrial Applications

Three major Industries were selected to be discussed: Oil and gas, Pharmaceutical and Food and Beverage Industries (Figure 3.12).

3.2.8.4.1 Oil and Gas Industry

One possible application of FO process is the concentration (volume reduction) of oil and gas wastewaters and production of high quality reuse waters. Typically, oil and gas wastewaters from drilling sites are rarely treated and transported to be disposed of in deep injection wells (Coday & Cath, 2014). The challenges associated with these wastewaters are high scaling affinity, high feed NTU and SDI, and the distinctive chemistry for each well (Lampi & Shethji, 2014). Figure 3.19 is a diagram depicting an FO water mass exchanger treating pit-waters. Concentrated brine is used as the DS and the FO process concentrates the wastewater by up to 90% producing diluted brine that can be used for hydraulic fracturing (Coday, Holloway, et al., 2014). This process is ideal if there is a beneficial use for the diluted draw solution, which is not always the case.

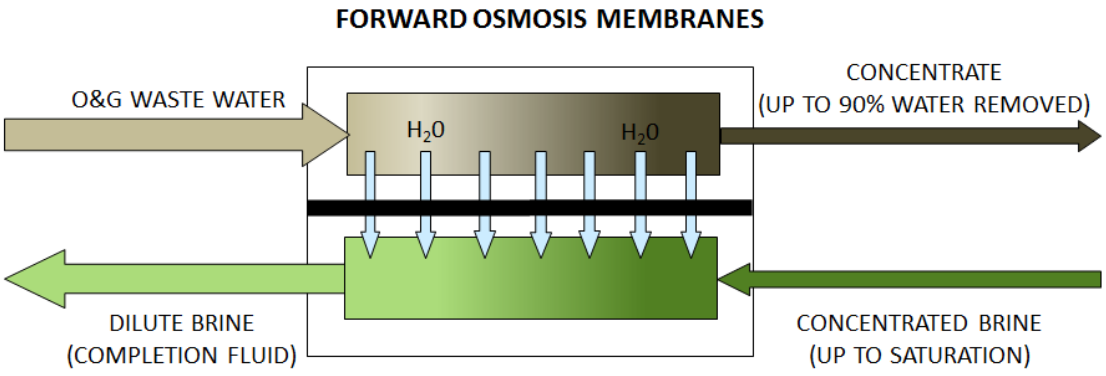


Figure 3.19 - Schematic of dewatering of oil and gas produced water by FO technology as a simple mass exchanger (Lampi & Shethji, 2014)

Usually, it is required to have clean low-TDS water for reuse or direct discharge. In this case, brine re-concentration step must be employed which is accomplished similar to the Landfill Leachate application with a hybrid FO/RO system described previously (Figure 3.20).

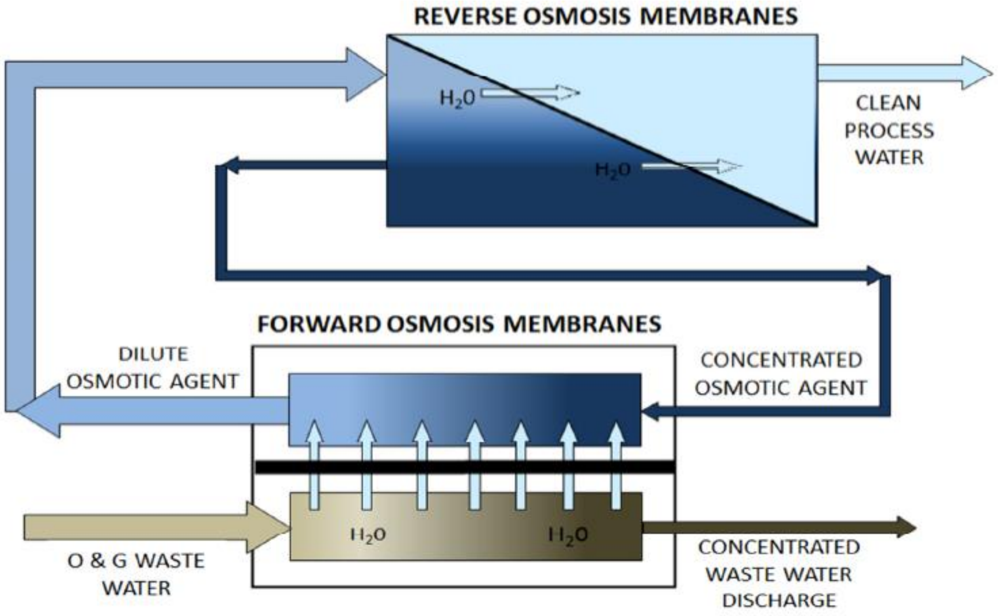


Figure 3.20 - Schematic of hybrid FO/RO system to treat oil and gas produced waters (Lampi & Shethji, 2014)

3.2.8.4.2 Pharmaceutical Industry

Oral administration of drugs may have its limitations since sometimes extended release, targeted delivery, or accurate dosage of a medicine in the body is necessary (T. Cath et al., 2006). Controlled drug delivery system is one possible FO application through the use of pharmaceutical osmotic pumps. Osmosis offers a major advantage as a driving force for constant pumping of drugs, which is precise mass transfer. In addition, controlled drug delivery decreases dosing frequency, provides regular drug concentration in the blood, supports bioavailability, increases patient compliance, and minimizes side effects (Siew, 2013).

As T. Cath et al. (2006) describes, an osmotic pump system is composed of a titanium cylindrical basin with a semi-permeable membrane separating the DS (mixture of NaCl and pharmaceutical excipients) compartment from the drug chamber containing a tiny piston (Figure 3.21). Water flows across the membrane due to the osmotic gradient created between the tissue water and the DS, increasing the pressure inside the DS compartment. As the piston is continuously pushed, the drug is delivered into the body through a small opening located on the other side of the cylinder.

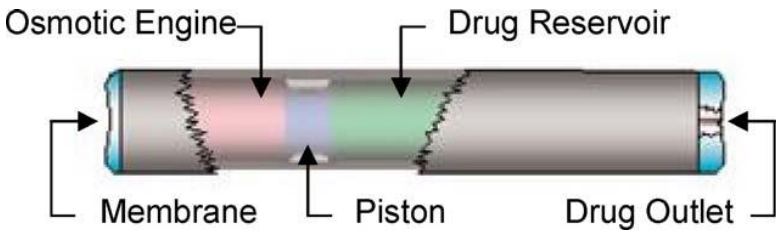


Figure 3.21 - The principal components of a typical osmotic drug-delivery system (T. Cath et al., 2006)

3.2.8.4.3 Food and Beverage Industry

Huge volumes of liquid food and beverages are industrially concentrated in order to reduce storage, packaging, handling and transportation costs. Vacuum evaporation or RO are the most common methods used by the food industry to produce liquid food concentrates, despite serious drawbacks such as poor product quality and high energy demand (Petrotos & Lazarides, 2001). Heat generation and vapor losses negatively impact food color, taste, and potentially the nutritional value of the final product (Coday, Xu, et al., 2014). FO could be applied to overcome the disadvantages of currently used concentration methods. Not only would FO improve final product quality and yield rate, but also it will reduce water usage, overall costs of wastewater treatment and environmental impact, thus making manufacturing process efficient, flexible and sustainable (Jin, n.d.). FO applications in the Food and beverage industry include liquid foods concentration with original nutritional properties maintained, recovery of valuable co-products, waste solids concentration (which can be turned into revenue) and wastewater treatment and recycling (Petrotos & Lazarides, 2001).

FO treatment of red raspberry juice was compared to traditional vacuum concentration. Using a high fructose corn syrup DS, the resulting FO concentrate was found to be of equal or higher quality than that produced by vacuum evaporation (Coday, Xu, et al., 2014). In addition, production of tomato sauce, tomato paste, catsup and pizza sauce is very energy intensive because fresh tomatoes are approximately 94% water (T. Cath et al., 2006). Common industry practice is to evaporate up to 90% of the water by multiple effect evaporators powered by fossil fuels (Petrotos & Lazarides, 2001). FO pre-concentrates tomato solids before evaporation eliminating 20% to 65% of the water and the brine DS is regenerated by sea-water RO (Figure 3.22) reducing the consumption of fossil fuels by as much as 85% (Coday, Xu, et al., 2014). FO process is also applicable to other food and beverages industries such as milk and dairy, sugar, edible oil, fruits vegetable juices and alcoholic drinks (Jin, n.d.).

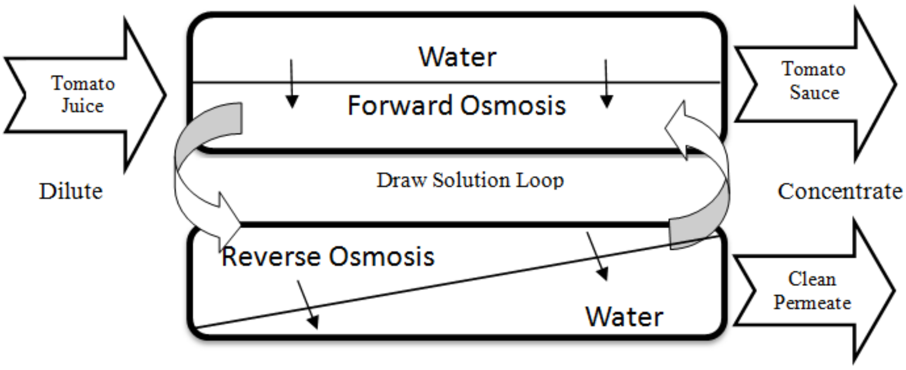


Figure 3.22 - Typical FO Process for Food and Beverage Industry (adapted from Lampi, 2014)

3.3 Fertilizers for Food Production

This section will discuss different types of fertilizers used for food production worldwide. Since fertilizers are an important factor in FDFO application, it should be highlighted.

3.3.1 Types of Fertilizers Used for Food Production

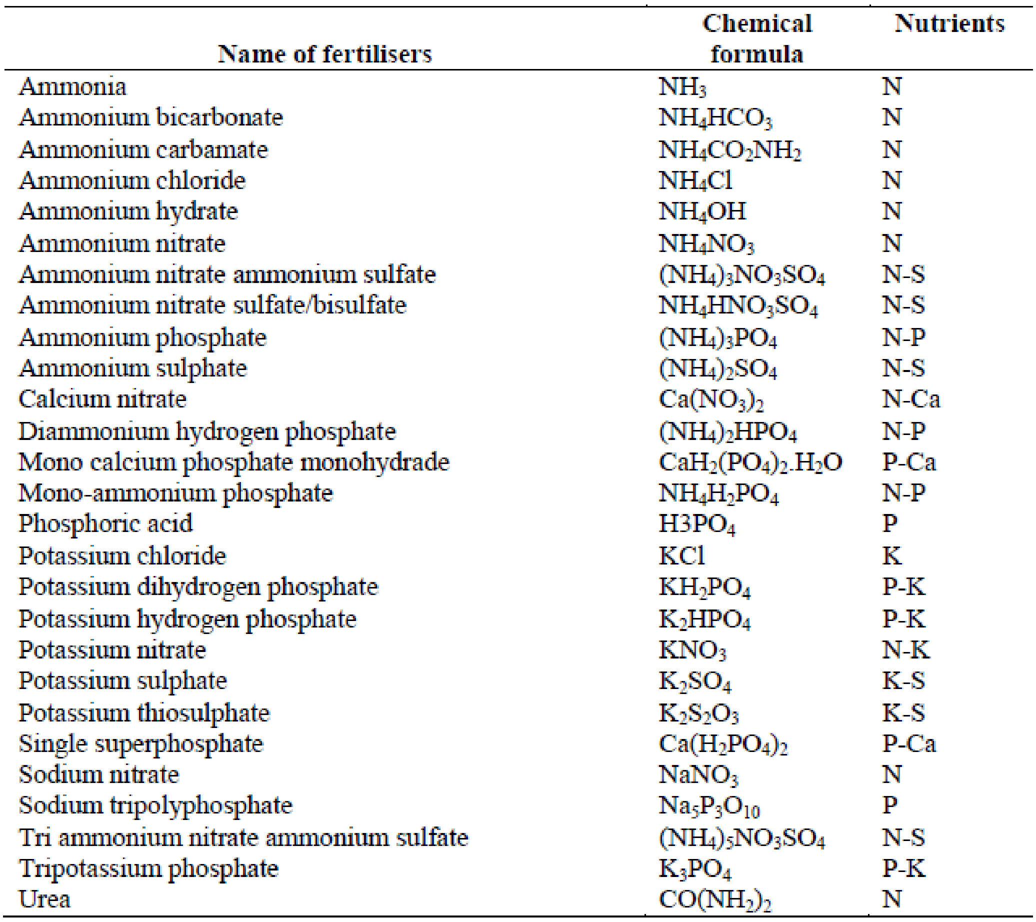
Sixteen elements, divided into 4 groups, are known to be essential for the growth of plants. First group contains C, H, O, N and S which are major constituents of organic substances. Second group containing P and B are needed for energy transfer reactions and carbohydrate movement. Third group contains M, Mg, Ca and Cl, which are required for maintaining ionic balance. Finally, the fourth group contains Cu, Fe, Mn, Mo and Zn, which are needed to enable electron transfer and function as enzyme catalysts (Kafkafi & Tarchitzky, 2011). Essential elements (C, H, O and N) are derived directly or indirectly from the air making up more than 90% of plant material. The other six essential elements (Ca, Mg, P, K, Fe, and S) are derived from the soil. Crop type, cropping seasons and other factors affect plant requirements, although all these elements are essential for healthy plant (Kafkafi & Kant, 2005). The elements that need special consideration are N, P, K, Ca and S. Out of these, NPK are the main nutrients of great importance for mineral or synthetic fertilizers (Phuntsho, Shon, Majeed, et al., 2012). Depending on the types of major elements needed by plants, fertilizers are classified as nitrogen, phosphorous or potassium fertilizers (NPK). The number of major elements present in each fertilizer determines their classification as single, compound or mixed fertilizers (Kafkafi & Tarchitzky, 2011).

3.3.1.1 Nitrogen Fertilizers

Nitrogen forms a major component of proteins and chlorophyll in plants. N is essential for the healthy growth of the plant (FAO, 2005a). Not only is N responsible for increases in crop yield, but also it is taken up in large quantities amongst the major NPK nutrients. A frequent regulated amount of N is more desirable than large amounts with less frequency maintaining healthy plant growth and reducing nutrient leaching. Excessive N results in excessive leaf growth with low fruit yield (Kafkafi & Kant, 2005).

Almost 79% (by volume) of the Earth's atmosphere contains N in the form of nitrogen gas. Yet, only a limited number of plant types can make use of this N directly from the air. Thus, for most plants, N must be made available to the soil in a dissolved form for proper cropping (FAO, 2004). Urea is the most widely used N fertilizer in the world and Egypt is no exception. Inorganic N in urea, is produced by fixing N from the atmosphere using natural gas (El-Gabaly, 2015). Table 3.4 shows some of the most commonly used fertilizers as a main source of N for agricultural production.

Table 3.4 – List of chemical fertilizers used worldwide (Phuntsho, Shon, Majeed, et al., 2012)



Name of fertilisers	Chemical formula	Nutrients
Ammonia	NH_3	N
Ammonium bicarbonate	NH_4HCO_3	N
Ammonium carbamate	$NH_4CO_2NH_2$	N
Ammonium chloride	NH_4Cl	N
Ammonium hydrate	NH_4OH	N
Ammonium nitrate	NH_4NO_3	N
Ammonium nitrate ammonium sulfate	$(NH_4)_3NO_3SO_4$	N-S
Ammonium nitrate sulfate/bisulfate	$NH_4HNO_3SO_4$	N-S
Ammonium phosphate	$(NH_4)_3PO_4$	N-P
Ammonium sulphate	$(NH_4)_2SO_4$	N-S
Calcium nitrate	$Ca(NO_3)_2$	N-Ca
Diammonium hydrogen phosphate	$(NH_4)_2HPO_4$	N-P
Mono calcium phosphate monohydrade	$CaH_2(PO_4)_2.H_2O$	P-Ca
Mono-ammonium phosphate	$NH_4H_2PO_4$	N-P
Phosphoric acid	$H3PO_4$	P
Potassium chloride	KCl	K
Potassium dihydrogen phosphate	KH_2PO_4	P-K
Potassium hydrogen phosphate	K_2HPO_4	P-K
Potassium nitrate	KNO_3	N-K
Potassium sulphate	K_2SO_4	K-S
Potassium thiosulphate	$K_2S_2O_3$	K-S
Single superphosphate	$Ca(H_2PO_4)_2$	P-Ca
Sodium nitrate	$NaNO_3$	N
Sodium tripolyphosphate	$Na_5P_3O_{10}$	P
Tri ammonium nitrate ammonium sulfate	$(NH_4)_5NO_3SO_4$	N-S
Tripotassium phosphate	K_3PO_4	P-K
Urea	$CO(NH_2)_2$	N

3.3.1.2 Phosphorous fertilizers

Phosphorus is a vital component of every living cell. It has an important role in many physiological and biochemical processes because it cannot be replaced by other elements. P has more than one role at it is needed for stimulating cell division, promoting plant growth and root development, accelerating ripening and improving the quality of grain (R. D. Armstrong et al., 2015).P, like N, is a nutrient that plants require in large quantities. P has low mobility in the soil so its application is needed a few weeks before planting. Efficient use of P is vital as P is a non-renewable resource and its irresponsible wasting could lead to eutrophication of water bodies (Phuntsho, Shon, Majeed, et al., 2012). Table 3.4 shows some of the fertilizers used as a source of P for agricultural production.

3.3.1.3 Potassium fertilizers

Potassium (K) is the third major nutrient required for plant growth. K provides a number of important functions for the plants, such as activating enzyme actions facilitating the transport of nutrients; maintaining the structural integrity of plant cells;

mediating the fixation of N in leguminous plant species; and protecting plants from certain plant pests and diseases (FAO, 2004). In addition, K helps maintain an electrical balance within plant cells. Almost 95% of the K source in the world come from potassium chloride (KCl) (FAO, 2004). The various mineral fertilizers containing potassium are listed in Table 3.4.

3.4 Fertilizer Drawn Forward Osmosis

3.4.1 Basic Concept

Fertilizer Drawn Forward Osmosis (FDFO) is a technique in which concentrated fertilizer solution is employed as the draw solute, and the diluted fertilizer after desalination can straightaway be used for fertigation, eliminating the need for draw solution separation and recovery (Phuntsho, Shon, Hong, et al., 2012). Fertigation is defined as “the application of fertilizer nutrients (dissolved form or suspended form) to the crops with irrigation water instead of broadcast application” (Figure 3.23) (Kafkafi & Tarchitzky, 2011). Such technique would supply irrigation water loaded with nutrients from any saline or brackish water source, as fertilizers are widely used in agriculture.

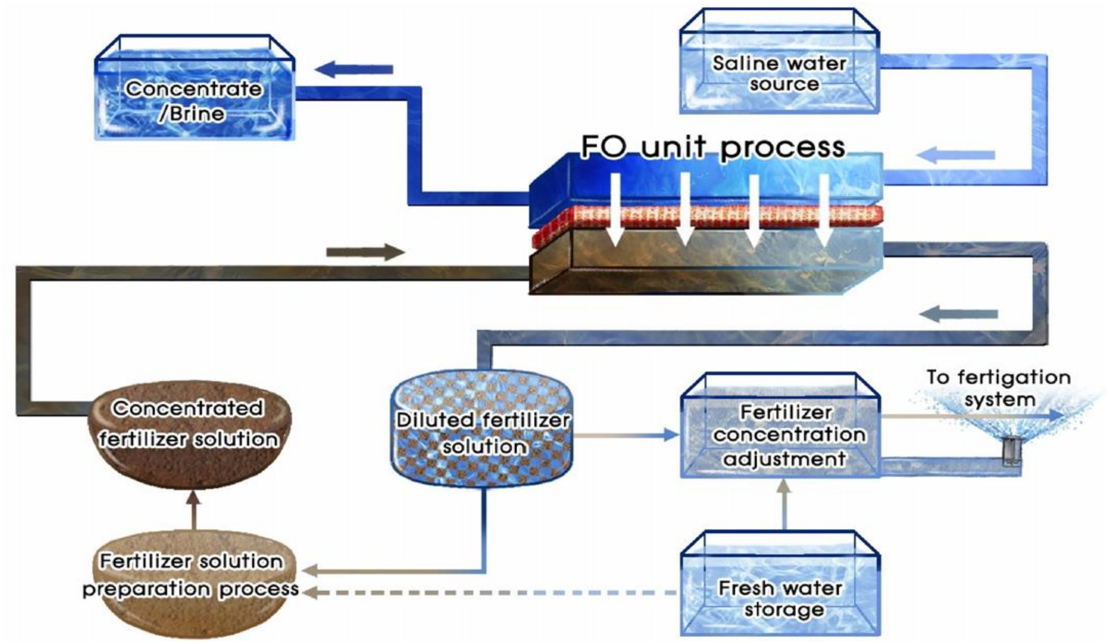


Figure 3.23 - Basic notion of FDFO for direct fertigation (Phuntsho et al., 2011)

The final fertilizer product water can be utilized directly for fertigation only if it complies with the permissible irrigation water quality standards and limits in terms of nutrient content. Yet, in case the final nutrient concentration surpasses the recommended limit, supplementary dilution is needed before using it for irrigation (Phuntsho, Shon, Hong, et al., 2012).

3.4.2 Advantages of Fertilizer Drawn Forward Osmosis

3.4.2.1 Energy Requirement

FO is mainly operated by concentration difference between DS and FS. No external force is needed to push the water through the membrane. Yet, energy is solely needed is to maintain the cross-flow of the FS and DS making sure they are in contact with the membrane surface and providing sufficient shear force to minimize the CP. Figure 3.24 shows the relative energy requirement for different desalination technologies.

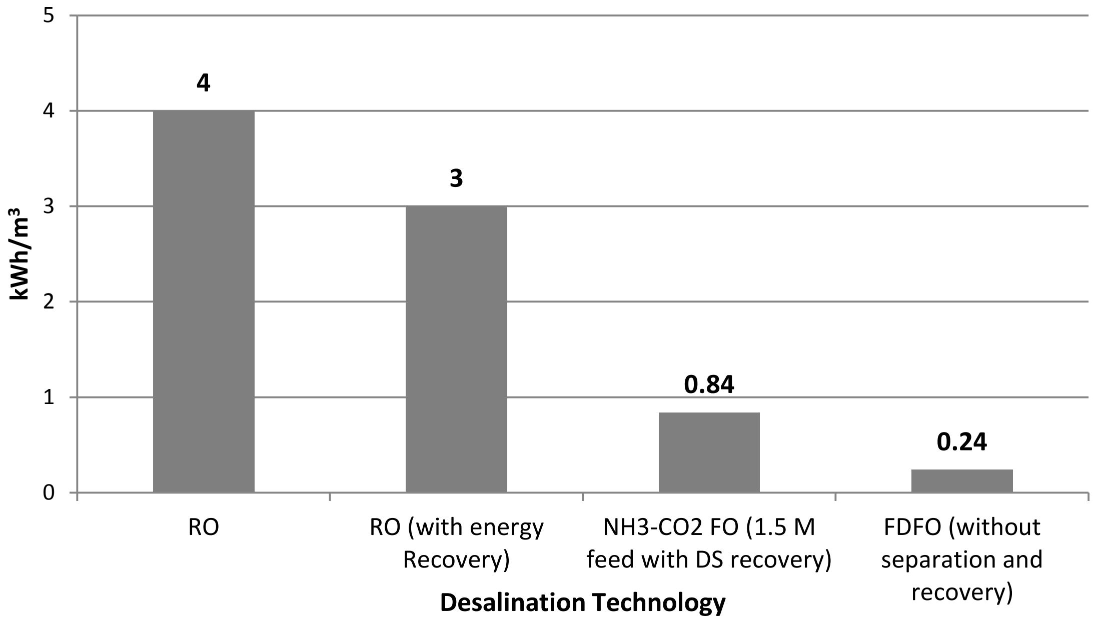


Figure 3.24 - Comparison of average energy requirements for different desalination technologies (Phuntsho, 2012)

The performance of NH_3-CO_2 as DS could vary from the fertilizer DS (Phuntsho et al., 2011). Yet, given the fact that the recovery of draw solutes from the diluted draw solution is not necessary, the estimates in Figure 3.24 signals that the energy required for FDFO will be significantly lower. From Figure 3.24, it can be concluded that FDFO consumes less than half the energy needed for ammonium bicarbonate FO application with DS feed recovery. This amount of energy when compared to other current desalination technologies, up to 85% of energy can be saved and used for other applications (Robert L. McGinnis & Elimelech, 2007).

Since FO desalination is not energy intensive, it could be easily powered by renewable energy, such as wind and solar energy, rendering it a green desalination technology (with no carbon foot print). Renewable energy, especially solar energy, is abundant in most remote communities in Egypt, therefore can be easily utilized for such purposes.

3.4.2.2 Fertilized Irrigation

Agricultural productivity is mostly affected by fertilizers and water availability. Agriculture is by far the largest consumer of potable water, accounting for about 80% of water consumption worldwide (ESCWA, 2009). Therefore, a little savings in agricultural water through improved efficiency will provide significant quantities of water available for the community and the environment. Energy efficient desalination techniques could be a promising way for providing water for irrigation. Besides making irrigation water available at lower energy from saline water sources, FDFO desalination provides nutrient-rich water for fertigation. According to Kafkafi & Tarchitzky (2011), fertigation has some pros in contrast with the use of water and fertilizers independently. Advantages are such as:

- minor losses through leaching,
- optimizing nutrient content by providing nutrients straight to the plant root,
- optimum management of soil mineral content,
- substantial savings in labor and energy costs
- accommodating and flexible technology as it can be easily integrated in any already-existing fertigation scheme
- suitable for application in mixtures with other micronutrients such as pesticides

3.4.3 Limitations of Fertilizer Drawn Forward Osmosis

3.4.3.1 Forward Osmosis Membranes

The most prominent limitation to the commercialization of the FO is the lack of a suitable high-flux membrane. The ideal FO membrane should have high water permeability and salt rejection, should be thin without a porous support layer minimizing the ICP effects and should also have good mechanical strength (Lay et al., 2010). However, providing a thin membrane without support layers is a challenge since it does not provide adequate mechanical strength to carry the water flow inside the membrane module (Zhao, Zou, Tang, et al., 2012). Several advancements have been reported on membrane manufacturing recently. The thin film composite (TFC) FO membranes are reported to have much higher water flux and salt rejection than the existing CTA FO membrane (Yip et al., 2010). Because of its exceptional properties, such as high salt rejection, high chemical resistance and high mechanical strength, TFC membranes have been long used for RO desalination (Phillip et al., 2010). However, the thick and dense support layer used for TFC-RO is not suitable for FO process as it causes severe ICP. The innovative claim for this TFC has been the modification of the support layer which is thinner and porous rendering it more proper for FO process. In particular, the hollow fiber thin film composite FO membrane is a significant breakthrough since flat sheet membranes are more complicated for the design of spiral-wound modules accommodating two different and independent flows in the module separately (R. Wang et al., 2010). With the commercialization of TFC-FO membranes, the future prospects of FO process and its applications are certainly high.

3.4.3.2 Choice of Suitable Fertilizer and the Performance of Fertilizers Draw Solution

Phuntsho, Shon, Hong, Lee, & Vigneswaran (2011) concluded that the majority of soluble fertilizers are candidates draw solution for FO desalination. However, pH compatibility of the fertilizer solution with the membrane used is of great importance. The wider the pH range of the membrane the better. Phuntsho, Shon, Hong, Lee, & Vigneswaran (2011) anticipated that a unit kilogram of fertilizer have the ability to absorb 11 to 29 liters of fresh water from seawater and 90 to 215 liters of fresh water from brackish feed. As feed salinity drops, fertilizers have the ability to extract additional water.

The permeation of pure water through the membrane will take place until osmotic equilibrium is achieved (Phuntsho et al., 2011). Full recovery is not realistic as at higher DS concentration as scaling of the feed solution starts to manifest itself, decreasing water flux. Knowing that water from natural sources such as sea or groundwater usually includes many dissolved elements such as Calcium and Magnesium, precipitation is expected earlier. In addition, more energy is needed to keep the fluid flowing due to the viscosity of the FS at high concentrations.

Reverse permeation of draw solutes (SRSF) also takes place during the FO process, affecting process performance as discussed previously (Achilli et al., 2010). The severity of reverse permeation depends on the formed species properties, pH and membrane properties (Phuntsho et al., 2011). For that reason, it is vital to put in mind such aspects when choosing a candidate fertilizer DS.

3.4.3.3 Lower-than-expected Water Flux

Lower-than-expected water flux is a result of concentration polarization phenomena explained earlier. ECP reduces the water flux considerably. The ECP effect is alleviated by insuring shear as well as turbulence on the membrane surface as a substitute to the dead end filtration (Zhao, Zou, & Mulcahy, 2012). Internal concentration polarization is inherent to FO process and is discovered to be significant as it takes place inside the membrane support layer (Lay et al., 2010). In fact, it has been discovered that the key aspect in charge of reducing the water flux in the FO is ICP, particularly the dilutive form (Gray et al., 2006).

Also, dilutive concentration polarization is another reason for the lower-than-expected water flux in FO. This phenomenon decreases the osmotic potential of the DS close to the plane of the membrane. That being said, the differential osmotic pressure is reduced, which lowers the pure water flux (Gray et al., 2006). On the other hand, with the continuous improvement in membrane design, it is feasible to avoid the polarization consequences to some degree.

Moreover, since the DS is diluted as it moves along the membrane module, the net differential pressure in the membrane is expected to be reduced. This in turn will decrease the flux, thus the osmotic equilibrium between DS and FS might not reached by a single FO stage. Consequently, there may be a need for multiple FO stages, which will increase the total membrane area, raising the capital cost required.

3.4.3.4 Fouling and Biofouling

Due to the nonexistence of high pressure, membrane fouling in FO process is described as reversible fouling (Lee et al., 2010). Such fouling is minimized by engineered design optimization of operating conditions (Zhang et al., 2012). Yet, there is rare information discussing FO fouling prosperity in literature.

Biofouling is an additional important problem that requires concern in FO. Since the membrane is continuously in contact the water, microorganisms and biofilm eventually grow. Biofouling is deemed unavoidable as it is uninfluenced hydrodynamically (Yoon, Baek, Yu, & Yoon, 2013). Since nutrients are known to be precursors to biofouling, the latter is inevitable in FDFO implementation (Ivnitsky et al., 2010). Biofouling is mainly due to the microbial activity, yet, modest literature is available about the topic (Ivnitsky et al., 2010).

3.4.3.5 Feed Salt Rejection and Reverse Permeation of Draw Solute

As the ideal FO membrane does not exist yet, the solute rejection is therefore expected to be slightly less than 100% (Phillip et al., 2010). Solute permeation can happen in one of two directions: 1) forward movement of feed salt, which is considered as rejection, and 2) reverse permeation of draw solutes (T. Cath et al., 2006). Reverse solute movement is mostly significant as fertilizer draw solution contains nitrogen and phosphorus. These elements could be damaging to the process of brine management Such elements could possibly cause eutrophication of receiving water bodies in case they are discharged to the environment haphazardly (Kafkafi & Tarchitzky, 2011). The presence of sodium chloride in produced water would also cause sodium toxicity to plant life, as previously discussed (Phuntsho, Hong, Elimelech, & Shon, 2013).

The degree of salt rejection and reverse permeation of draw solute mainly relies on: 1) membrane characteristics, 2) the DS properties (Phillip et al., 2010). Unfortunately, the current commercially available CTA FO membrane exhibit low salt rejection (Lay et al., 2010). Reverse solute flux differs significantly for each fertilizer, depending on the solute properties. It should be noted that, DS containing ions of large hydrated diameter, exhibited less reverse permeation than ions with smaller hydrated size (C.H. Tan & Ng, 2010; Zhao, Zou, & Mulcahy, 2012).

3.4.3.6 Meeting Irrigation Water Quality Standards

Any DS can extract fresh water from saline FS, provided that the fertilizer DS is soluble in water and has osmotic pressure more than the salty FS (Phuntsho, Shon, Hong, et al., 2012). There is an ultimate limit to which the osmotic process can continue occurring (Phuntsho et al., 2011). In other words, each DS can extract water only up to the “osmotic equilibrium”, which is defined as “the concentration where the DS osmotic potential equals that of the feed water” (Phuntsho, Shon, Hong, et al., 2012). Beyond this point, the DS cannot be further diluted. At this equilibrium point, depending on the feed salinity, the fertilizer concentration may be too high for direct fertigation. The fertilizer final nutrient concentration may possibly surpass the maximum limit and thus may cause problems to vegetation.

Depending on the osmotic pressure of the feed water, the limit to which the DS could achieve its final concentration is established. The salinity of the feed water is directly proportional to the final fertilizer DS concentration. The optimum nutrient content for fertigation relies on numerous aspects such as: crop type, season, soil nutrient conditions, etc. (Kafkafi & Tarchitzky, 2011). Using seawater as FS, it is expected that a large volume of water will be needed to reduce the nutrient content of the product water before fertigation. Thus, FDFO desalination is more appropriate for brackish water.

In case the nutrient concentration does not meet the fertigation standard, the DS must be further diluted to make the desalted water fit for fertigation. Dilution is achievable if the site has access to a source of potable water for irrigation. However, if this is not the case then this is a challenge. Since maintaining the required nutrient concentration is necessary for fertigation, an additional process could be augmented with the FO unit. According to Phuntsho, Shon, Hong, Lee, Vigneswaran, et al. (2011), to achieve lower nutrient concentration in the final FDFO product water, possible options are: 1) Pretreatment of feed water, 2) Post Treatment of feed water, 3) Use of blended fertilizer, 4) Hybrid FO system. These four options are discussed below.

3.4.3.6.1 Pre-treatment of Feed Water

As shown in Figure 3.25, FDFO desalination process may be incorporated with Nanofiltration (NF) pretreatment process to decrease the TDS of the feed water. NF is advantageous as it can reject up to 80% of monovalent and up to 99% of divalent ions (Zhao, Zou, & Mulcahy, 2012). Since brackish groundwater usually contains divalent ions such as Ca^{2+}, Mg^{2+}, SO_4^{2+}, etc., NF can be used to lessen the total dissolved solids and the osmotic pressure of the FS. In addition, any decrease in the divalent ions would reduce the scaling likelihood of the FS, improving the recovery rate (T. Cath et al., 2006). So, feasible nutrient concentration is achievable and direct fertigation is possible.

Not only will NF achieve high water flux, but also will operate at low hydraulic pressure. NF is not energy intensive and thus has low operation and maintenance costs (C.H. Tan & Ng, 2010).

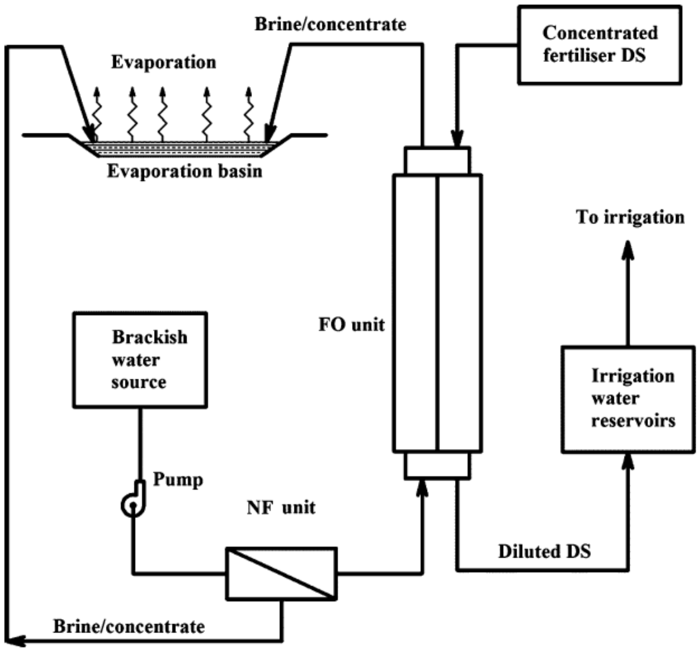


Figure 3.25 - FDFO desalination process integrated with NF pretreatment process (Phuntsho, Shon, Hong, et al., 2012)

3.4.3.6.2 Post-treatment of Feed Water

Nano-filtration can be adopted as a post-treatment instead of a pre-treatment option, as discussed previously. NF can be utilized to concentrate and reuse the DS. Permeate with considerably low nutrient content can be deployed straightaway for fertigation and the concentrate with high nutrient concentration is recycled as draw solution to desalinate more FS (Figure 3.26).

It has been reported that two-staged NF post treatment is capable of recovering divalent draw solutes meeting World Health Organization drinking water quality standards (C.H. Tan & Ng, 2010). One additional benefit of the NF post-treatment is the fact that NF is more efficient as the process effluent does not contain any foulants but contains just diluted fertilizer as any undesired foulants in the FS is eradicated in the previous FDFO step (C.H. Tan & Ng, 2010).

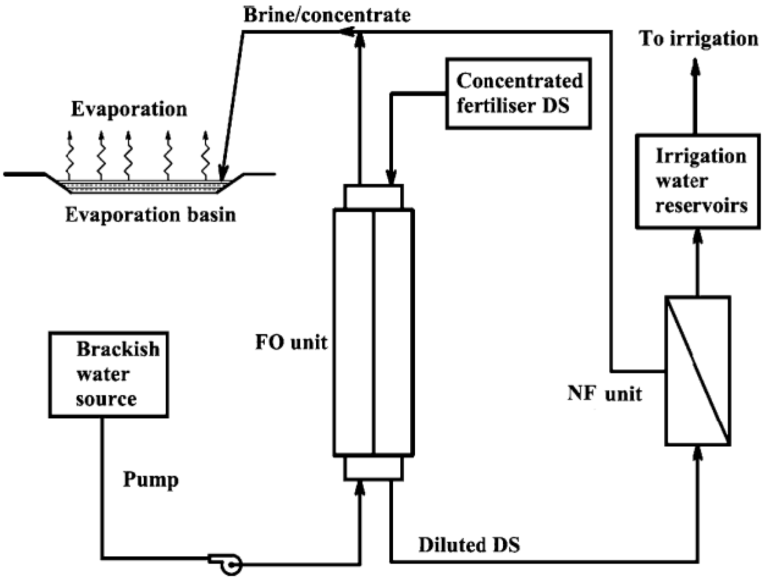


Figure 3.26 - FDFO desalination process integrated with NF post-treatment process (Phuntsho, Shon, Hong, et al., 2012).

3.4.3.6.3 Blended Fertilizers

Another potential alternative is to use a blend of thermolyte fertilizers as DS in FDFO process (Figure 3.27). Lower nutrient content in the final DS is achievable by utilizing a DS with several ionic species. This can be done by mixing two or three fertilizers with other elements such as pesticides and insecticides. Doing that would significantly raise the osmotic potential of the draw solution as well as lower the final nutrient content.

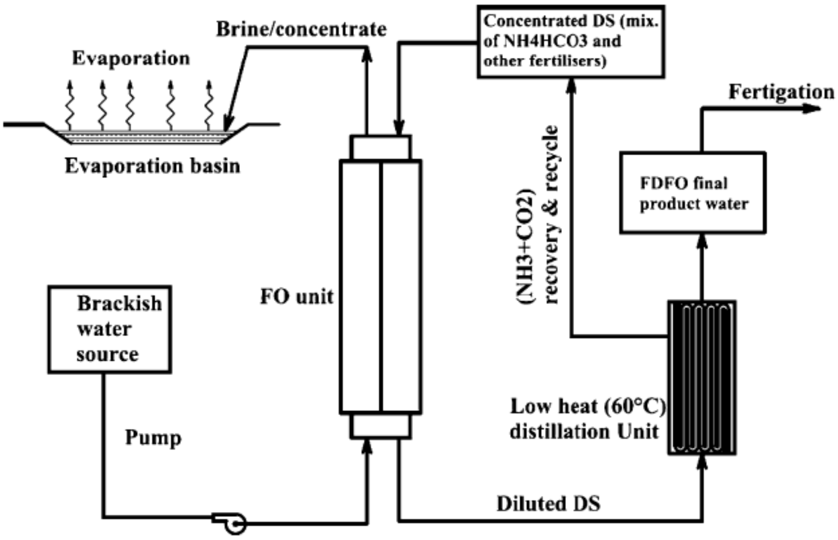


Figure 3.27 - FDFO desalination process using DS containing blended fertilizers (Phuntsho, Shon, Hong, et al., 2012).

Using blended fertilizer will overcome another problem related to the variable dilution factors required when fertilizers containing more than one nutrient are used as DS. For example, a fertilizer containing N and P may require a dilution factor of 2.5 for N concentration and 10 for P concentration. Such an issue exists with fertilizers like Mono-Ammonium phosphate (MAP), KNO_3 and KH_2PO_4.

3.4.3.6.4 Hybrid Forward Osmosis Systems

Another option is to utilize wastewater effluent to dilute the fertilizer solution. The basic idea is to employ a multiple two-staged FO process for concurrent WW treatment and desalination of brackish water (Figure 3.28) (T. Cath et al., 2006). The brackish water passes by the first FO stage to be desalinated using a fertilizer as the DS. Then, the diluted fertilizer DS passes through FO stage 2 in which water is extracted from the WW effluent. FO stage2t not only treats wastewater effluent to the required irrigation standard, but also provides additional dilution to the fertilizer solution decreasing its nutrient concentration deeming it fit for direct fertigation (Phuntsho, Shon, Hong, et al., 2012).

On the other hand, a second option would be designed differently. Brackish water could be employed as the DS in the first FO stage to absorb pure water from WW effluent. The product of the first FO stage (diluted brackish water) can then be the FS of the second FO stage, with concentrated fertilizer as the DS. For either option, final nutrient concentration in product water is minimized.

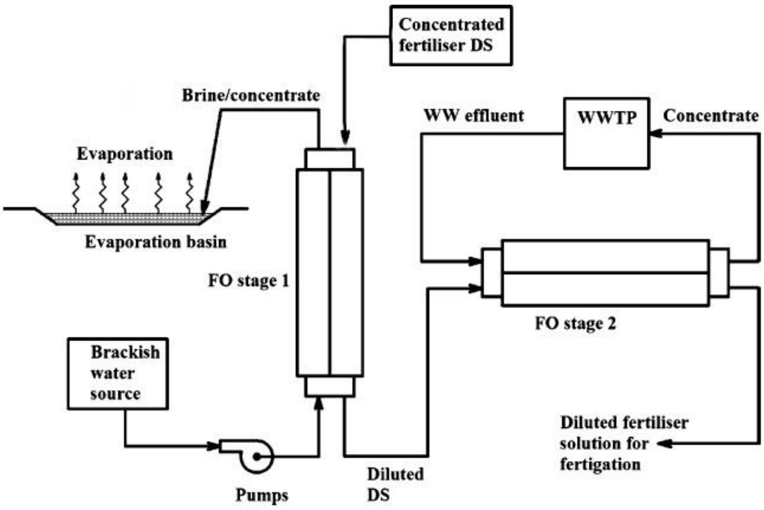


Figure 3.28 - Hybrid FDFO desalination process using 2 stage FO process with additional dilution water from a secondary WWTP effluent (Phuntsho, Shon, Hong, et al., 2012).

CHAPTER 4 - SELECTION OF POTENTIAL LOCATIONS FOR FERTILIZER DRAWN FORAWD OSMOSIS APPLICATION IN EGYPT

4.1 Introduction

The FDFO desalination process is a promising technology that could be applied in any part of the world where fresh water resources are scarce for irrigation and where saline or brackish water is abundant. The impact of such technology on the agricultural segment in Egypt is expected to be huge where brackish water is abundant in the form of groundwater in inland areas. The following chapter focuses on the application in Egypt, where the water debate has been a public issue for decades. The outcome of this chapter is a published paper entitled "The potential of groundwater desalination using forward osmosis for irrigation in Egypt".

4.2 Irrigation in Egypt

Due to the small quantity of rainfall in the country, almost all agricultural land in Egypt is irrigated. The Ministry of Water Resources and Irrigation (MWRI) manages a vast irrigation network occupying around 13% of the agricultural land area (ICARDA, 2011). The network is fed through River Nile and extends along 1,200 km from Aswan till the Mediterranean. The Ministry supplies farmers with water through 33,200 km of main and sub-canals, about 80,000 km of private water canals, and about 22,700 km of drains (Abo Soliman & Halim, 2012). Surface irrigation is considered the most common irrigation method in Egypt (Figure 4.1). While drip irrigation is used on 10%, and sprinkler irrigation on 8% of the agricultural land, surface irrigation is used on almost 82% of the agricultural lands (FAO, 1985).

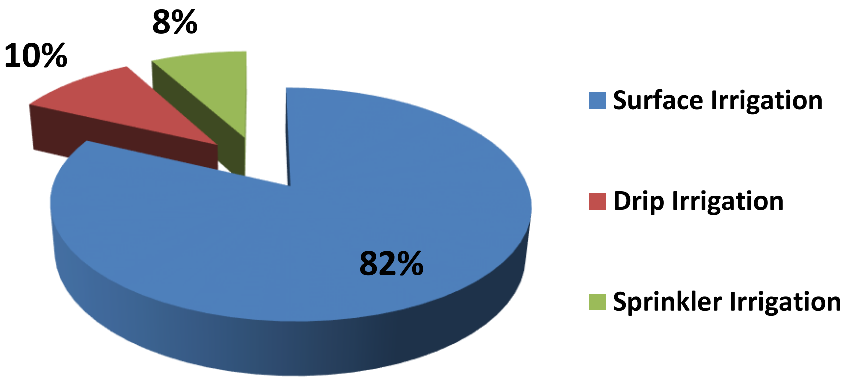


Figure 4.1 - Most common irrigation methods in Egypt (FAO, 1985)

In the Nile Valley, Egypt utilizes a hybrid gravity and water lifting system for irrigation. There are seven barrages to facilitate abstraction downstream of the High

Aswan Dam (Abo Soliman & Halim, 2012). As MWRI (2009) elaborates, the main canal system is fed from the head regulators which are located upstream of the Nile barrages. Water is then disseminated along branches where the flow is continuous. Distributaries get water according to a certain schedule. Water is then pumped from the distributaries to farming lands. Surface irrigation is prohibited in the reclaimed areas located at the outer edge of the irrigation system as such areas are more at risk of water scarcity. Farmers are encouraged to employ more efficient techniques of irrigation such as sprinkler or drip irrigation (MWRI, 2009).

4.2.1 Status of Egyptian Brackish Ground Water Use in Irrigation

4.2.1.1 Nile Valley and Delta

The main source of groundwater in this area is seepage water from the Nile, the irrigation networks and agricultural lands. Almost 6.3 billion cubic meters have been abstracted from the groundwater reservoir during the year 2007-2008 (El Tahlawi, Farrag, & Ahmed, 2007). Luckily, this is within the safe yield margins of the shallow reservoir in the Nile and Delta, which is estimated as 7.5 billion cubic meters per year. That being said, it is planned to increase the abstraction of GW by an additional 1.2 billion cubic meters by the year 2017 (Abo Soliman & Halim, 2012).

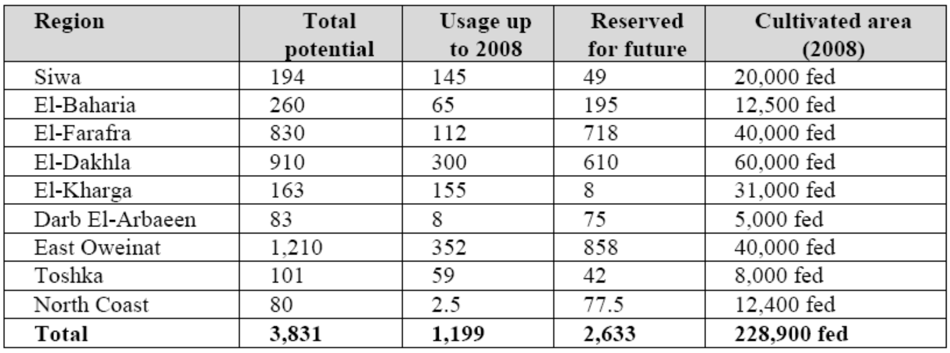
4.2.1.2 The Sinai Peninsula

The annual GW abstraction volumes from Sinai aquifers are estimated at 1.1 billion cubic meters originating from 3 aquifers (El Tahlawi et al., 2007). The agricultural area that is irrigated in the Sinai from these groundwater resources is about 8,080 feddan. These are distributed on the boundary strip (1,890 feddan), the coastal strip (2,040 feddan), middle Sinai (2,080 feddan), and 2,120 feddan in south Sinai (Abo Soliman & Halim, 2012). Some developments are planned by 2017 in the boundary strips, which will enable reclamation and cultivation of an additional 2,410 feddan (1,689 feddan in north Sinai and 730 feddan in south Sinai) using the available groundwater resources (ICARDA, 2011).

4.2.1.3 West Desert and Oasis

There are considerable GW resources in the western desert, including the Oases of Dakhla, Kharga, Farafra, Siwa, East Oweinat and Darb El-Arbaeen. However, the feasible amount that can be utilized is rather limited (Talaat et al., 2003). The total potential of these reservoirs is estimated to be 3.8 billion m^3/year. Table 4.1 shows the potential and general location of these reservoirs. Currently only 1.7 billion cubic meters are used annually, and the remaining 2.1 billion cubic meters per year are available for future developments (Abo Soliman & Halim, 2012).

Table 4.1 - GW potential in the western desert and Oases -million m^3/year (Abo Soliman & Halim, 2012)



Region	Total potential	Usage up to 2008	Reserved for future	Cultivated area (2008)
Siwa	194	145	49	20,000 fed
El-Baharia	260	65	195	12,500 fed
El-Farafra	830	112	718	40,000 fed
El-Dakhla	910	300	610	60,000 fed
El-Kharga	163	155	8	31,000 fed
Darb El-Arbaeen	83	8	75	5,000 fed
East Oweinat	1,210	352	858	40,000 fed
Toshka	101	59	42	8,000 fed
North Coast	80	2.5	77.5	12,400 fed
Total	**3,831**	**1,199**	**2,633**	**228,900 fed**

4.2.1.4 West of Cairo–Alexandria Desert Road (El-Faregh Valley)

El-Faregh valley is located west of Alexandria (between km 50 and km 80 from Cairo). It has about 1,800 water wells, pumping about 0.50 billion cubic meters of water annually (Abo Soliman & Halim, 2012). This amount is almost double the sustainable GW potential of the reservoir causing a considerable drop of water table. That is why, it is planned to supply this area with Nile water through the West Delta project. Also, there are an additional 300 wells to the west of the valley, and north of the road to the Baharia Oasis that can be used to irrigate an area of about 20,000 feddan (Abo Soliman & Halim, 2012).

4.2.1.5 El-Natroun Valley

El-Natroun Valley is located westward the Cairo-Alexandria desert road (between km 80 and km 110) and has about 1,200 water well. These wells are producing water at a rate of almost double the sustainable potential of the GW reservoir, which has led to excessive drawdown of GW levels. There is also a potential area of 10,000 feddan at the entrance of the Al-Alamein International road (north of El-Natroun Valley up to km 30). This area has sufficient groundwater and is ready for irrigation (Abo Soliman & Halim, 2012).

4.2.1.6 El-Moghra Basin

El-Moghra basin is located between El-Natroun Valley in the east and El-Kattara depression to the west dominating an area of 90 km by 30 km. The water quality of this basin has a salinity ranging between 3000 to 6000 ppm, which is suitable for olive trees and date palm (RIGW, 2002). This reservoir is not efficiently utilized until now, in spite of its high potential in terms of water quantity.

4.2.1.7 Nile Valley Fringes in Upper Egypt

Groundwater exists in the Nile valley fringes in the sedimentary reservoir in the governorates of El–Menia, Assiut, Qena and in the fractured limestone rocks in the governorates of El–Menia, Assiut and Sohag. The sedimentary reservoir has limited potential and its salinity ranges between 1,000 to 3,000 ppm (Abo Soliman & Halim, 2012). This reservoir can supply water to cultivate an area of about 20,000-30,000 feddan (ICARDA, 2011).This GW resource is distinguished by a potential quality and quantity with a water salinity not exceeding 1,000 ppm. It already supplies water to around 40,000 feddan, which can be further increased if more salt-tolerant crops are chosen (El Tahlawi et al., 2007).

4.3 Illegal Abstraction of Groundwater

According to Abo Soliman & Halim (2012), there are around 37,500 illegal abstraction wells distributed in the country and their majority is sited in Lower Egypt. The number of legal wells in Egypt is about 22,000 for agricultural use. In addition, there are 4,500 unlicensed wells used for potable water. In the last two decades, touristic areas and residential resorts have been established which include golf courses, swimming pools, artificial lakes, and other structures that consume large quantities of water for luxurious activities (El Tahlawi et al., 2007). Abstraction from the groundwater aquifer led to excessive drawdown and deterioration of water quality (RIGW, 2002). Most of the resorts are located by Cairo-Alexandria desert road, in the New Cairo area and other places. The establishment of these resorts was accompanied by large investments and was sold to the public many years ago. Effective measures from the government were absent to control/stop such action. In addition, the current laws and water regulations are not flexible enough to easily control these recent changes and deal with them effectively (El Tahlawi et al., 2007). The easy solution in this case would be to decommission these wells, keeping in mind that many of them are drilled without permits. However, this would be through demolishing huge investments, which is a big financial loss. Therefore, it may be appropriate to correct and legalize the status of these resorts and create non-traditional procedures to assure water management and sustainability while preserving the large investments made.

These procedures include the installation of water meters on the wells and collection of fees for water used in non-agricultural activities and elaboration of relevant regulations and control measures (Abo Soliman & Halim, 2012).

4.3.1 Salt-Affected Soil in Egypt

Soil salinity problems are common in Egypt. Approximately 30-40% of the irrigated lands are salt-affected (Figure 4.2) (ICARDA, 2011). In the Nile Valley region, more than 25% of irrigated land is salt-affected. Similarly, reclaimed lands bordering the Nile Valley and Delta areas also experience water-logging and high salinity (Mabrouk et al., 2013). Such soils have high soluble salt concentration such as sodium chloride. As a result, soils build up sodium causing poor physical and chemical properties, as discussed previously, negatively impacting plant growth and yield (Domenico & Schwartz, 1998). According to GRA (2009), soil salinization is mainly due to:

- Excessive and inappropriate use of irrigation water
- Irrigation using water of poor quality such as mixed drainage water
- Irrigation using low quality saline groundwater
- Inefficient salt leaching processes
- Ineffective drainage
- Direct evaporation from water table contributing to root-zone salinity

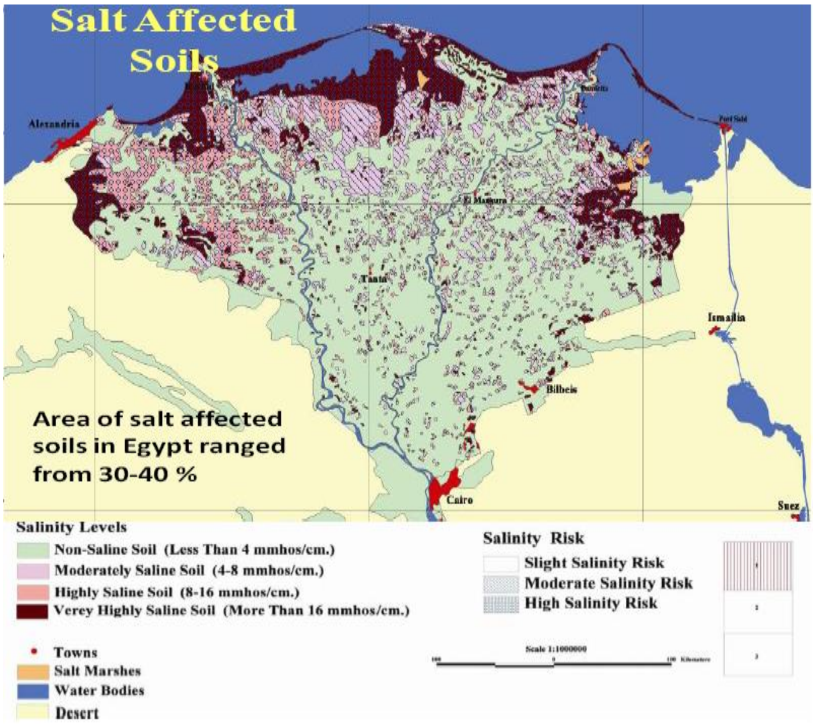


Figure 4.2 – Egypt soil salinity status (Abo Soliman & Halim, 2012)

4.4 Groundwater in Egypt

Although rainfall is scarce in Egypt, groundwater is still considered one of the most important water resources (Sharaky, Atta, El Hassanein, & Khallaf, 2007). The quantity of groundwater in Egypt is estimated to be around 6.1 billion m^3/year in the Nile Valley and Delta. Generally, the total volume of water (renewable, non-renewable) that is available in aquifers is predicted to be 11.565 billion m^3/year (Table 4.2) (Abo Soliman & Halim, 2012).

Table 4.2 - Quantity of groundwater in Egypt for the years 2006-2007 (Abo Soliman & Halim, 2012)

Source of groundwater in Egypt (2006-2007)	**Quantity (Billion m^3/year)**
Renewable groundwater	5.69
Non-renewable groundwater	3.785
Groundwater in Nile Valley and Delta (Renewable and non-renewable)	2.09

Egyptian groundwater can be classified into two major classes (Figure 4.3). The first includes GW of the Nile Valley and Delta system and the second includes groundwater of Western Desert (or sometimes called Nubian Sandstone Aquifer) (Sharaky et al., 2007). The volume of Nile Valley GW aquifer is estimated to be 200 billion m^3 and its salinity is approximately 800 ppm (Abo Soliman & Halim, 2012). On the other hand, the volume of the Delta aquifer is estimated to be 300 billion m^3. Currently, the annual groundwater withdrawal rate of from Nile Valley and Delta aquifer is 6.13 billion m^3/year (Abo Soliman & Halim, 2012).

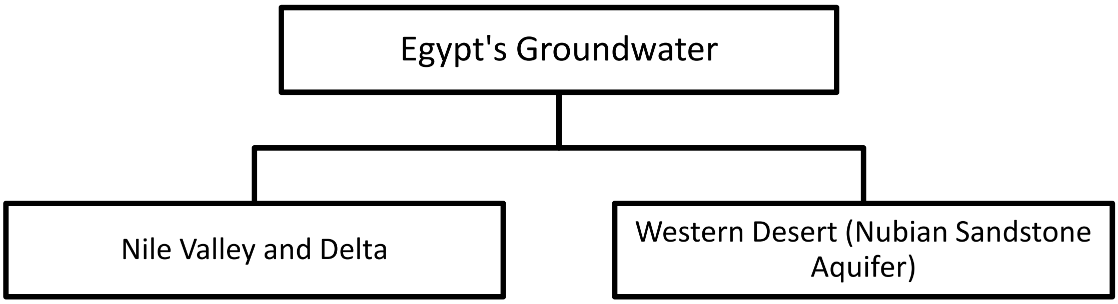


Figure 4.3 - Major classes of Groundwater in Egypt

The second class is the groundwater located in the Western Desert, which is mostly nonrenewable and deep. Due to its depth, utilization potential of this aquifer relies on the abstraction cost (El Arabi, 2012). In north Sinai, seasonal rainfall refills shallow aquifers. The aquifer's thickness ranges between 30 to 150 m and its salinity ranges between 2,000 to 9,000 ppm (Abo Soliman & Halim, 2012). Recent investigations in South Sinai discovered a number of aquifers with a small capacity. Regarding the groundwater aquifers by the North coast and the Red Sea, the present abstraction rate is almost 2 million m^3/year (Abo Soliman & Halim, 2012).

4.4.1 Egypt's Groundwater Aquifers

According to RIGW (2002), the hydrogeological structure of Egypt consists of six main aquifers, as shown in Figure 4.4.

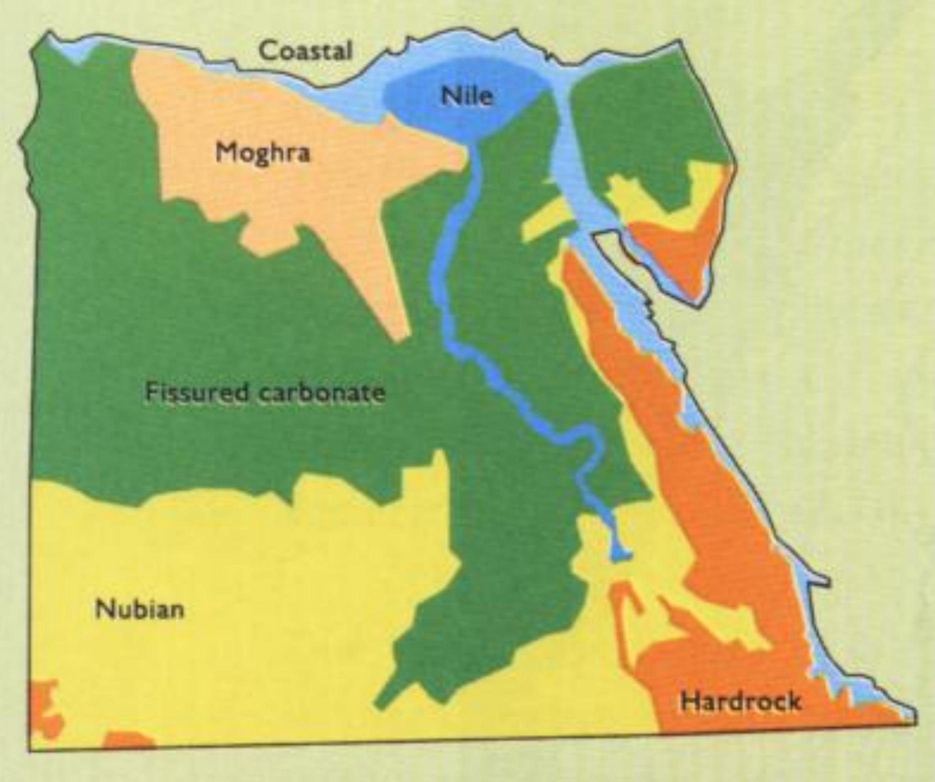


Figure 4.4 - - Main aquifer system in Egypt (Abo Soliman & Halim, 2012)

4.4.1.1 The Nile Aquifer

The Nile aquifer covers the Nile flood plain and desert fringes (Figure 4.5). The thickness of this aquifer is estimated to be 300 meter (El Tahlawi et al., 2007). There are impermeable clayey deposits below this aquifer hindering its connection with the Nubian Sandstone aquifer (RIGW, 2002). The water of this aquifer is primarily utilized for domestic purposes as well as irrigation. The average salinity of the Nile Aquifer is less than 1,500 ppm (El Tahlawi et al., 2007).

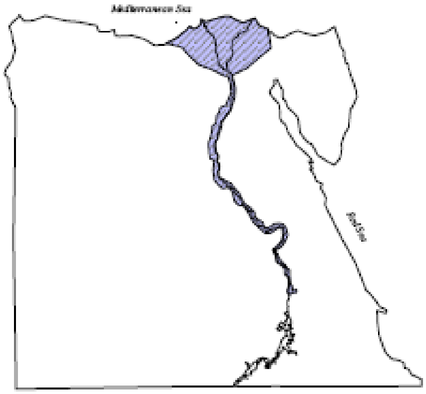


Figure 4.5 - Nile Aquifer geographic location (Abo Soliman & Halim, 2012)

4.4.1.2 The Nubian Sandstone Aquifer

This aquifer occupies large area in the Western Desert as well as sections of the Eastern Desert and Sinai (Figure 4.6). This aquifer is non-renewable with an estimated volume of 200,000 billion cubic meters (El Tahlawi et al., 2007). Yet, due to its existence at large depths with high cost of extraction, this aquifer has limited potential. The Nubian Sandstone Aquifer is designated as the largest groundwater reservoirs worldwide (RIGW, 2002). With an area of almost two million square kilometer, this huge aquifer is shared by Egypt, Sudan, Libya and part of Chad (Abo Soliman & Halim, 2012).

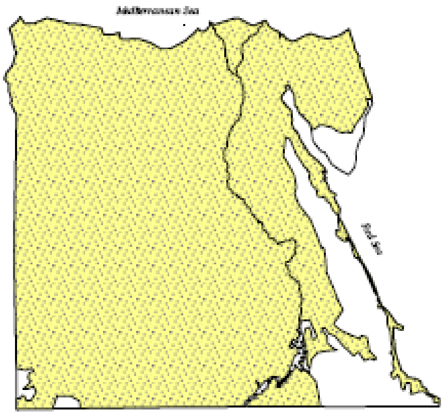


Figure 4.6 – Nubian Sandstone Aquifer geographic location (Abo Soliman & Halim, 2012)

4.4.1.3 The Moghra Aquifer

The Moghra Aquifer occupies mainly the western edge of the Delta (Figure 4.7). According to El Tahlawi et al. (2007), the Moghra aquifer is positioned westward of Delta and is around 50 to 250 m thick. The aquifer's area is almost 50,000 km^2. The salinity of this aquifer ranges between 3000 to 6000 ppm, which is suitable for olive and palm trees irrigation. In spite of its high potential in terms of water quantity, this reservoir is not been fully utilized (Abo Soliman & Halim, 2012).

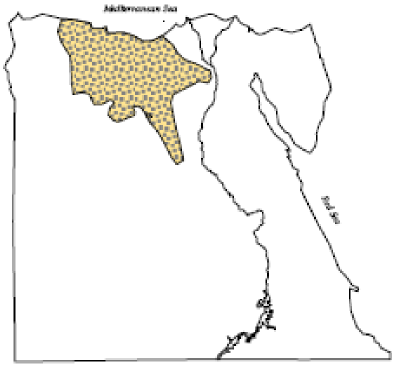


Figure 4.7 – El Moghra Aquifer geographic location (Abo Soliman & Halim, 2012)

4.4.1.4 The Coastal Aquifer

The Coastal Aquifer, occupying the north western and eastern coasts (Figure 4.8). The coastal aquifers occupy around 20,000 km^2 and has a capacity of 2 billion m^3 (Abo Soliman & Halim, 2012). There are two subcategories of coastal aquifers:

a) Mediterranean Sea Aquifer: The Mediterranean coastal zone is known by its heavy rainfall, which is estimated to be 200 mm/year (El Tahlawi et al., 2007). Rainfall forms a 1 m thin layer which floats on the salty water coming from seawater intrusion (RIGW, 2002).

b) Red Sea Aquifer: The Red Sea coastal aquifers, existing in Sinai, encompass the Quaternary Fluviatile and Tertiary Aquifers (El Tahlawi et al., 2007). According to El Tahlawi et al. (2007), the former aquifer has evolved at the delta area where the water is under phreatic conditions. The salinity of the aquifer is between 2,000 to 2,500 ppm (RIGW, 2002). El Tahlawi et al. (2007) states that Wadi El Qa'a aquifer, near El-Tor in Sinai, is an example of Red Sea coastal aquifer. This aquifer is more than 100 meter thick and is regenerated through runoff from the neighboring high lands.

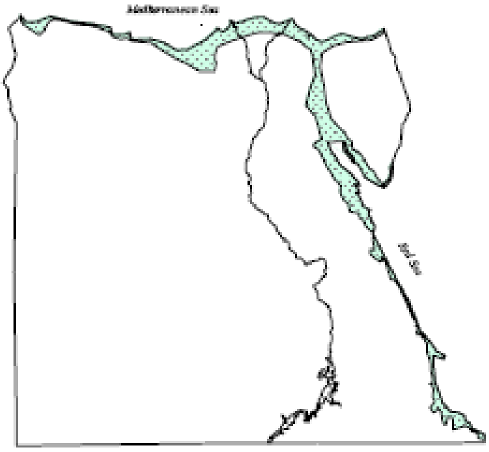


Figure 4.8 - Coastal Aquifer geographic location (Abo Soliman & Halim, 2012)

4.4.1.5 The Karstified Carbonate Aquifer

This aquifer occupies mainly the north and middle parts of the Western Desert (Figure 4.9). Although it dominates around half of Egypt's area, this aquifer is the least utilized nationwide. This aquifer occupy around 500,000 km^2 and has a capacity of 5 billion m^3 (Abo Soliman & Halim, 2012). According to RIGW (2002), the aquifer is split into three horizons. The three horizons are segregated by two impervious clay layers. The carbonate rocks lay over the Nubian Sandstone complex. Rainfall and seepage from the Nubian Sandstone aquifer recharge the aquifer (Abo Soliman & Halim, 2012). In Siwa Oasis, fissured limestone complex exist in the upper layer, with a thickness of about 650 m and lying on the Nubian Sandstone aquifer (El Tahlawi et al., 2007).

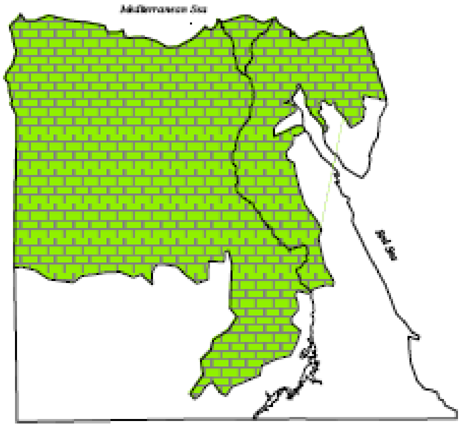


Figure 4.9 - Karstified Carbonate Aquifer geographic location (Abo Soliman & Halim, 2012)

4.4.1.6 The Fissured and Weathered Hard Rock Aquifer

This aquifer occupies the Eastern Desert and Sinai (Figure 4.10). According to El Tahlawi et al. (2007), groundwater mobility is minimal due to tectonic factors. The cracks in the volcanic rocks are present in the Egyptian south eastern desert, where the GW exists in a free state (RIGW, 2002).

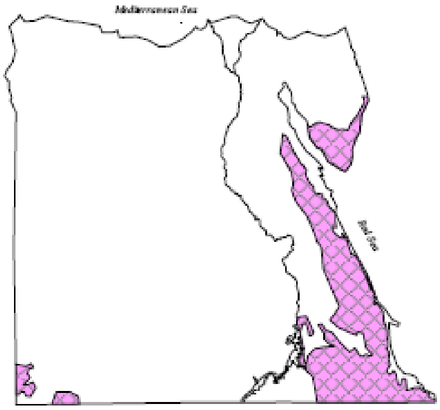


Figure 4.10 – Fissured and Weathered Hard Rock Aquifer geographic location (Abo Soliman & Halim, 2012)

Table 4.3 summarizes hydrological characteristics of main Egyptian brackish water aquifers with respect to their location, average area, reasons for salinity, average salinity, exploitable volume and average depth to groundwater level.

Table 4.3 - Hydrogeological characteristics of Egypt's main aquifers (adapted from Abo Soliman & Halim, 2012; Allam & Allam, 2007; Nashed et al., 2014)

Aquifer	**Location**	**Area (km^2)**	**Reason of GW salinity**	**Average salinity (ppm)**	**Exploitable Volume (m^3)**	**Depth to GW level (m)**
Coastal	Along Mediterranean and Red Sea coasts	20,000	Sea water intrusion	>2,000	< 2 billion	15-70
Nile Valley	Nile valley and Delta	30,000	Seawater intrusion, lateral seepage of saline water from the adjacent aquifers and upward leakage from deep aquifers	800-3,000	≈ 4 billion	0-5
El Moghra	West of the Nile Delta	10,000	--	3,000 – 6,000	> 1 billion	0-200
Nubian Sandstone	Parts of Western, Eastern Desert and Sinai	100,000	Fossil GW (will be depleted by natural and artificial processes)	1,000 – 10,000	> 500 billion	0-50
Fissured Carbonate	Parts of Eastern Desert and Sinai	500,000	-	1,000-12,000	≈ 5 billion	20-220
Hard Rocks	South Sinai and Eastern Desert	-	tectonic, and litho-logic	1,000-2,000	-	>50

4.4.2 Egypt's Groundwater Quality

Brackish groundwater exists in about all aquifer systems (Figure 4.11). However, Abo Soliman & Halim, (2012) argue that the utilization of this resource is still inadequate due to a number of challenges, including:

- Far-fetched dynamics of groundwater (quality varies over time);
- Existence of brackish groundwater in non-water-scarce areas;
- Problems related to the disposal of effluent;
- The salinity range of groundwater is estimated to be between 1,000 and 30,000 ppm. The salinity is expected to rise with time, especially for the coastal aquifer systems;
- The main deployment of groundwater at present is by carried out by native Bedouins as they use it for small farming activities and as a potable source for their farm animals;
- The total exploitation is anticipated to be 19 million m^3/year, mostly from the salinity range 1,000 to 10,000 (brackish range).

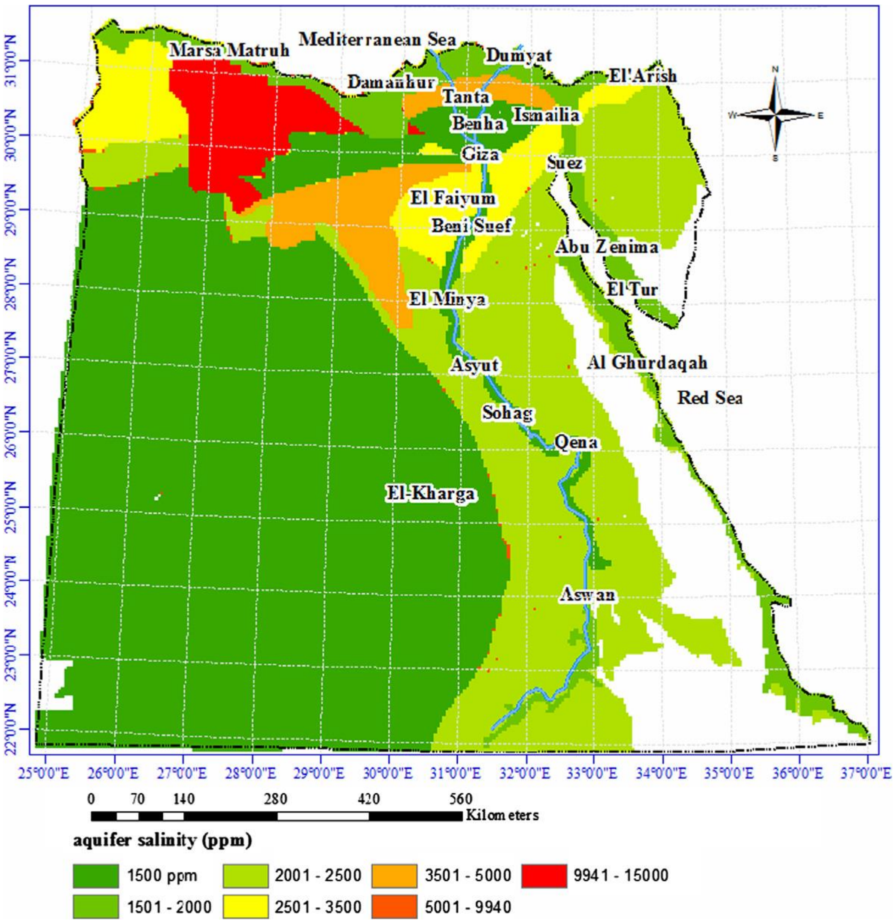


Figure 4.11 - Classification of aquifer salinity in Egypt (Salim, 2012)

According to Abo Soliman & Halim (2012), 41 priority areas have been selected and studied carefully covering a large part of the country through a comprehensive groundwater quality monitoring program. Almost 60 % of the monitoring wells were selected to be located in the Nile Basin. The reason behind the large number of wells in the Nile Basin is that this aquifer is heavily used and that the areas in this region face serious a pollution problem.

4.4.2.1 Chloride

Chloride is a unique element affecting the groundwater quality. Compared with the drinking water guidelines, the chloride content in groundwater is high in the Eastern Desert, Sinai and Cairo. Yet, low chloride contents are found in the Nile Delta and the Western Desert. The possible reasons behind the high chloride concentrations are dissolution from soil salts (halite), evapotranspiration and salinization processes by intrusion or seepage through faults (Abo Soliman & Halim, 2012).

4.4.2.2 Sulphate

Sulphate content in groundwater is noticeably high in the Eastern Desert, Delta regions, and Sinai. About one quarter of the collected samples contain high sulphate content exceeding the guideline values for drinking water (Abo Soliman & Halim, 2012). This could be due to the dissolution of soluble materials from fertilizers and the pumping of water from greater depths (Domenico & Schwartz, 1998).

4.4.2.3 Nitrate

Nitrate is considered an indicator for domestic and agricultural pollution (Freeze & Cherry, 1979). About half of the monitored groundwater samples exceed WHO standards for drinking water and about 3% exceed FAO standards for irrigation water (FAO, 1985). Nitrate content in groundwater is very high in the reclaimed areas along the Nile Valley and the Delta regions (Abo Soliman & Halim, 2012).

4.4.2.4 Calcium

High calcium concentration is present in the Eastern Desert, some significant areas of the Nile Valley (El Fashn and Samalut) and in Sinai. Values as high as 900 mg/l are noted at the edges of the Eastern Desert and Nile Valley. The high calcium content in groundwater is typically due to permanent water-rock contact and dissolution of carbonate rocks such as limestone, dolomite and gypsum (Abo Soliman & Halim, 2012).

4.4.2.5 Sodium

Sodium content is one of the key factors in determining groundwater quality, especially for drinking and irrigation (FAO, 1985; Fipps, 2003). High sodium concentrations in groundwater are present in some areas, possibly due to recharge from wastewater sources and the dissolution from clay layers that occupy the Eastern and Western edges of the Nile Valley and Delta (Domenico & Schwartz, 1998; Freeze & Cherry, 1979).

4.4.2.6 Total Dissolved Solids (TDS)

Highest TDS values are present in the Eastern Desert region. This is caused by the existence of sodium, calcium, chloride and sulphate elements (Y. Wang & Jiao, 2012). High TDS values happened in the monitoring wells in the fringes of the Nile Valley and Delta, where values exceeded 4 g/l (Abo Soliman & Halim, 2012).

4.4.2.7 Trace Elements in Groundwater

In addition to the major elements discussed previously, some heavy metals and trace constituents are significant for the study of groundwater quality. Many of heavy metals in groundwater are pertaining to dissolution of sediments (Domenico & Schwartz, 1998). The hydrochemical characteristics of the soil have significant influence on the transport of pollutants through the soil (Weert et al., 2009). Following is a presentation of the concentration of some heavy metals exceeding the WHO standard for drinking water.

4.4.2.7.1 Manganese

High manganese concentrations are noticed in the groundwater samples of the Nile Valley, Delta and low frequency wells in greater Cairo region. Typically, manganese is dissolved from the aquifer sediments where manganese is present as manganese oxides and hydroxides (Abo Soliman & Halim, 2012).

4.4.2.7.2 Iron

High iron concentrations can be spotted in the some wells in the Nile Valley, Delta, and Western Desert and in the Greater Cairo region. The guideline value for iron in drinking water was recommended by WHO to be 0.3 mg/l (Abo Soliman & Halim, 2012). It is discovered that remarkably elevated iron concentrations are in the same areas of high manganese concentrations. The justification of this phenomenon is that provided anaerobic conditions, iron and manganese oxides and hydroxides discharge soluble ions in groundwater (Domenico & Schwartz, 1998).

4.4.2.7.3 Boron

Elevated boron concentrations are found in the groundwater of the Eastern Desert and in the Nile Valley and Delta regions. Such high concentrations of boron in groundwater could be attributed to boron-containing minerals such as tourmaline and due to agricultural activity from fertilizers and pesticides (GRA, 2009; Sharaky et al., 2007).

4.4.2.8 Pesticides

As the different samples were analyzed for some of the most commonly used pesticides in Egypt, none indicated pesticides content in groundwater. This is possibly due to decay of the pesticides before they reach big depths at which the monitoring wells are present (Abo Soliman & Halim, 2012).

4.5 Selection Criteria

Although FDFO is applicable to most areas where brackish groundwater is abundant, there are certain locations in Egypt that have high potential for such an application. The proposed scheme would maximize its return if certain criteria are met. Such criteria could be used by decision makers in Egypt for implementation purposes, as will be elaborated in the next section.

4.5.1 High Irrigation Water Demand

As the proposed scheme provides additional water for irrigation, it is very promising for implementation in areas with high irrigation water demand. Even under-populated regions that are far from Nilewater, water transportation cost becomes a burden, deeming this proposal competitive. Nile Delta is one of the areas with a high water demand for irrigation and it will be discussed in details later in the writing.

4.5.2 Availability of Arable Land

Availability of neighboring arable land is required to benefit from the proposed scheme since FDFO provides water suitable for direct irrigation. In the case that arable land is not at proximity, cost related to transportation of desalinated water by pipeline becomes significant and should be considered. Yet, instead of spending money on infrastructure of canals delivering fresh water from Nilewater to irrigate newly developed areas, it is currently more convenient and economical to desalinate the already available groundwater. This does not only save on irrecoverable water losses due to high rates of evaporation, evapotranspiration and seepage, but also minimizes on-farm losses. It is reported that water losses through conveyance from Lake Nasser to delta region reaches around 50% (MWRI, 2009).

4.5.3 Proximity to Fresh Water Source

Due to process nature, FDFO on its own is not capable to produce water of suitable quality for irrigation without requiring additional water to dilute the fertilizer to create the draw solution. Also, as the FDFO product water requires further dilution to meet nutrient content limits for irrigation, available water can be combined with the FDFO product water for fertigation. Thus, proximity of a fresh water source is recommended. In some cases such fresh water in not available, requiring the integration of RO to produce fresh water.

4.5.4 Sustainability of Groundwater

In order to consider this solution sustainable, it is desirable to employ it where groundwater is renewable, making sure that the abstraction rate does not exceed the recharge rate. If this is not the case, unstudied exploitation will lead to short period of use, which does not contribute to solving the problem. For example, the oases area in the Western Desert where many wells were dug in the Nubian aquifer stopped to produce water naturally due to heavy extraction and the wells being close to each other (El Tahlawi et al., 2007; Nashed et al., 2014), which eventually compromises the sustainability of the community relying on GW.

4.5.5 Ease of Brine Disposal

Due to the nature of the process, the production of brine (or reject) is inevitable. The disposal of brine in an environmentally sound manner is vital. If the desalination facility is located near the sea, the potential for a problem will be considerably less severe through brine disposal directly in the sea using an outfall pipe (Buros, 1990). Brine usually sinks to the sea floor as it is denser than seawater with a concentration ranging between 50 to 75 g/l. Proper mixing, diffusion and dilution of brine concentrate should be insured to minimize the negative impacts of the salt load on the flora, marine life and any other human activities (Lenntech, 2014).

4.6 Potential Areas of Application in Egypt

Although there are many potential areas of FDFO application in Egypt, this section highlights two potential areas of application. The first area is the Nile Valley and Delta region, the second is Red Sea coast in Eastern Desert and Sinai (Figure 4.12). Each selected areas will be discussed in more details in the next section.

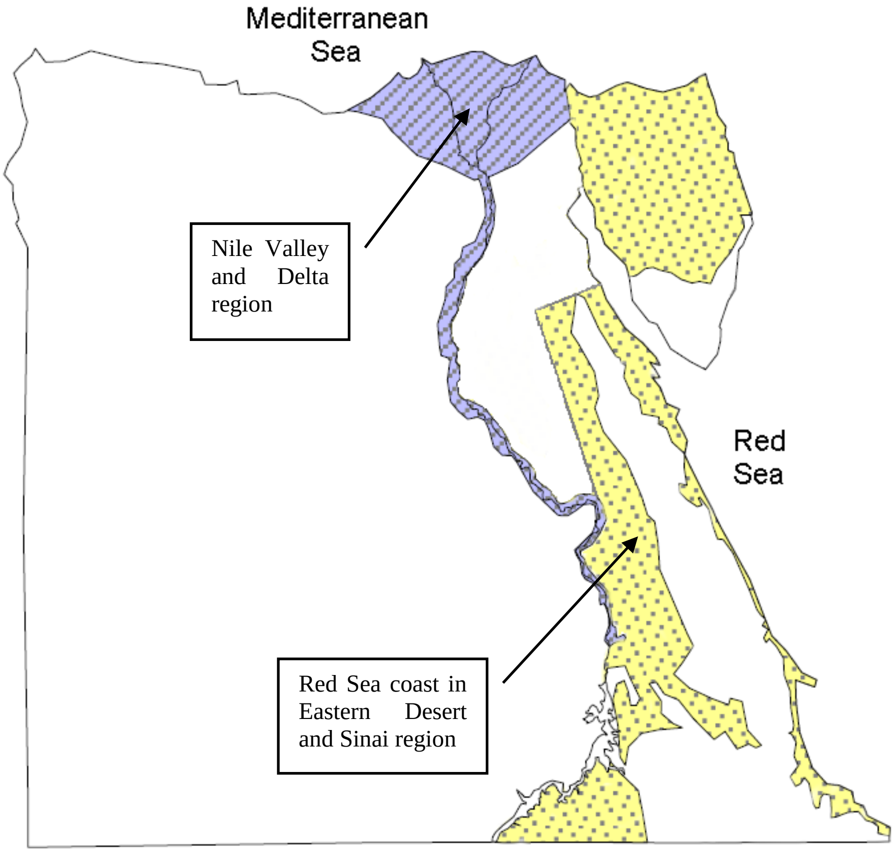


Figure 4.12 – Selected Areas for potential FDFO application in Egypt (Nasr & Sewilam, 2015b)

4.6.1 Nile Valley and Delta Region

The total area of cultivated land at present in Egypt is 8.6 million feddan where 6.5 million feddan is in the Nile Valley and Delta region (ICARDA, 2011). In other words, almost 75% of the irrigated land in Egypt lies in the Nile valley and Delta region, which is almost entirely dependent on Nile water. The Delta and Nile valley is the most populated region in Egypt. Expected increases in the consumption of Nile water for domestic use, industry, and tourism will certainly affect agriculture. Regional challenges, mainly with the African basin countries, are expected to affect the Nile water and the delta region will be the first to suffer from any water shortage in the future. In order to overcome this difficulty, innovative ideas are needed to increase irrigation water supply. Average rainfall in the delta is very small as it ranges from 25 mm/year in the South and middle part of the Delta to 200 mm/year in the North (Mabrouk et al., 2013). Thus, it may be concluded that the rainfall-induced recharge is neglected because it is very small, compared to other recharge methods.

The underlying aquifer in Delta has a high potential. Not only does it have a massive exploitable volume of more than 4 billion m^3/y, but also a salinity range between 1,500-10,000 ppm which can be desalinated using FDFO technology (Mabrouk et al., 2013). The aquifer is continuously recharged by fresh water from Nilewater and infiltration from irrigation (El Tahlawi et al., 2007). The annual overall groundwater recharge to the aquifer is estimated at 6.70 billion m^3/year (Sefelnasr & Sherif, 2014). In the Nile valley, the underlying aquifer thickness decreases from 300 m at south Sohag to a few meters in north near Cairo and south near Komombo, as per Figure 4.13. The depth to the groundwater level is not more than 5 m, which saves on groundwater abstraction cost.

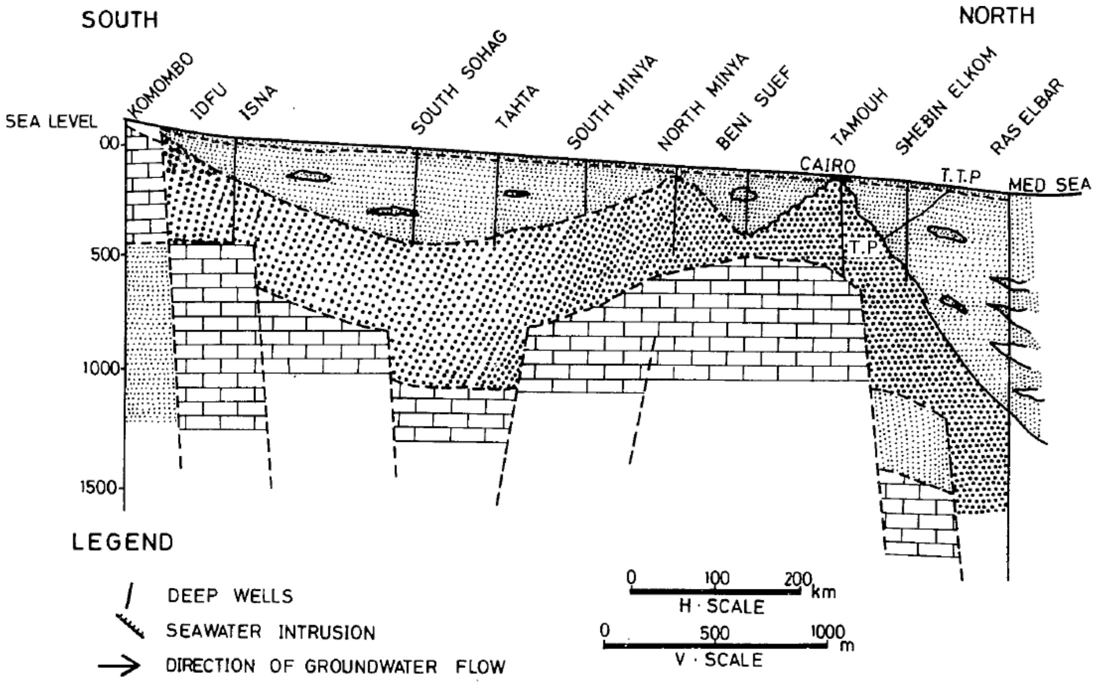


Figure 4.13 – Hydrological profile through Nile valley and Delta (Hefny, Farid, & Hussein, 1992)

The salinity of the groundwater in the Nile valley aquifer increases northwards from Cairo to reach its maximum along the Mediterranean coastline (Sefelnasr & Sherif, 2014). An intermediate mixing zone of a salinity range 1,000-35,000 ppm can be outlined (Figure 4.14). Mediterranean seawater intrusion, lateral seepage of saline water from the adjacent aquifers and upward leakage from deep aquifers proved to be the main reasons behind aquifer salinity (Mabrouk et al., 2013). Abstraction from this aquifer will decrease the groundwater level in the area from Upper Egypt to south of Cairo, which is a favorable condition, as this puts the aquifer under phreatic conditions allowing for the storage of about 5 billion m^3 of water that could be used as an annual or seasonal reservoir of groundwater (Abo Soliman & Halim, 2012).

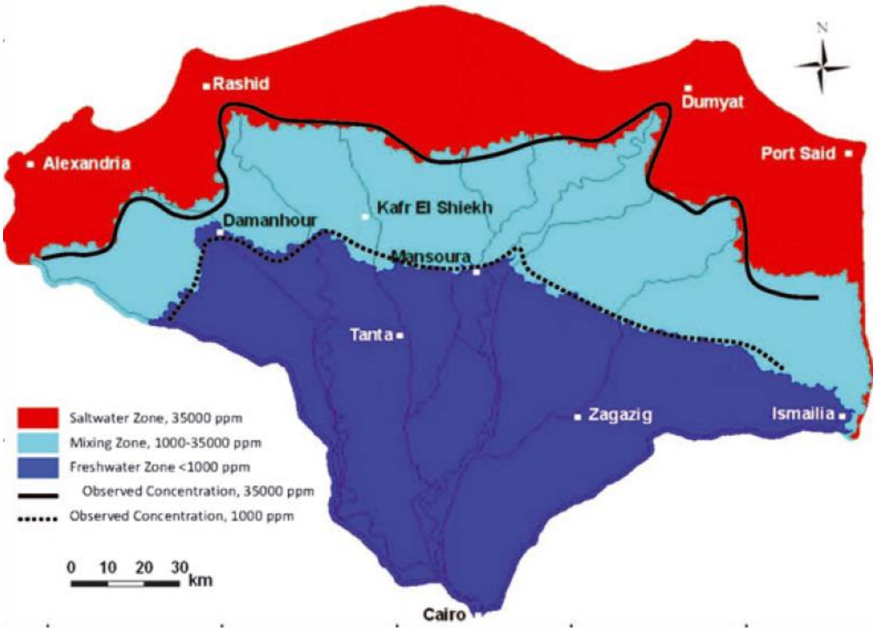


Figure 4.14 - Groundwater salinity in Nile Delta Aquifer (Sefelnasr & Sherif, 2014)

The proposed scheme has a number of advantages:

- The use of groundwater will reduce the pressure on Nile River making more water available for environmental flows in the river which will eventually lead to a healthy river ecosystem
- Fresh Nile water can be used as additional water source to dilute the fertilizer to create the draw solution and to dilute product water to meet nutrient content limits for irrigation
- The solution promotes sustainable use of groundwater as the underlying aquifer is renewable.
- The proposed technique will optimize fertilizers application and save labor cost related to fertigation.
- Brine could be disposed of in Mediterranean Sea, taking into account the environmental requirements and conditions, as discussed previously.
- The proposed technique works towards minimizing further soil salinization which is a reported problem in the delta region, as it is estimated that 35% of

the agricultural land in Egypt is suffering from salinity which negatively affects crop yield (Abo Soliman & Halim, 2012).

- This technology is appropriate for use during dry seasons when water availability is low.
- Low abstraction cost as depth to groundwater level is few meters

Currently, traditional surface (flood) irrigation is the main irrigation scheme used in Nile valley cultivated lands, consuming more than 60% of the total water resources available (ICARDA, 2011). Coupled with FDFO technology, changing this system can save considerable amounts of irrigation water. Localized irrigation technique is a better alternative, where frequent, slow application of water to specific root zone area of the plant, by surface and subsurface drip is deployed. Most fruit trees and vegetables react positively to localized irrigation systems, such as drip irrigation. As per Figure 4.15, localized irrigation could save around 42% of water used when compared to traditional surface (flood) irrigation typically used in Delta region nowadays.

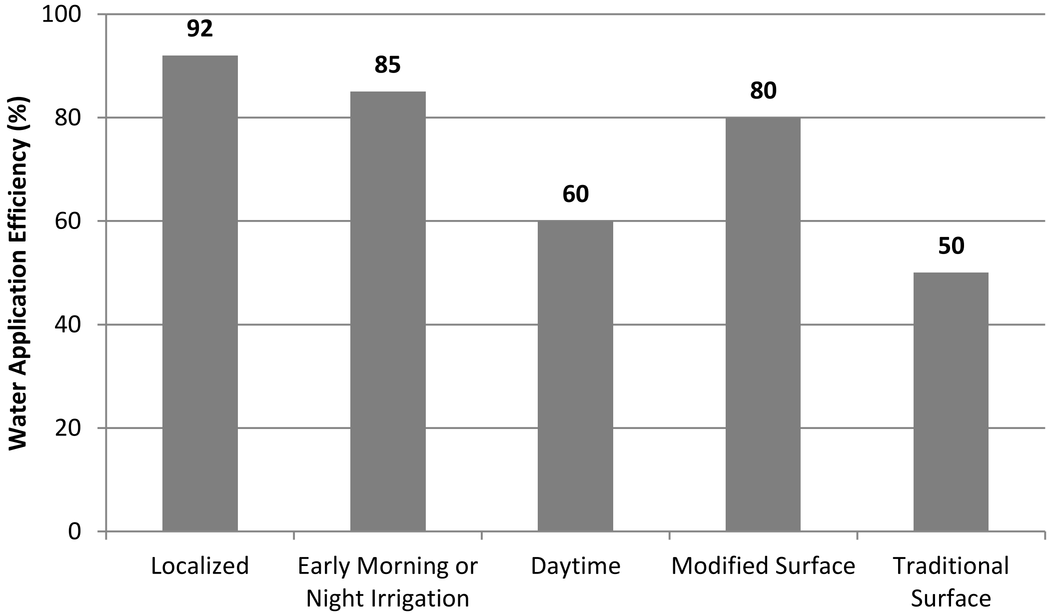


Figure 4.15 - Water-application efficiency for different irrigation methods (ICARDA, 2011)

It is important to quantitatively estimate the return of employing the proposed scheme in terms of the cultivable area using the renewable 4 billion m^3/year groundwater. According to Nile Water balance, 58 billion m^3/year of water is used to irrigate 8.6 million feddan for agriculture in all Egypt (ICARDA, 2011).Thus, water consumption rate could be estimated to be 6,750 m^3/feddan (using inefficient flood technique). If localized irrigation is used, 40% of the used water can be saved (ICARDA, 2011). So water consumption could be estimated to 4,050 m^3/ feddan. Thus, the cultivable area using the renewable 4 billion m^3/year of groundwater would amount to around 1 million feddan.

4.6.2 Red Sea Coast (Eastern Desert and Sinai)

Another potential area for FDFO application is the Red Sea coastal area in Eastern Desert and Sinai (Figure 4.12), where large quantities of brackish groundwater are available from different aquifers (Nubian Sandstone, Coastal aquifer and Hard Rock Aquifer), as per Table 4.3. According to El Tahlawi et al. (2007), the annual recharge in Red Sea Coast in southeastern desert is relatively high due to rainfall as the Red Sea hills attract orographic rainfall. Today, the average rainfall received by the southeastern Desert annually reaches up to 50 mm annually (Byrnes, 2007). The Tertiary aquifers are recharged by runoff water, by infiltration from the Quaternary aquifers and by upward leakage from deep aquifers, rendering it a renewable aquifer. The salinity ranges between 2,000 to 2,500 ppm (RIGW, 2002). The water is under phreatic conditions and is at a depth of around 70 m from ground surface. The salinity of this aquifer is about 1,500 ppm. In addition to the phreatic water conditions, high pressure water is a characteristic of this aquifer giving it a high potential.

Brackish groundwater desalination by FDFO technology in Red Sea Coast region is a sustainable solution for the water scarcity problem. As the area suffers from a severe water scarcity problem limiting its development, supply of supplementary water will help irrigation of new lands. The proposed scheme has a number of advantages:

- More arable lands will be available encouraging quick development of eastern desert and Sinai as well as creation of new employment opportunities.
- The Eastern Desert is bordered by populated areas (along Red Sea coast) which allow a gradual expansion of decentralized communities.
- The available RO facilities can be utilized and integrated to provide the fresh water required to create the DS and to dilute of the product water
- GW desalination by FDFO is probably more economical than seawater desalination in the Eastern Desert as the latter is separated from the Red Sea coast by the Red Sea hills, which is an obstruction for water conveyance and transportation.

- Brine can be disposed of directly into the Red Sea taking into account the environmental requirements and conditions, as outlined previously.
- The proposed technique insures sustainable use of groundwater as underlying aquifer is renewable.
- The water currently transported to Sinai is mixture of Nilewater and recycled drainage water (ratio 1:1), which has significant negative environmental impact. The proposed scheme will minimize such an environmental hazard as drainage water is no more used.

Due to the availability of land in the region under discussion, it is suggested to employ a new scheme different from present collective intensive cultivation. The proposed system entails distant limited cultivation, where decentralized small-scale farms (not exceeding 2,000 feddan) are set up, rather than hundreds of thousands of feddan as is common in Delta and Nile valley regions. Under such proposed scheme, the water losses will be greatly reduced, with the possibility of maintaining the desalinated water at a competitive price. Development of decentralized communities increases the resiliency of the population especially when the workplace is in the area where people are living. Developing decentralized communities away from the Nile Valley and Delta region will not only prevent further degradation of arable lands, but also will result in a redistribution of the population since currently 97% of the population are concentrated in less than 4% of the country's area (CAPMAS, 2013). If such scheme is combined with FDFO technology, large amounts of water will be available.

4.7 Concluding Remarks

FDFO is applicable to any area where brackish groundwater is abundant. Yet, there are certain locations in Egypt that have high potential as the proposed scheme would maximize its return if certain criteria are met. After investigating irrigation scheme and groundwater aquifers in Egypt, the two proposed locations presented in this work are 1) Nile Valley and Delta region and 2) Red Sea coast in Eastern Desert and Sinai region. It is anticipated that the impact of such technology on the agricultural segment in Egypt would be profound.

CHAPTER 5 - SELECTION OF POTENTIAL FERTILIZER DRAW SOLUTION FOR FERTILIZER DRAWN FORWARD OSMOSIS APPLICATION IN EGYPT

5.1 Introduction

The choice of a proper draw solution is vital in FO desalination process. A draw solution could be any aqueous solution with high osmotic pressure. It should provide sufficient force to cause passage of water across the membrane and therefore it is an essential part of the FO process. As the osmotic pressure of the draw solution is the driving force in the FO, it is crucial to select an appropriate concentrated solution for any application (Achilli et al., 2010). The osmotic pressure relies on concentration, number of species generated, the MW of the solute and the temperature. Osmotic pressure is independent on the type of species generated in the solution (colligative property). The less the MW of the DS and the higher its water solubility, the more the osmotic pressure generated and the higher the flux (McCutcheon et al., 2005).

It is worth noting that sections of this chapter were incorporated in the published paper entitled “Investigating Fertilizer Drawn Forward Osmosis Process for Groundwater Desalination for Irrigation in Egypt”.

5.2 Draw Solution Selection Criteria

According to McCutcheon et al. (2005) and (Zhao et al. (2012), an efficient DS solute must have the following distinctive properties:

1. It must exhibit a high osmotic driving force
2. It has to be soluble in water
3. It preferably has a small molecular weight
4. It must be non-toxic
5. It must be chemically matched with the membrane
6. The DS solute should be easily and inexpensively recovered (if not needed in the product water)

A flow diagram that displays the DS selection criteria is shown in Figure 5.1

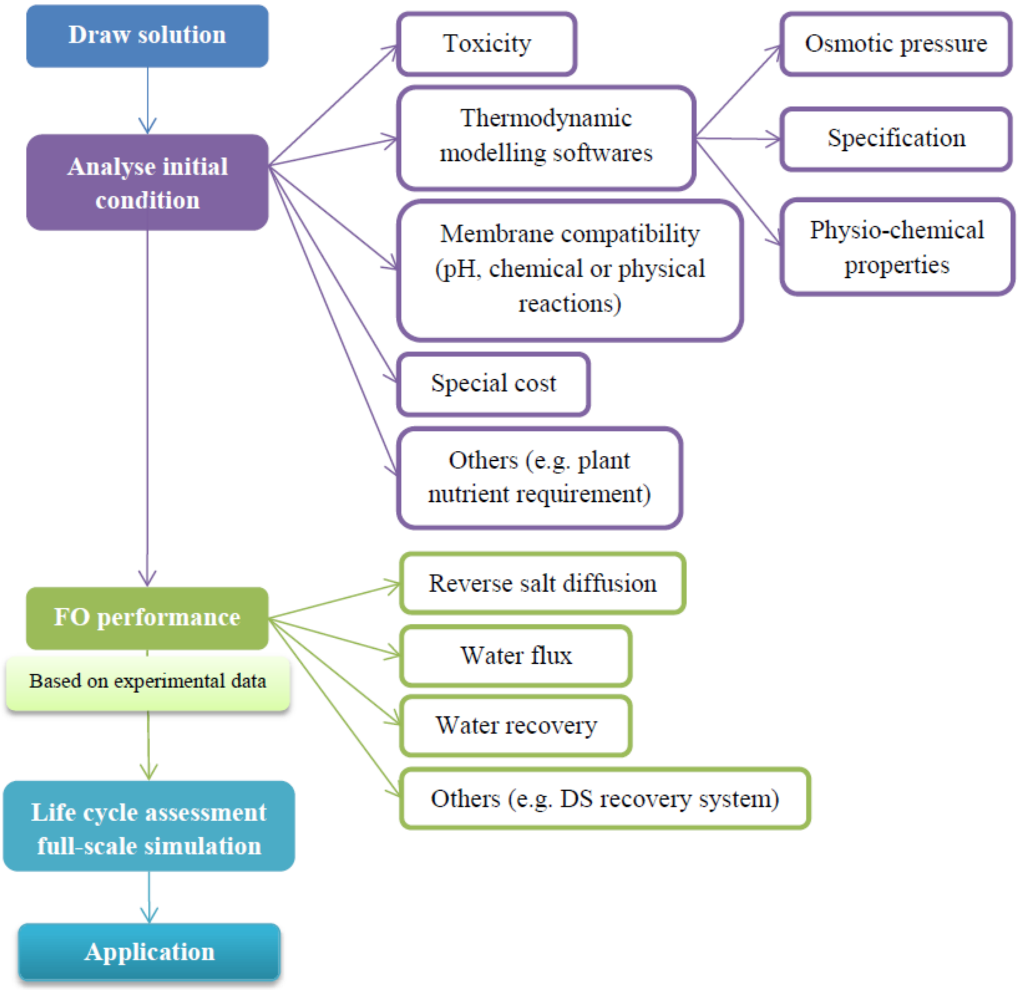


Figure 5.1 - Flow diagram for selecting a suitable DS in FO process (J. E. Kim, 2013)

5.2.1 Fertilizers as Draw Solutes

The choice of fertilizer DS for FDFO application will be based on a number of factors, which are fertilizer availability, economics and performance.

5.2.1.1 Fertilizer Availability

To have a sustainable FDFO process, the selected fertilizer should be readily available in the local market. Preferably, the fertilizer would be locally produced to avoid problems and delays related to importing from abroad. Being a central aspect of the system, fertilizer scarcity would significantly affect process efficiency.

5.2.1.2 Fertilizer Economics

Current fertilizer prices are related to high demand due to an increasing worldwide need for more food and a more diverse diet. Fertilizer is a world market commodity subject to global market forces, volatility, and risks. Yet, as the fertilizer is a key component of the FDFO scheme, for FDFO to be cost effective, the chosen fertilizer should not be expensive or costly.

5.2.1.3 Fertilizer Performance

The selected fertilizer should have suitable physiochemical properties to serve as a DS in FDFO process, such as solubility, pH compatibility with selected FO membrane, molecular weight, osmotic pressure, water extraction capability and final nutrient content in product water (Achilli et al., 2010). In addition, the DS should not chemically react with the FS to create unwanted species impeding the osmotic process or the final intended utilization of the produced water (irrigation in case of FDFO).

5.3 Fertilizers in Egypt

Although there are many types of chemical fertilizers used in agricultural industry in many parts of the world, only those fertilizers commonly used in Egypt were considered for assessment as DS for FDFO. In addition, chemical composition of commercially available blended fertilizers remains proprietary and thus they were excluded in this work.

For Egypt, fertilizer existed a long time ago. As previously discussed, fertilizers are divided into two groups organic and inorganic fertilizers (Kafkafi & Tarchitzky, 2011), where the latter are used intensively in Egypt compared to the former. Inorganic fertilizers include three main categories which are Nitrogen, Phosphate and Potassium fertilizers. Figure 5.2 illustrates the percentages of fertilizers consumed in Egypt by type. Mason (2003) claims that more than 8.5 million tons (86% of total fertilizers) of nitrogenous, 11.3 million tons (11%) of phosphorus and 29 million tons (3%) of potassium fertilizers are used in Egypt. Thus, nitrogen fertilizers come to be the most consumed type of fertilizer in Egypt and this group includes urea, ammonium nitrate, ammonium sulphate and calcium nitrate. Local consumption of Nitrogen fertilizers increased by 14.3% in 2008 compared to 2004. Presently, the annual use for Nitrogen fertilizers is almost 9 million ton (AlexBank, 2012).

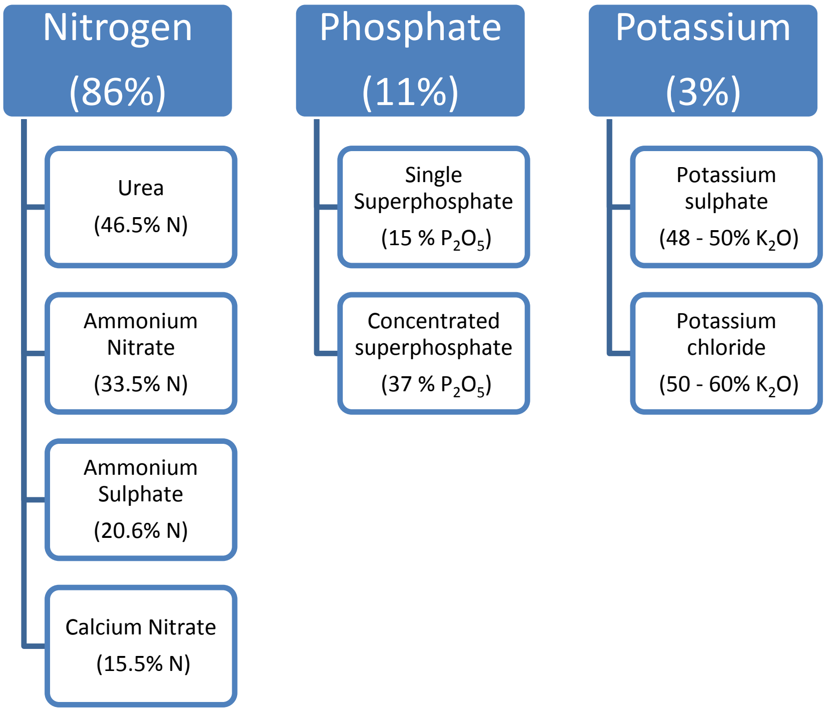


Figure 5.2 - Main types of fertilizers Egypt. Amounts presented are consumption percentages (Adapted from FAO, 2005a)

Fertilizer-use in Egypt boomed during the last three decades. For instance, in 2002 the total fertilizer consumption exceeded 1.3 million tons (FAO, 2005a). Figure 5.3 illustrates production, import, exports and consumption of different fertilizers types in Egypt. There are 14 major Egyptian fertilizer-producing companies such as Semadco, Abu Qir Co., Abu-Zaabal Fertilizer and Chemical Company and others (El-Gabaly, 2015).

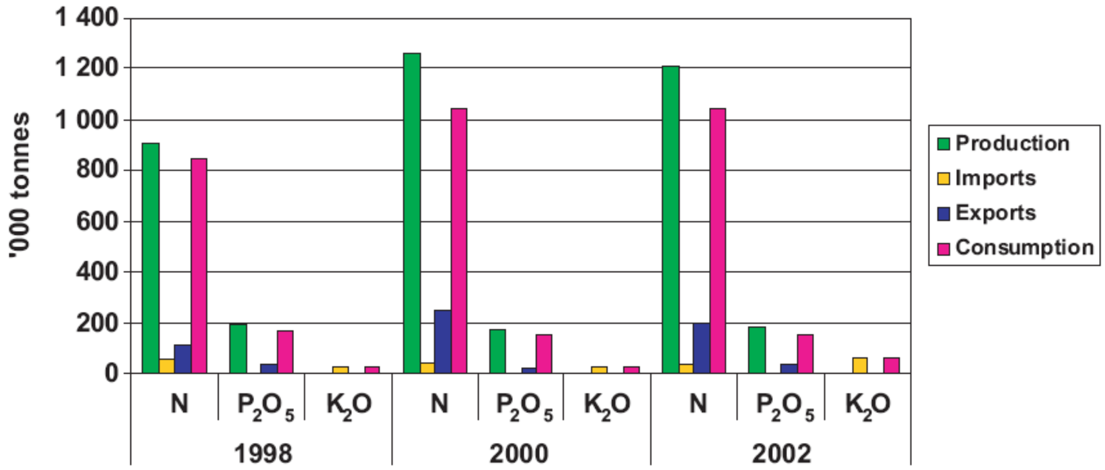


Figure 5.3 - Production, imports, exports and consumption of fertilizers in Egypt (FAO, 2005a)

As Nitrogenous fertilizers are by far the most commonly produced and consumed fertilizers in Egypt, this study will focus only on them (Figure 5.2 and Figure 5.3).

5.3.1 Fertilizer Screening According to Availability

The four selected fertilizers are available in the market (Figure 5.2). Yet, nitrate containing fertilizers (ammonium nitrate and calcium nitrate) were not easy to obtain as they are categorized as explosive material.

5.3.2 Fertilizer Screening According to Economics

Average local market prices of both highly-pure and less-pure fertilizers have been collected from different suppliers. Prices of highly pure (99% purity) chemical fertilizers were used for comparison. As each fertilizer contains a different amount of nitrogen content, comparison is carried out on a kg of Nitrogen basis, as per Table 5.1. Urea contains the highest nitrogen content (46%) followed by ammonium nitrate, ammonium sulphate and calcium nitrate. While urea contains the largest percent of nitrogen, it is considered more expensive (in terms of kg N) than calcium nitrate and ammonium sulphate.

Table 5.1 – Fertilizer price comparison

Fertilizer	**Less pure fertilizer Price (LE/kg)**	**Highly Pure fertilizer Price (LE/kg)**	**% Nitrogen**	**Pure fertilizer Price (LE/ kg N)**
Urea	2.8	253	46%	116.4
Ammonium Nitrate	3	462	34%	157.1
Ammonium Sulphate	1.9	71	21%	14.9
Calcium Nitrate	3	440	15.5%	68.2

The prices of the four selected fertilizers are illustrated in Figure 5.4. Ammonium Nitrate is the most expensive fertilizer costing 462 LE/kg, followed by Calcium Nitrate, urea and ammonium sulphate. The order changes if the basis for comparison is kg of N as follows: Ammonium Nitrate followed by urea, calcium nitrate and ammonium sulphate.

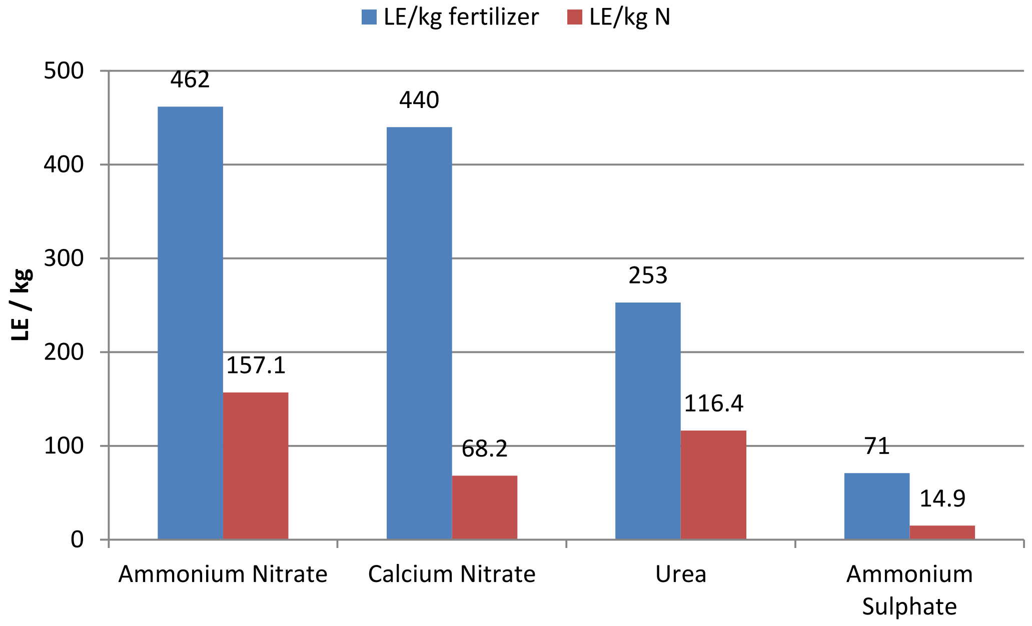


Figure 5.4 - Price comparison of four selected fertilizers (Nasr & Sewilam, 2016a)

5.3.3 Fertilizer Screening According to Performance

A performance screening of Nitrogen based fertilizer for the DS is conducted to determine basic properties (Table 5.2). OLI Stream Analyzer software 9.1, a software that employs thermodynamic modeling from published experimental data to forecast properties of solutions at different concentrations, was used to determine DS solubility, pH, speciation and osmotic pressure.

Table 5.2 - List of most popular Nitrogenous fertilizers in Egypt. Solubility and osmotic pressure data obtained from OLI Stream Analyzer Software 9.1 (OLI Systems, Inc., 2015)

Name of fertilizer	**Chemical Formula**	**Molecular Weight**	**pH at 2 M**	**π at 2 M (atm)**	**Max. Solubility**
Urea	$CO(NH_2)_2$	60.05	7.00	46.1	19.65 M
Ammonium Nitrate	NH_4NO_3	80.04	4.87	64.9	Highly Soluble
Ammonium Sulphate	$(NH_4)_2SO_4$	132.1	5.46	92.1	5.7 M
Calcium Nitrate	$Ca(NO_3)_2$	164.1	4.68	108.5	7.9 M

5.3.3.1 Osmotic pressure

The osmotic pressure relies on the number of species produced rather than the species' nature (Hancock & Cath, 2009). Figure 5.5 shows the osmotic pressure of the four selected fertilizers DS at variable concentrations. Calcium nitrate produces the largest osmotic pressure of 600 atm at its maximum solubility. This is because $Ca(NO_3)_2$

when dissolved generates the largest number of species in comparison to other fertilizers.

If a comparison is made at the same molar concentration (say at 2.0 M) from Table 5.2, the next maximum osmotic pressure observed is for Ammonium Sulphate (92.1 atm). The least osmotic pressure witnessed is for urea (46.1 atm at 2.0 M). Yet, as urea is readily soluble in water, it possesses osmotic pressure more than 200 atm at concentrations more than 10 M (Figure 5.5). Figure 5.6, Figure 5.7, Figure 5.8 and Figure 5.9 provide the type and concentration of each species present as well as the expected osmotic pressure at different concentrations of the four selected fertilizers. Analysis was done by the help of OLI stream Analyzer 9.1 software.

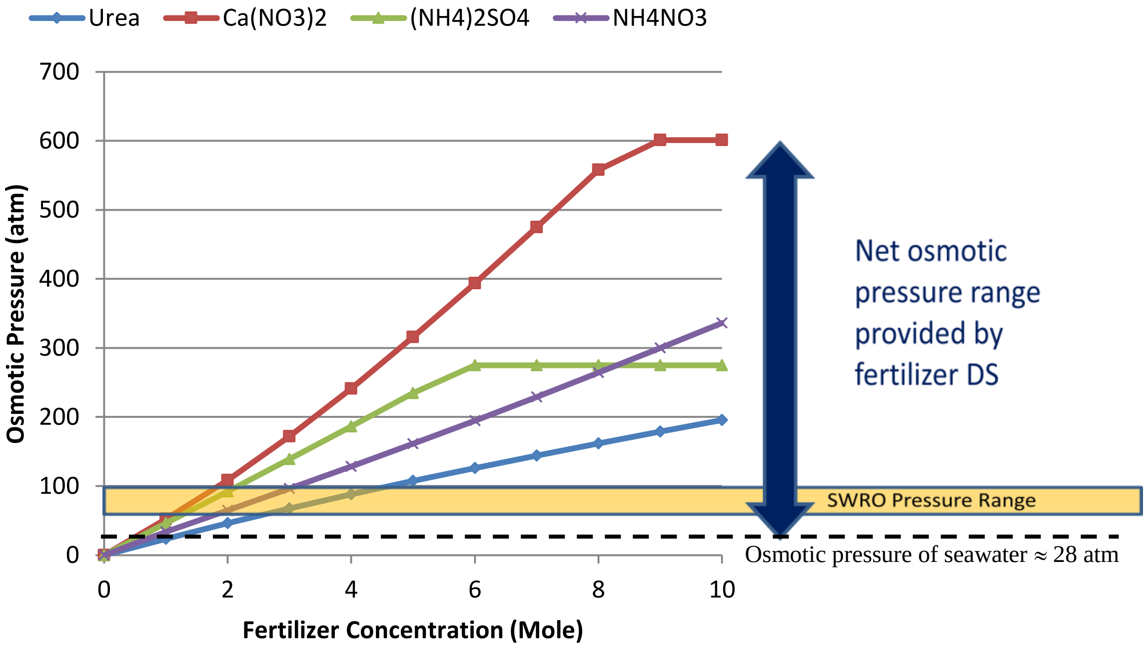


Figure 5.5 – Osmotic pressure of different nitrogenous fertilizers DS at 25 C analyzed using OLI Stream Analyzer 9.1

It is worth noting that SWRO pressure range is between 60 and 100 atm and that the osmotic pressure of seawater is estimated to be around 28 atm (Altaee, Zaragoza, & van Tonningen, 2014; Lenntech, 2014; Shaffer, Yip, Gilron, & Elimelech, 2012). Comparing these values to the osmotic pressures of the four fertilizers under study, it is clearly inferred that the four fertilizers possess osmotic pressure much more than that of seawater and SWRO (Figure 5.5).

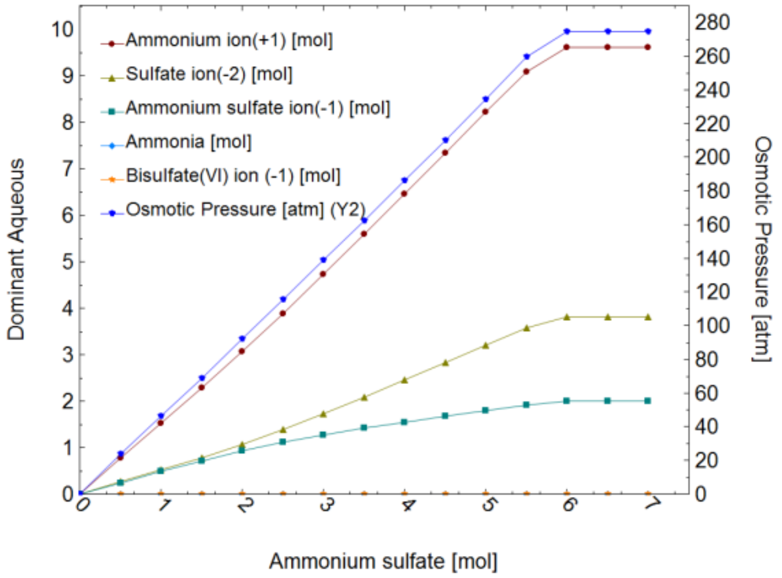


Figure 5.6 - Species generated and osmotic pressure of ammonium sulphate. Analysis carried out using OLI stream Analyzer 9.1 at 25°C temperature and 1 atm pressure (OLI Systems, Inc., 2015)

For Ammonium sulphate, three dominant aqueous species exist, which are ammonium ion, sulphate ion and ammonium sulphate ion. Ammonia and bisulphate ion are not considered from the dominant species (Figure 5.6). Osmotic pressure of ammonium sulphate seems to increase as concentration increases up to 5.5 molar concentration due to its maximum solubility.

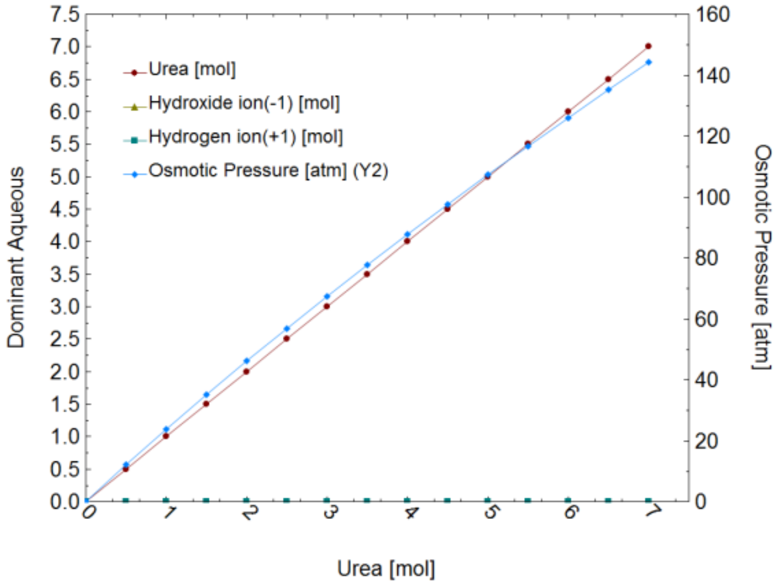


Figure 5.7 - Species formed and osmotic pressure of urea. Analysis carried out using OLI stream Analyzer 9.1 at 25°C temperature and 1 atm pressure (OLI Systems, Inc., 2015)

Urea has only one dominant aqueous species (Figure 5.7). The osmotic pressure lineally increases as urea concentration increases. Osmotic pressure reaches up to 150 atm at a 7 molar concentration.

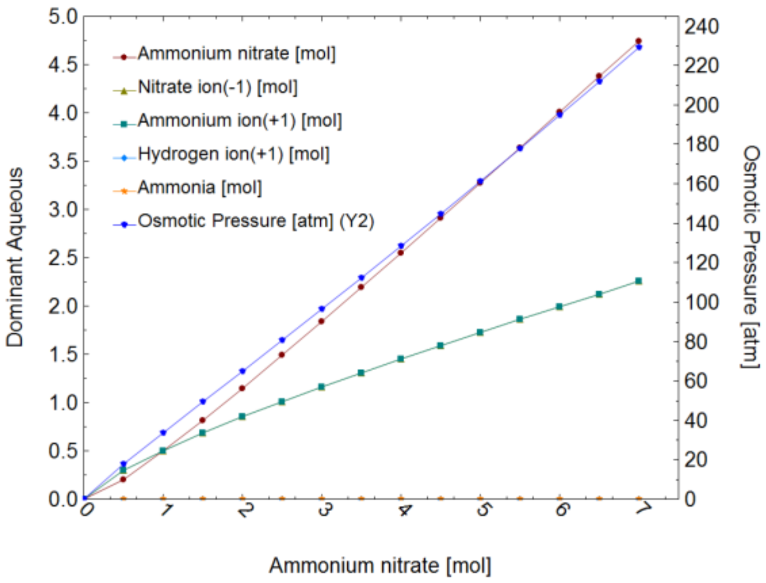


Figure 5.8 - Species formed and osmotic pressure of ammonium nitrate. Analysis carried out using OLI stream Analyzer 9.1 at 25°C temperature and 1 atm pressure (OLI Systems, Inc., 2015)

For Ammonium nitrate, two dominant aqueous species exist, which are ammonium nitrate and ammonium ion. Ammonia and nitrate ion are not considered from the dominant species (Figure 5.8). Osmotic pressure of ammonium nitrate seems to increase proportionally as concentration increases reaching 230 atm at 7 molar concentration.

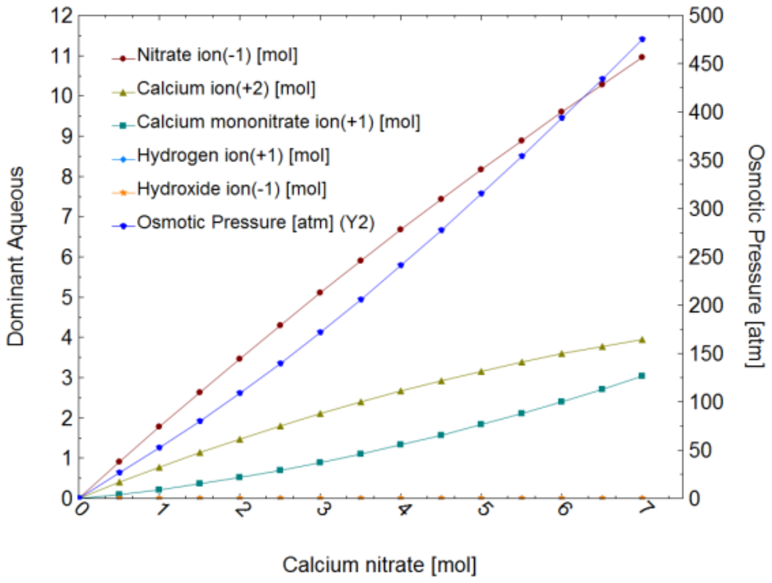


Figure 5.9 - Species formed and osmotic pressure of calcium nitrate. Analysis carried out using OLI stream Analyzer 9.1 at 25°C temperature and 1 atm pressure (OLI Systems, Inc., 2015)

Calcium nitrate has three dominant aqueous species, which are nitrate ion, calcium ion and calcium mono-nitrate ion (Figure 5.9). Osmotic pressure of calcium nitrate seems to increase proportionally as concentration increases reaching 475 atm at 7 molar concentration.

Any draw solute should exhibit higher osmotic pressure than that of the feed solution. For example, sweater has an osmotic pressure of 26 atm. So, if sweater is the feed solution, the DS must exhibit an osmotic pressure a lot more than 26 atm. Such conclusion signifies that all the investigated fertilizers produce osmotic pressure that is much way than seawater or brackish water, indicating their suitability for use as an osmotic DS.

5.3.3.2 Water Extraction Capacity

Water extraction capacity of the draw solute plays a major role in any FO process. DS can extract water from the FS until the osmotic pressure of the DS reaches equilibrium with the osmotic pressure of the FS (Phuntsho et al., 2014). When different draw solutes are used a number of species are formed in solution and the osmotic pressure of the DS depends on their osmotic coefficient. According to Phuntsho et al. (2014), the total volume of water (V) a kilogram of draw solute can extract from an FS can be estimated using the following relationship:

$$V = \frac{1000}{M_w}\left[\frac{1}{C_{D,E}} - \frac{1}{C_{D,Max}}\right]$$ **Equation 5.1**

Where: M_w is molecular weight of draw solute used (mol/g) - Table 5.2

$C_{D,E}$ is the molar concentration of the DS that generates equal bulk osmotic pressure (osmotic equilibrium condition) with the osmotic pressure of a FS (mol)

$C_{D,Max}$ is maximum solubility of the draw solute (mol) - Table 5.2

Osmotic pressure of six different TDS FS are considered for comparative reasons (1, 2, 5, 10, 20 and 35 g/l NaCl). Using OLI Stream analyzer 9.1, the osmotic pressures of these FS were estimated to be 0.8, 1.59, 3.91, 7.76, 15.52 and 28 atm, respectively.

For example, to calculate volume of water extracted using urea DS and a 5g/l NaCl FS, $C_{D,E}$ is first estimated. The 5 g/l NaCl FS has osmotic pressure equal to 3.91 atm and the equivalent concentration of urea at this osmotic pressure ($C_{D,E}$) is equal to

0.1607 M (Figure 5.7). OLI stream analyzer software 9.1 was utilized in these calculations. Substituting the relevant values in Equation 5.1, the volume of water extracted will equal 103 L/kg.

As per Figure 5.10, the water extraction capacity of the DS declines severely upon gradual increase in feed Total Dissolved Solids. It can also be concluded that the 4 fertilizers almost show similar water extraction capacities. Yet, NH_4NO_3 exhibits slight more water extraction especially at low TDS feeds. For example, at a feed TDS equal to 1 g/l NaCl, while NH_4NO_3 extracts 700 l/kg of pure water, $Ca(NO_3)_2$ extracts only 488 l/kg. As FS concentration increases from 1 to 35 g/l NaCl, the difference in extraction capacities of the 4 fertilizers significantly decreases.

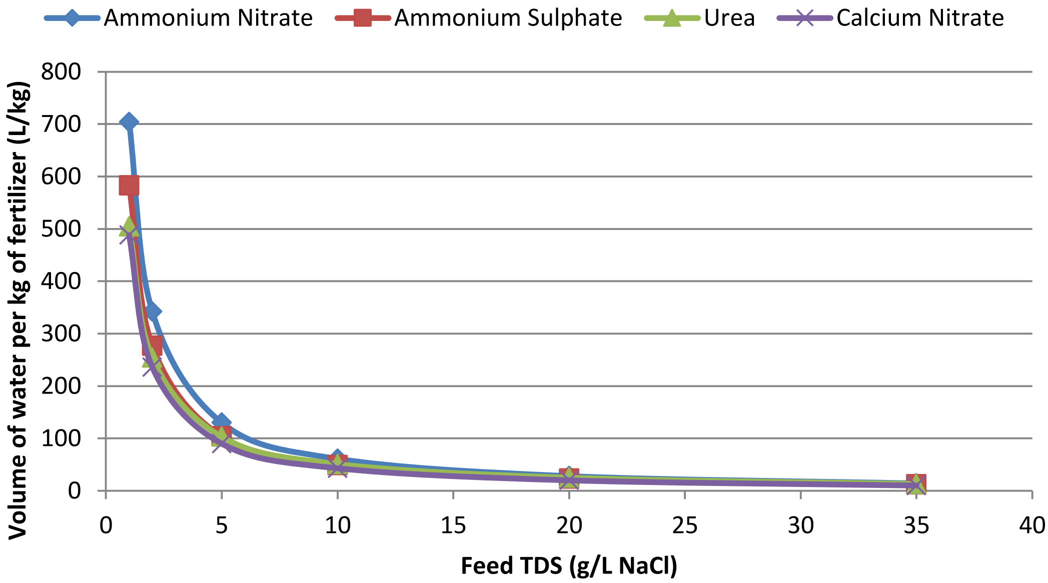


Figure 5.10 - Variation of water extraction capacities of the draw solutes by FO process at different feed TDS using different draw solutes

5.3.3.3 Expected Final Nutrient Concentration in Product Water

Regardless of which initial DS concentration is used, the FO process will continue to take place until the osmotic pressure of the diluted DS is in equilibrium with the FS. Thus, the molar concentrations of each fertilizer DS can be determined according to the osmotic pressure of the FS. The feed waters of six different TDS (1, 2, 5, 10, 20 and 35 g/l NaCl) are considered to assess the expected nutrient content in the final product water after desalination.

The nutrient content is assessed in terms of Nitrogen content and is presented in Figure 5.11. For example, urea's final concentration at 5 g/l NaCl as FS (osmotic pressure equal to 3.91 atm) is expected to be 0.1607 M. This concentration of urea contains $\left(0.1607\ \frac{\text{mol}}{\text{l}} * 28\ \frac{\text{g}}{\text{mol}}\right)$ g/l of N, or 4.5 g/l of N.

It is obvious from Figure 5.11 that the final nutrient concentrations in FDFO rely on the type of fertilizer used and the TDS of the FS. Feed TDS and final nutrient concentration of product water are directly proportional. The lowest N concentration was observed for $Ca(NO_3)_2$, with 349 mg/L with feed TDS of 1 g/L; however this increases to 0.72, 1.87, 3.89, 8.2 and 14.8 g/L of N with 2, 5, 10, 20 and 35 g/l Feed TDS, respectively. Urea will result in highest N content in the final product water for all feed concentrations. These results indicate that when high N containing fertilizers such as urea are used as DS, the N content in the product water will be considerably higher than in the other fertilizers containing low nitrogen (Phuntsho, Shon, Majeed, et al., 2012). Another reason for high N concentration with urea is that it generates one of the lowest osmotic pressures amongst all the fertilizers at equimolar concentration, in spite of its high solubility (Figure 5.5 and Table 5.2).

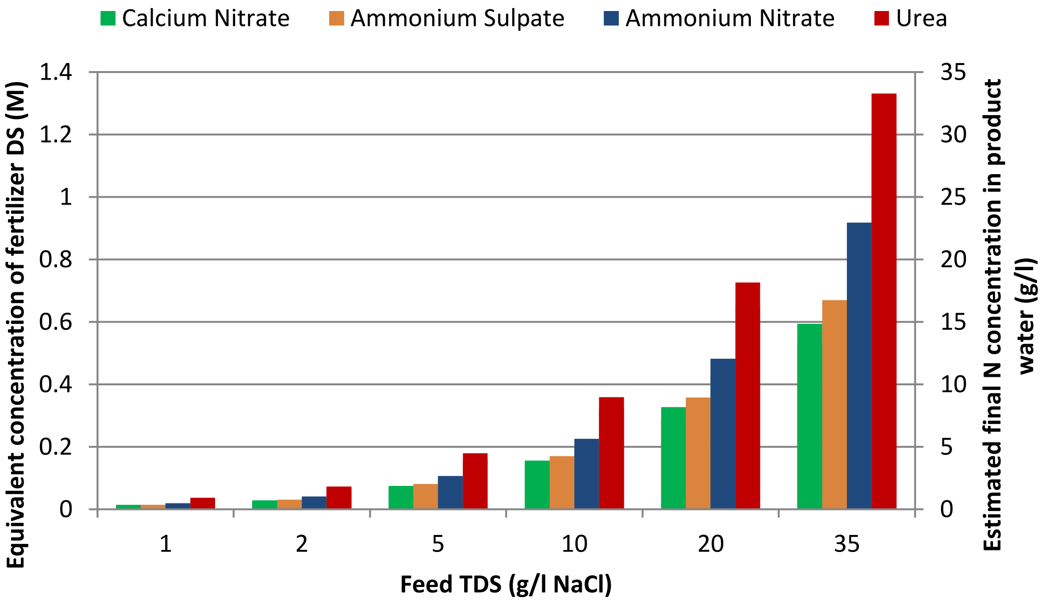


Figure 5.11 – Equivalent concentration of fertilizer DS and estimated final N concentration in product water for different feed TDS concentrations

5.3.3.4 Dilution Requirement

If the final product water from the FDFO desalination plant is to be used directly for fertigation, the nutrient concentration must meet the water quality standards for irrigation. Therefore, it is important that the final FDFO produced water meets the nutrient concentration; otherwise further dilution is required before applying for fertigation. Excessive fertilizer nutrient can be harmful to plants because it increases not only salinity but also toxicity (Kafkafi & Tarchitzky, 2011). In addition, leaching of fertilizer nutrients when excessive fertilizer is used in the water can cause undesired pollution of groundwater bodies (Freeze & Cherry, 1979).

Figure 5.12 provides the highest recommended N concentrations for different types of plant crops. Plant requirement from nutrients varies depending on numerous factors, such as types of crop, cropping season, soil nutrient condition, etc. (Kafkafi & Kant, 2005). Generally, the required N nutrient concentrations ranges between 50 and 200 mg/L for N, function of the crop and growing time of year (Phocaides, 2007). Comparing the information in Figure 5.12 to that of Figure 5.11, it can be easily concluded that it will not be possible to achieve the required water quality standards by the FDFO desalination process only, especially if feed salinity is more than 1 g/l. The N concentrations are significantly higher, especially for feed with higher TDS, indicating that a high dilution factor is needed to achieve recommended concentrations. This means that the additional dilution required is of several orders of magnitude before it can be used for direct fertigation.

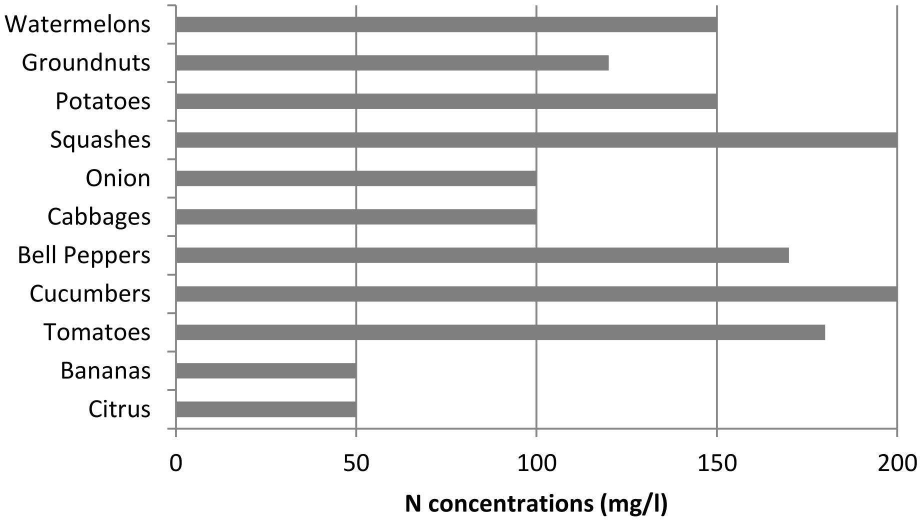


Figure 5.12 - Highest recommended N concentrations for different types of plant crops (Phocaides, 2007)

For example, if the target crop is potatoes, being an important Egyptian crop, it is necessary for the N nutrient concentration to be 150 mg/L (Figure 5.12). None of the four fertilizers achieve an acceptable N concentration for the potatoes without dilution before the fertilizer solution can be used for fertigation even with the lowest FS concentration of 1 g/l NaCl. Using the selected four fertilizers as the DS will require a dilution factor of at least 4 to make the N concentration acceptable for the potatoes at 150 mg/L using feed with TDS of 2 g/l. The dilution factor for $Ca(NO_3)_2$, SOA, NH_4NO_3 and Urea are 4.8, 5.0, 6.8 and 12.2, respectively, when used with FS TDS of 2 g/L. As the FS TDS increases, the dilution factor will increase.

5.4 Fertilizer Selection

In light of the above screening, Ammonium Sulpahte was selected as the best draw solute for FDFO application in Egypt. The selection was based on the following justifications:

- Ammonium Sulpahte is the most non-expensive fertilizer, which will save operational costs (Figure 5.4). It has been used in Egypt a long time ago and it is produced locally by numerous fertilizer factories (AlexBank, 2012). Although domestic demand for the granular ammonium sulphate is low, the crystal form is popular in Egypt since it is relatively cheap (Thapliyal, 2013). It is reported that Egyptian market consumed 140,000 ton of ammonium sulphate in 2012 (Factfish, 2015).
- Ammonium Sulpahte produced osmotic pressure that is way higher than seawater (~28 atm) and brackish water, indicating its suitability to be used as an osmotic DS (Figure 5.5)
- Ammonium sulphate provides the plant with nitrogen and sulphur at the same time as it contains approximately 21% nitrogen and 24% sulphur, promoting plant growth and crop yield. Because Ammonium sulphate contains mainly ammonium nitrogen, it secures a lasting and sustainable nitrogen source. In the meantime, it minimizes nitrogen washing out from the soil. In addition, ammonium sulphate promotes the availability of secondary nutrients like manganese, iron, and boron in the soil (Kafkafi & Kant, 2005; Kafkafi & Tarchitzky, 2011).
- Cost of ammonium sulphate is not affected by the fluctuating costs of natural gas because it is a byproduct of other industries such as steel and polyester compounds. Certain by-products that contain ammonia or sulfuric acid are commonly converted to ammonium sulphate for use in agriculture (“Ammonium sulfate,” 2015; Norton, 2015).

- Ammonium Sulpahte is not hygroscopic (tendency to absorb moisture from the air), thus long storage duration is possible (UNIDO & IFDC, 1998)
- Compared to urea, ammonium sulphate is more resistant to valorization
- Ammonium sulphate is the preferred fertilizer for flood irrigation used for rice cultivation, while nitrate-based fertilizers are a bad option due to significant denitrification losses (UNIDO & IFDC, 1998)
- Ammonium Sulpahte exhibits moderate final Nitrogen concentration in product water so it can easily meet irrigation water quality (Figure 5.11)
- Ammonium sulphate has SO_4^{2-} ionic species which exhibit a large hydrated diameter compared to other fertilizer species. The effective diameter of the hydrated NH_4^+ and SO_4^{2-} ions are $250x10^{-12}$ and $400x10^{-12}$ m respectively, making it hard to pass through the membrane material (Achilli et al., 2010). Consequently, ammonium sulphate is expected to perform well in terms of RSF (Phuntsho, Shon, Hong, et al., 2012).
- Ammonium sulphate is highly soluble in water, non-flammable and less hazardous than other draw solutes (Norton, 2015)

Other three fertilizers were overlooked due to the following reasons:

- Urea is not the best candidate as a DS. Not only because it exhibits the lowest osmotic pressure compared to other DS, but also because it results in the highest final Nitrogen concentration in final product water which will lead to need for dilution to meet water quality standards. In addition, other studies reported that urea suffers from significant reverse permeation of draw solutes compared to other DS. The high RSF/SRSF of urea can be attributed to its low rejection by the membrane as urea is a neutral solute with the smallest molecular size in comparison to other DS (Phuntsho, Shon, Majeed, et al., 2012).
- Ammonium nitrate is hygroscopic (tends to absorb moisture from the air), less effective for flood irrigation and prone to leaching after application (UNIDO & IFDC, 1998).
- Calcium nitrate is hygroscopic and must be kept under air-tight storage conditions

- Ammonium nitrate and calcium nitrate are not easy to obtain as they are commercially banned being main constituents in explosives manufacturing.

CHAPTER 6 – INVESTIGATING THE PERFORMANCE OF AMMONIUM SULPHATE DRAW SOLUTION IN FERTILIZER DRAWN FORWARD OSMOSIS APPLICATION

6.1 Introduction

Chapter 5 concluded that Ammonium Sulphate is the best candidate for FDFO application in Egypt. This chapter further investigates the draw solution performance with respect to water flux, reverse permeation and rejection using a bench-scale forward osmosis (FO) setup. It must be mentioned here that, this particular study was conducted at University of Technology, Sydney. Only one FO membrane was tested in this investigation, which is a Thin Film Composite polyamide FO membrane obtained from Woongjin Chemicals, Korea. The outcome of this chapter is a publication entitled "Investigating the performance of ammonium sulphate draw solution in fertilizer drawn forward osmosis process".

6.2 Theory

The general equation describing water transport in FO is given by the following basic equation (McCutcheon et al., 2006):

$$J_w = A\,\sigma\,(\pi_{DS} - \pi_{FS})$$

Equation 6.1

where, J_w is the pure water flux,

A is the pure water permeability coefficient of the membrane,

σ is the reflection coefficient, usually assumed to be one, indicating total rejection of solute

π_{DS} is bulk osmotic pressure of the draw solution (DS)

π_{FS} is bulk osmotic pressure of the feed solution (FS)

Since polymeric membranes are not ideal membranes, they cannot totally reject the solutes. Thus, as per Figure 6.1, solute transfer could possibly occur on both sides of the membrane (Phuntsho et al., 2014). For the draw solute to permeate across the asymmetric membrane into the feed solution, where its concentration C_F is negligible, it must be transported across the support layer of thickness t_S, and the active layer of thickness t_A. C_i^S and C_i^A represent the draw solute concentrations on the support layer side and active layer side of the support layer-active layer interface, respectively (Phillip et al., 2010). So, Reverse Solute Flux (J_s or RSF) defines the diffusion of draw solutes occurring in reverse direction to the water flux.

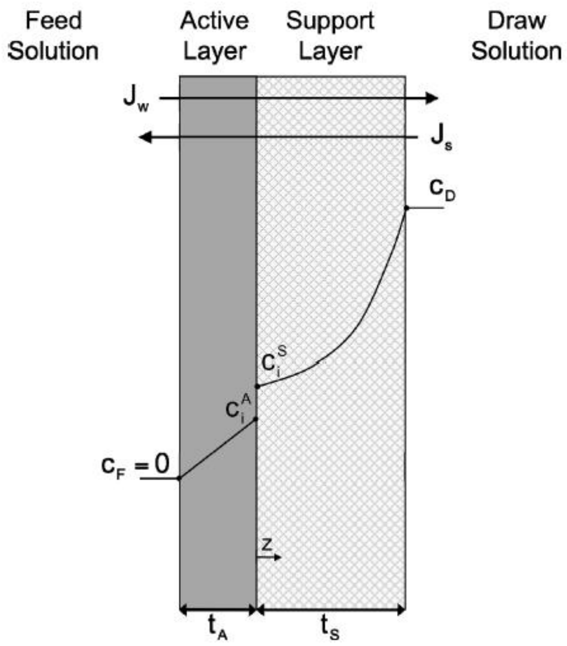


Figure 6.1 - A schematic of draw solute leaking into the feed solution. The high concentration of solute in the draw solution, C_D , creates a chemical potential gradient that drives both the forward water flux, J_w, and the reverse flux of solute, J_s . Boundary layer for draw solute on feed/membrane interface is disregarded (Phillip et al., 2010)

Considering the RSF in the FO process is pivotal due to a number of reasons. Reverse diffusion of draw solutes is an economic loss because lost draw solutes cannot be recovered and fresh draw solutes need replenishment (T. Cath et al., 2006). In addition RSF is a significant parameter when nitrogen- and phosphorus- containing DSs are used as these compounds eventually cause eutrophication in the receiving water environment (Phuntsho, Shon, Hong, et al., 2012). Reverse salt permeation can be detrimental for FO because not only may it upset feed water concentrate management and reduce the net osmotic driving force, but also it increases the fouling potential of the FS by forming complexes with the feed ions (T. Cath et al., 2006; Lay et al., 2010). Therefore it is essential to assess the performance of fertilizer draw solution in terms of RSF.

The RSF of an individual solute through any semi-permeable membrane is governed by concentration gradients between the two solutions [i.e. $J_s \propto f(\Delta C)$] and can be calculated as follows:

$$\mathrm{RSF} = \mathrm{J_s} = \frac{(\mathrm{V_i} - \Delta \mathrm{V}) * \mathrm{C_S}}{\text{membrane area} * \text{time}}$$ **Equation 6.2**

where: V_i is the initial volume of FS

ΔV is the total volume of water that enters the DS from the FS

C_s is the concentration of the draw solutes in the FS at the end of the experiment

RSF in Equation 6.2 does not account for the amount of pure water transferred through the membrane. That is why; Specific Reverse Solute Flux (SRSF) is introduced to relate the amount of draw solutes lost by reverse diffusion per unit volume of water extracted from the FS (T. Cath et al., 2006). SRSF can be calculated using the following relation:

$$\mathrm{SRSF} = \frac{J_s}{J_w} \qquad \textbf{Equation 6.3}$$

A higher SRSF value denotes a lower membrane selectivity and poorer FO efficiency (Zhao, Zou, & Mulcahy, 2012). SRSF relates to the selectivity of the active layer of the membrane and is independent of the DS concentration and membrane support structure, as will be shown later (Hancock & Cath, 2009; Phillip et al., 2010).

The forward rejection of the feed solutes is estimated using the following relation:

$$R_s(\%) = \left(\frac{C_i - C_p}{C_i}\right) * 100 \qquad \textbf{Equation 6.4}$$

where: C_i is initial concentration of the ion in FS

C_p is final concentration of the ion in permeate, which is equal to $\left(\frac{C_{p,D}(V_i+\Delta V)}{\Delta V}\right)$, where $C_{p,D}$ is the measured concentration of the ion in DS

6.3 Materials and Methods

The experimental investigations in this work were performed using a bench-scale crossflow filtration unit (Figure 6.2 and Figure 6.3). The FO unit consists of an FO cell with channel dimensions of 7.7 cm length x 2.6 cm width x 0.3 cm depth and a membrane area equal to 2 x 10^{-3} m^2 (Figure 6.4). A flow channel is provided on each side of the membrane to allow feed water to flow on one side of the membrane and draw solution on the side of the membrane. Rubber gaskets were used to support the membrane and provide adequate depth in each flow channel.

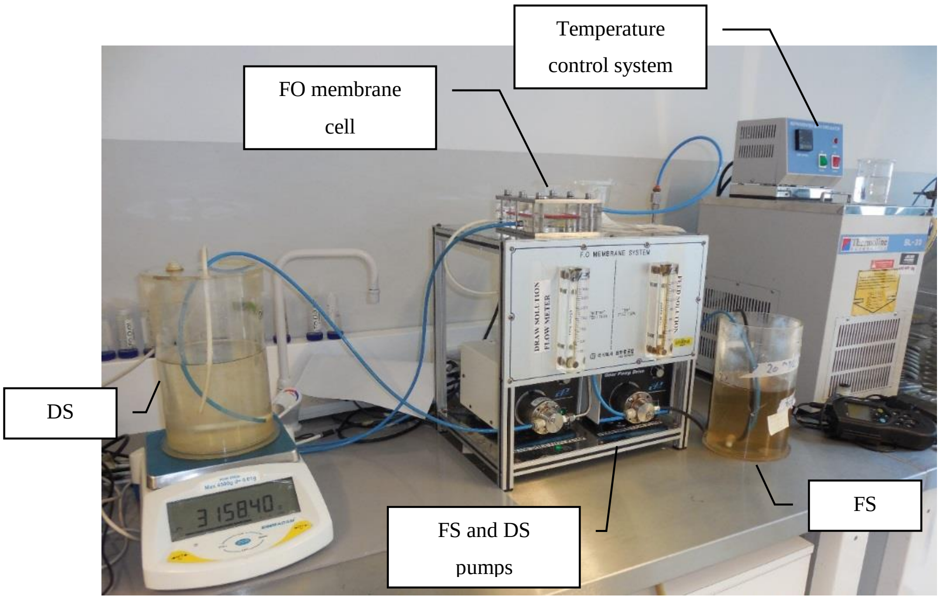


Figure 6.2 – Bench-scale system used for FO experimentation in University of Technology, Sydney

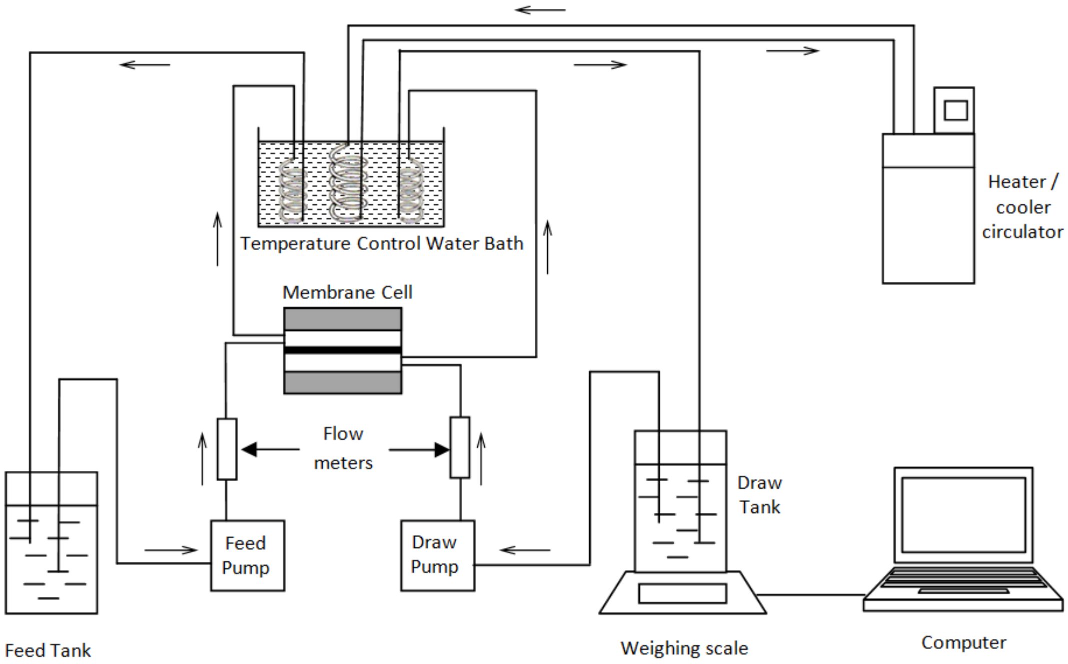


Figure 6.3 - Experimental Setup (Nasr & Sewilam, 2016b)

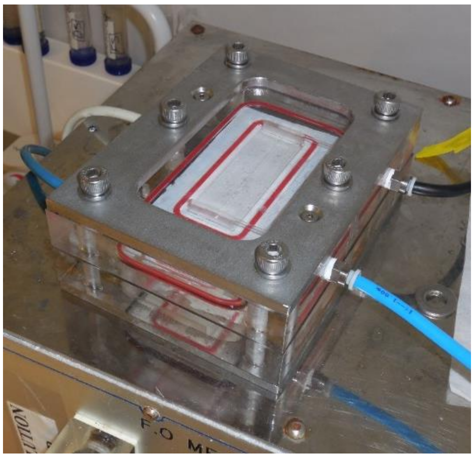


Figure 6.4 - FO membrane cell with effective membrane area of 2.002 x 10^{-3} m^2

Experiments in this study were carried out at a crossflow rate of 400 ml/min which is equivalent to a crossflow velocity of 8.5 cm/s. The crossflows were operated in counter-current flow directions using two variable speed peristaltic pumps (Cole Palmer model 75211-15, 50-5000 RPM and 0.07 HP, Thermo Fisher Scientific, USA). The temperature of all solutions was maintained at 25°C using a temperature water bath controlled by a heater/chiller[2]. Water flux across the membrane in the FO process was calculated from the change in the volume of the DS in the DS tank. The change in the DS volume was recorded continuously by connecting the DS to a digital mass scale connected to a computer for online data logging at three-minute intervals. The water flux J_w (in $Lm^{-2}h^{-1}$) was calculated using Equation 6.5, as shown below.

$$J_w = \frac{\Delta V}{\text{membrane area} * \text{time}}$$ **Equation 6.5**

The initial volume of both the DS and FS (V_i) was 2.0 L each. The solutions after passing through the membrane were returned to their respective tanks. This led to the continuous dilution of the DS and a continuous increase in the concentration of the FS, resulting in a decrease in water flux with time. However, the water flux was selected from the point at which a stable flux was observed from the plot of flux versus time, which usually happened within the first 50 minutes of operation. Most of the experiments were carried out for duration of at least six hours for adequate diffusion of draw solutes and help effective monitoring of the reverse diffusion of draw solutes.

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[2] Experimental settings were chosen similar to previous work done by the research team at University of Technology, Sydney which is published in Phuntsho, Hong, Elimelech, & Shon (2014).

6.3.1 Forward Osmosis Membrane

The FO membrane used in this study is supplied by Woongjin Chemicals, Korea. It is a polyamide based TFC flat sheet membrane. Basic properties of the membrane used in this study are shown in Table 6.1. Surface and cross-sectional SEM images of the FO membrane are shown in Figure 6.5. The membrane is composed of a polyamide selective layer over a polysulfone support layer placed over a fine polyester nonwoven fabric (Yip et al., 2010). A finger-like morphology is observed in the polysulfone support layer with sponge-like formations near the upper surface.

Table 6.1- Membrane properties – as provided by manufacturer, Woongjin Chemicals, Korea

Pure Water Permeability Coefficient, A ($Lm^{-2}h^{-1}bar^{-1}$)	3.036
Salt permeability coefficient of active layer, B ($Lm^{-2}h^{-1}$)	1.968
Rejection for 5,000 mg/L NaCl at 10 bar (%)	85.2%
Total membrane thickness (μm)	63.11
Material of active layer	Polyamide (PA)
Material of support layer	TFC Porous Polysulfone

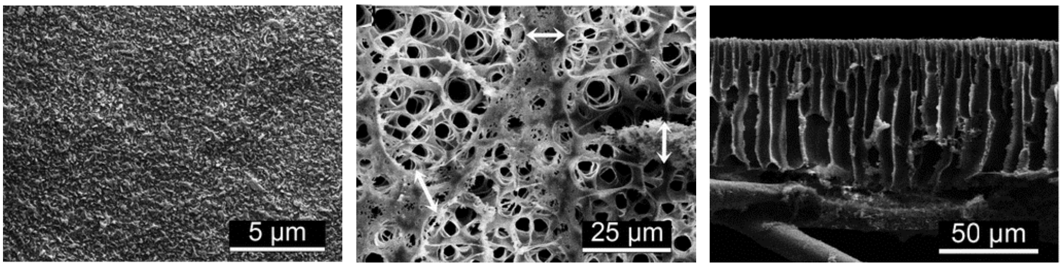

Figure 6.5- SEM images of the TFC membranes used (Yip et al., 2010)

The membrane orientation used in this investigation was FO mode, where FS faces the membrane active layer and the DS faces the porous support layer. In this setup, CECP occurs on the membrane active layer facing the FS while DICP takes place inside the membrane support layer facing the DS, as per Figure 6.6. The CP phenomena are the primary causes of the lower-than-expected water flux as they lead to a reduction in the net driving force across the membrane (Lay et al., 2010; Lee et al., 2010).

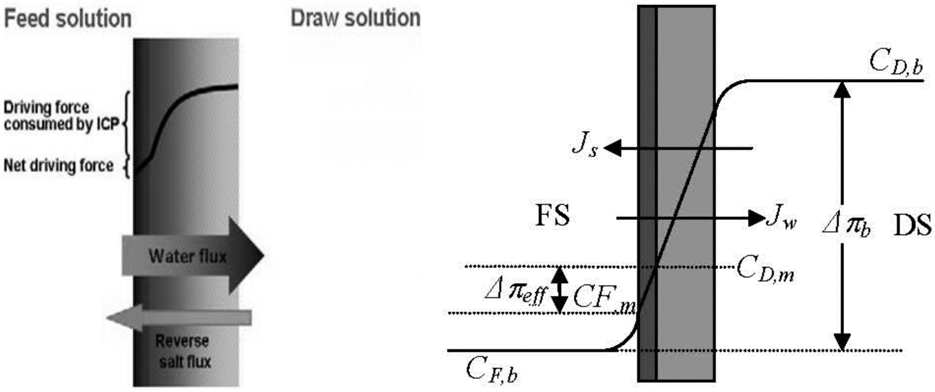

Figure 6.6 – Dilutive ICP in FO mode. *C*: refers to the solute concentrations that generate osmotic pressure. Subscripts *D*, *F*, *b* and *m* refer to the DS, FS, bulk solution and membrane boundary layer respectively. $\Delta\pi_b$ refers to the net bulk osmotic pressure and $\Delta\pi_{eff}$ refers to the effective osmotic pressure or effective driving force (Alsvik & Hägg, 2013; Phuntsho, 2012)

6.3.2 Draw Solution

An aqueous solution containing ammonium sulphate was selected as the DS for this investigation. Reason of this selection is discussed thoroughly in Chapter 5. Basic properties of ammonium sulphate are shown in Table 6.2. The speciation and the osmotic potential of ammonium sulphate were predicted using OLI Stream Analyzer software 9.1. Six different concentrations of DS were investigated: 0.5, 1, 1.5, 2, 2.5 and 3 M ammonium sulphate. Reagent grade $(NH_4)_2SO_4$ was used in this investigation and was supplied by Sigma-Aldrich, Australia.

Table 6.2 - Ammonium sulphate properties (OLI Systems, Inc., 2015)

Chemical Formula	$(NH_4)_2SO_4$
Molecular Weight	132.1 g/mol
Density	1.760 g/cm^3
pH at 2 M	5.46
π at 1 M (atm)	46.14
π at 2 M (atm)	92.1
Maximum Solubility	5.7 M (77g/100mL@25°C)
π at max solubility (atm)	274.8
Species formed in 2.0 M solution at 25 ◦C and 1.0 atm pressure	NH_4^+: 3.07 M, SO_4^{2-}: 1.07 M, $NH_4SO_4^-$:0.93M
Melting point	235 °C
Flash point	Non flammable

6.3.3 Feed Solution

Three different FS concentrations were selected for the experiments: 5 g/l, 10 g/l and 35 g/l NaCl. These concentrations were selected as the first two are representative of brackish groundwater and the last one represents seawater. Reagent grade NaCl was used in this investigation and was supplied by Sigma-Aldrich, Australia.

6.3.4 Experimental Plan

In addition to the 18 experiments outlined, six baseline (BL) experiments were run using 6 different concentrations of NaCl as DS and DI water as FS. NaCl was used in these experiments because it is highly soluble in water and its properties in solution are well-characterized.

The DS and FS were prepared by dissolving the salts in DI water with the help of magnetic stirrer at 200-300 rpm for at least 15 minutes to ensure that all salts were fully dissolved and uniformly mixed before starting the experiments.

When DI water was used as the FS, the RSF and SRSF were determined by measuring TDS using a TDS and EC meter (Hach HQ40D multi). However, when the FS consisted of saline water (NaCl), the draw solute concentration in the FS and feed solute concentration in the DS were measured using inductively coupled plasma-mass spectrometry (Spectroquant – Merck Millipore Nova 60). Analyzing the samples was a challenge, especially when high DS concentrations were used during the experiments because the concentrations of feed solutes were significantly lower in comparison to the DS. Each sample was analyzed using several dilution factors for accuracy purposes.

In addition, feed ions rejection was investigated being an important parameter in FO processes. In this study, the forward rejections of the feed solutes were measured by taking the DS sample at the end of each experiment and analyzing it for Na^+ and Cl^- ions. Equation 6.4 was used to calculate the feed ions salt rejection.

6.4 Results and Analysis

6.4.1 Water Flux

Figure 6.7 shows flux of baseline experiments where DI was used as FS and NaCl with different concentration as DS. As can be seen from Figure 6.7, as DS concentration increases, osmotic pressure increases and thus flux increases.

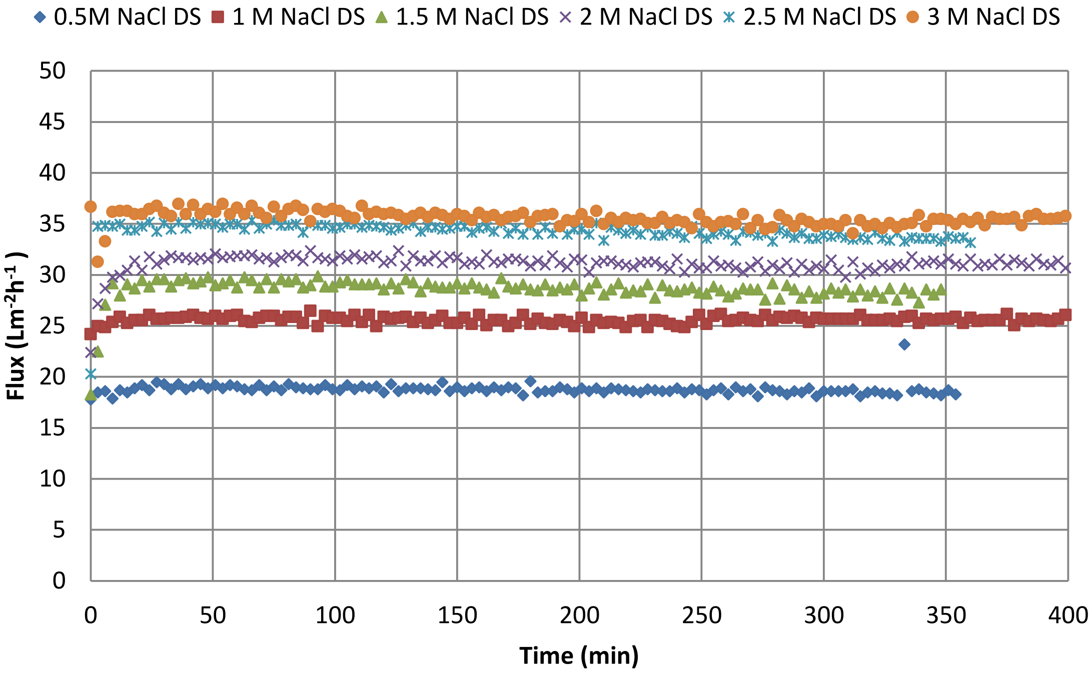

Figure 6.7 – Flux of baseline experiments (DI as FS and NaCl with different concentration as DS) (Nasr & Sewilam, 2016b)

Flux values obtained from Figure 6.7 are plotted versus Molarity of NaCl DS in Figure 6.8. It can be concluded that as concentration of the NaCl FS increases, the flux increases logarithmically. As CTA membranes have, historically, been the standard membrane material for FO, Figure 6.8 compares measured flux for each experiment to the results available from literature for CTA membrane under the same conditions (T. Cath et al., 2006; McCutcheon et al., 2006). TFC membranes perform better in terms of flux for same DS concentration, which is in agreement with previous studies (Gray et al., 2006; R. Wang et al., 2010; Yip et al., 2010; Zhao, Zou, Tang, et al., 2012). For both TFC and CTA membranes, flux and DS concentration can be correlated logarithmically. Despite further increase in DS concentration, water flux decreases gradually, which is due to increased severity of DICP effects that take place at high DS concentration (Gray et al., 2006; Zhao & Zou, 2011b). Importance of baseline experiments is that they report the flux in the absence of concentration polarization (as DI water is used as FS). After each experiment, baseline flux is re-checked to make sure that no scaling is taking place on the membrane material (Figure 6.9). In case flux curve after experiment did not converge with baseline flux, membrane sample is discarded and a fresh membrane sample is used.

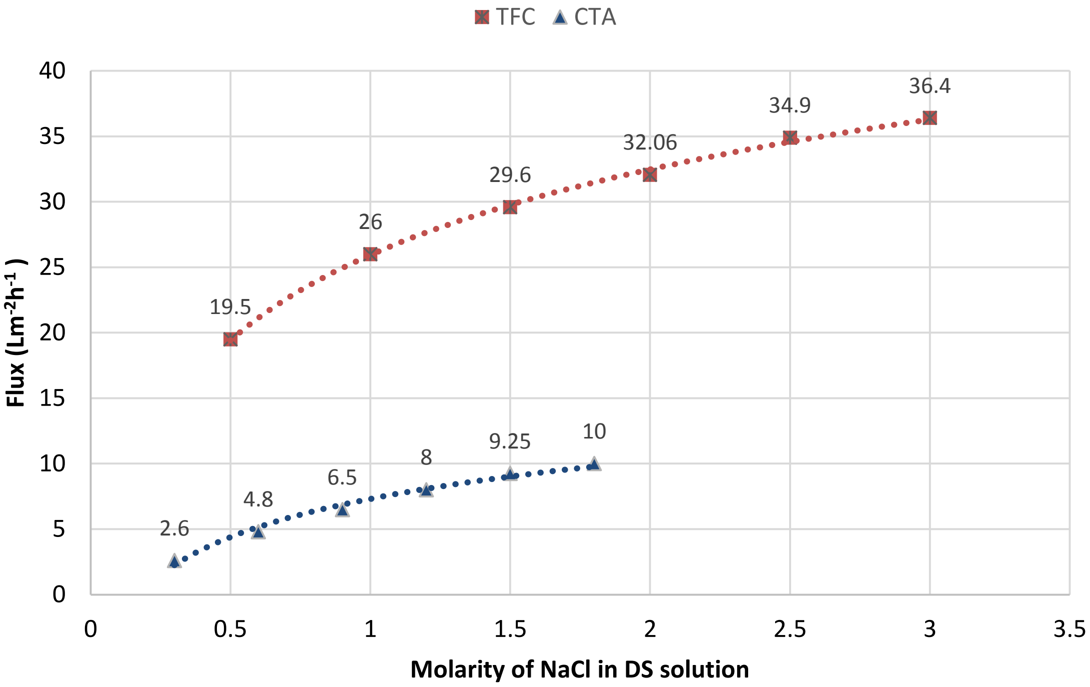

Figure 6.8 – Flux comparison of baseline experiments using NaCl as DS and DI water as FS (Nasr & Sewilam, 2016b). Membrane used is TFC membrane. CTA flux illustrated is from literature under the same conditions (T. Cath et al., 2006; McCutcheon et al., 2006)

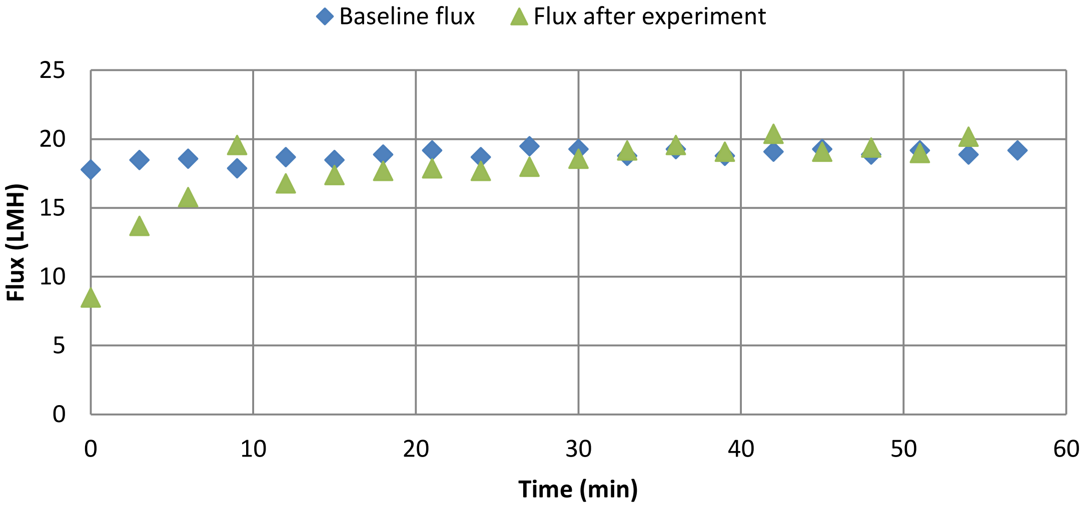

Figure 6.9 - Re-checking baseline flux. Convergence of the two flux curves indicates flux recovery and absence of signs of membrane scaling

In almost all experiments, flux stabilized after the passage of around 50 minutes. The water flux increased at higher molar concentrations of the $(NH_4)_2SO_4$ concentrations (Figure 6.10). The correlation between molar concentration and water fluxes was non-linear unlike osmotic pressure where the correlation with DS concentration was observed to be fairly linear. In fact, a logarithmic correlation was observed between DS concentration and the water flux and similar observation was reported in other studies (Hancock & Cath, 2009; Seppälä & Lampinen, 2004). This means that, although the water flux increased with the increase in DS concentrations, the increase in water flux at higher DS concentrations were not proportional to the increased osmotic pressure at some point almost flattening at high concentration. This flattening of the water flux at higher DS concentration is a result of the high severity of DICP effects at higher osmotic pressure. When the DS concentration is increased, the net osmotic pressure increases, generating higher water fluxes temporarily. Yet, the increased incoming water flux causes more DICP within the membrane support layer, thus keeping the overall gain in water poorer (Phuntsho et al., 2014). In addition, at higher DS concentrations, the water flux itself acts as a limiting factor and reduces the performance of the DS. An important implication of using highly concentrated DS is the increase of the pumping cost because of the increased specific weight and viscosity of the DS. The selection of the required pump is influenced by the fluid characteristics such as specific weight, viscosity, particulate content, and vapor pressure (Phuntsho, 2012).

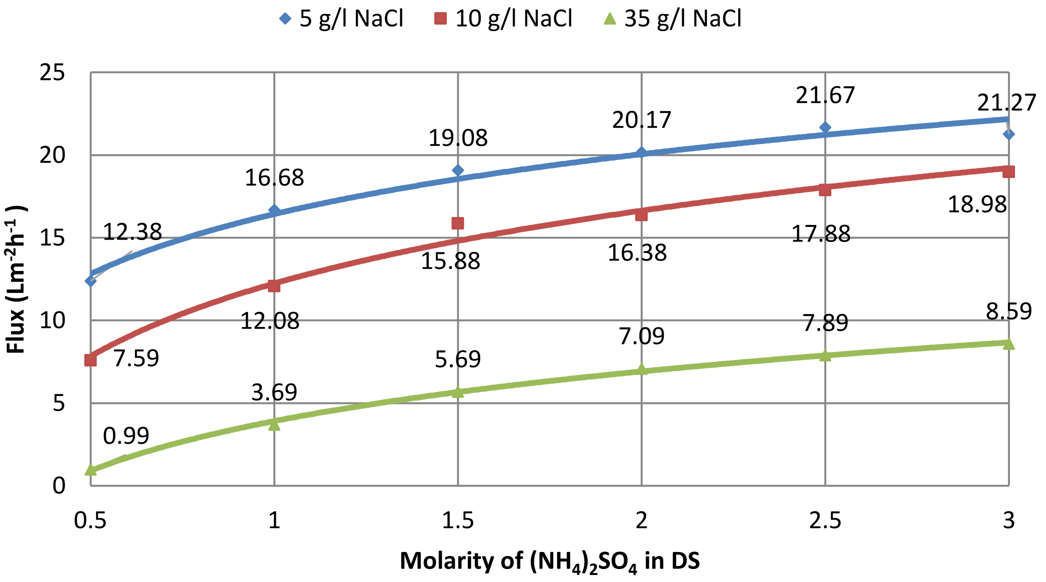

Figure 6.10 - Flux Comparison of 5, 10 and 35 g/l NaCl FS (Nasr & Sewilam, 2016b)

On the other hand, as the FS concentration increases from 5 g/l to 35 g/l the flux decreased significantly (Figure 6.10). For example, for 2.5 M $(NH_4)_2SO_4$ DS, flux decreased from 21.67 $Lm^{-2}h^{-1}$ for 5 g/l NaCl FS to 7.89 $Lm^{-2}h^{-1}$ for 35 g/l NaCl FS. The reason for this decrease is the drop in the differential bulk osmotic pressure caused by increasing FS concentration and keeping DS concentration constant.

6.4.2 Reverse Permeation

Equation 6.3 was used to calculate the SRSF values for NH_4^+ and SO_4^{2-} ions. Results can be summarized in Figure 6.11 below. It must be noted that a lower SRSF value indicates higher membrane selectivity and a developed FO process. The general trend of the readings indicate that at high water flux (more than 10 $Lm^{-2}h^{-1}$), SRSF value of NH_4^+ and SO_4^{2-} ions ranges between 0 and 2 g/l. On the other hand, at low flux (less than 10 $Lm^{-2}h^{-1}$), SRSF for both ions seems to be significantly high indicating a high reverse permeation of draw solutes. There is a high dispersion of data points in the area of low flux (less than 10 $Lm^{-2}h^{-1}$). As there should be a constant molar ratio between the two ions, it is probable that there is an ion exchange occurring due to different mobilities, which may cause an additional driving force of the Donnan potential across the membrane (J. E. Kim, Phuntsho, Lotfi, & Shon, 2015; Chien Hsiang Tan & Ng, 2008).

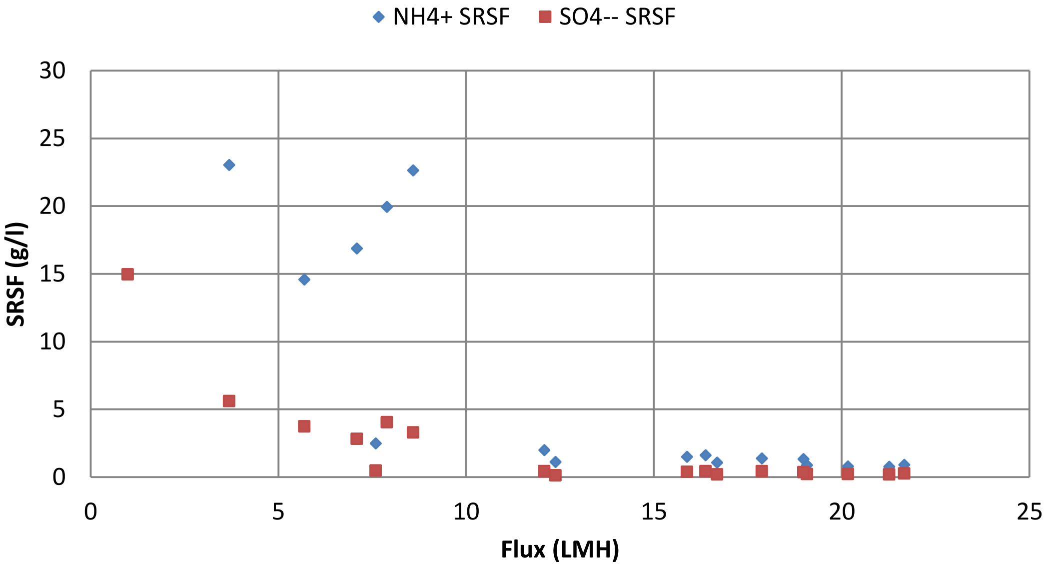

Figure 6.11 - NH4$^+$ and SO$_4^{2-}$ SRSF vs. flux (Nasr & Sewilam, 2016b)

Another way of presenting the result is shown in Figure 6.12 and Figure 6.13, showing SRSF as a function of DS concentration. It can be concluded that SRSF is almost constant irrespective of DS concentration. This is in agreement with a previous study done by Phillip et al. (2010), which proved that the SRSF is independent of not only the bulk draw solution concentration, but also of membrane structural parameter (S). The reason behind this phenomenon is that a high concentration of draw solute at the support/active layer interface is necessary to generate a large osmotic gradient, causing a high water flux. However, this higher concentration of draw solute also amplifies the concentration gradient across the active layer, which in turn increases the reverse salt flux (Phillip et al., 2010). For an ideal solution, the osmotic gradient is proportional to the concentration gradient, and, therefore, the ratio of the two quantities remains constant.

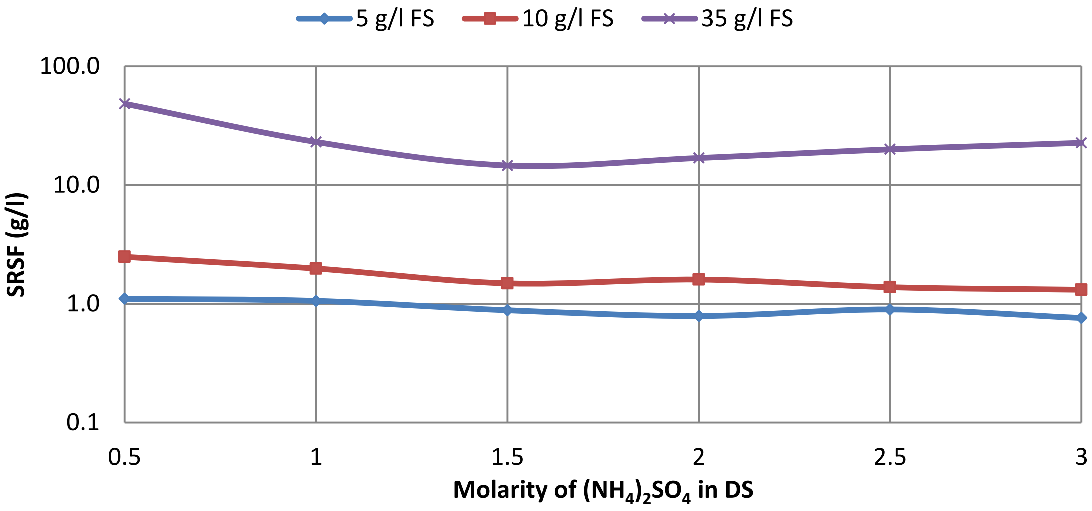

Figure 6.12 - NH_4^+ SRSF for different FS concentration (Nasr & Sewilam, 2016b)

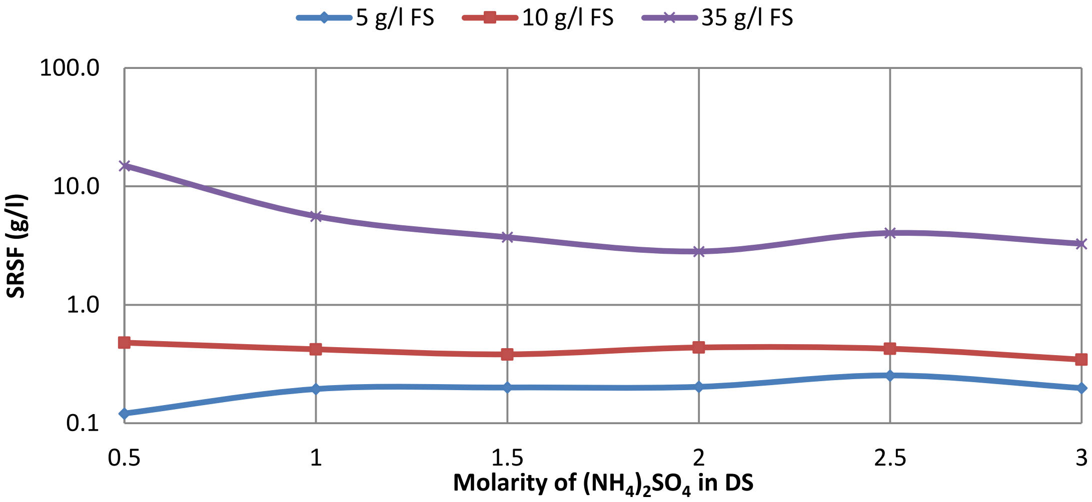

Figure 6.13 - SO_4^{2-} SRSF for different FS concentration (Nasr & Sewilam, 2016b)

From these illustrations, it is possible also to conclude the effect of FS concentration on the SRSF. As FS concentration increases from 5 to 35 g/l, SRSF increases. This could be justified by the relation between SRSF and the flux (Figure 6.11). For the same draw solution concentration, the lower the flux, the higher the SRSF and vice versa. By comparing Figure 6.10 to Figure 6.12 this relation is clear. For a DS concentration of 2 moles $(NH_4)_2SO_4$, flux for 35 g/l NaCl FS is 7.09 $Lm^{-2}h^{-1}$ and the NH_4^+ SRSF is 16.86 g/l. For the same DS concentration of 2 moles

$(NH_4)_2SO_4$, flux for 5 g/l NaCl FS is 30.17 $Lm^{-2}h^{-1}$ and the NH_4^+ SRSF is 0.79 g/l. In other words, as FS concentration decreased 85.7%, SRSF increased 95.7%.

6.4.3 Feed Ions Rejection

Equation 6.4 was used to calculate FS ions (Na^+ and Cl^-) rejection in this investigation. As can be seen from Figure 6.14, the membrane exhibited high rejection of FS ions for almost all DS concentrations except when operated at low DS concentration (0.5 M DS $(NH_4)_2SO_4$) and high FS concentration (35 g/l NaCl). Using a relatively low concentration of DS with a high FS concentration significantly decreases $\Delta\pi_{eff}$, which is the effective driving force in the FO process (Figure 6.6), so a poor rejection is expected.

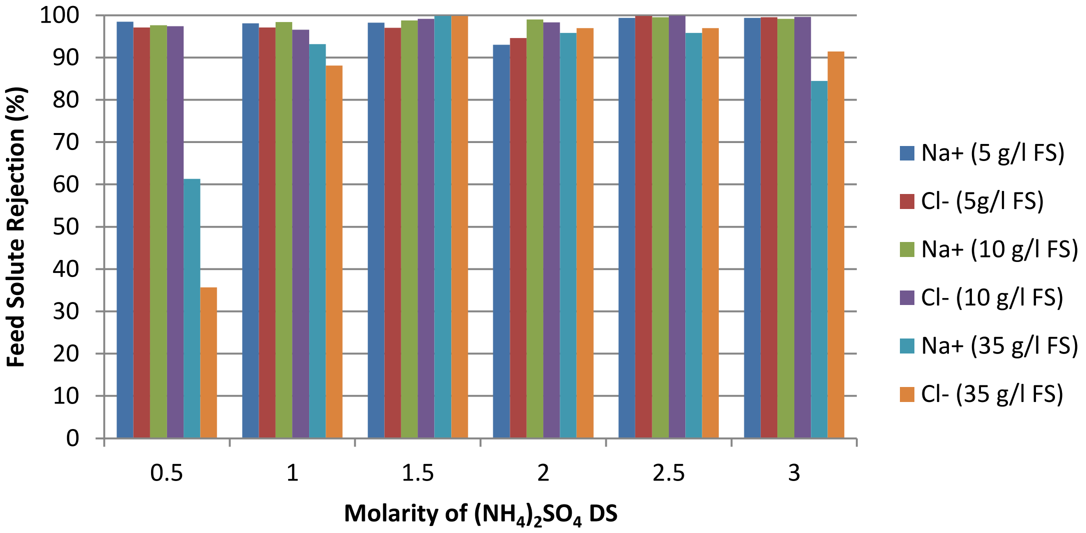

Figure 6.14 - Forward rejection of FS ions operated at different DS concentrations (Nasr & Sewilam, 2016b)

6.5 Conclusion

This study investigated the performance of Ammonium sulphate as a draw solution in a typical FDFO process. Although FDFO process cannot be a standalone process as the final nutrient concentration in the DS is usually higher than needed, an in-depth understanding of the efficiency of draw solutions is critical to the effective development of FDFO. Performance has been assessed by determining the water flux, reverse permeation of draw solute from the DS into the FS (SRSF) and the forward rejections of the feed solutes. It is concluded that flux and ammonium sulphate concentration can be correlated logarithmically. Further increase in ammonium sulphate concentration decreases water flux gradually due to increased severity of DICP effects that take place at high DS concentration. As the FS concentration increases, the flux decreased significantly due to the significant drop in the differential bulk osmotic pressures of the DS and FS.

As flux increases, SRSF for NH_4^+ and SO_4^{2-} ions drop, which is a favorable condition. SRSF values at flux less than 10 $Lm^{-2}h^{-1}$ is significantly higher than that for flux more than 10 $Lm^{-2}h^{-1}$. As a result, it is recommended to operate the process at a flux higher than 10 $Lm^{-2}h^{-1}$ to avoid loss of draw solute by reverse solute permeation.

SRSF is almost constant irrespective of ammonium sulphate concentration. As FS concentration increases from 5 to 35 g/l, SRSF increases which could be explained by the relation between SRSF and the flux. For the same DS concentration, the lower the flux, the higher the SRSF and vice versa.

TFC membrane used in this study exhibited high rejection of FS ions for almost all DS concentrations except when operated at low ammonium sulphate concentration and high FS concentration.

In conclusion, the system studied showed that ammonium sulphate is an efficient DS for FDFO process using TFC membrane when run at flux more than 10 $Lm^{-2}h^{-1}$ exhibiting high osmotic pressure, low reverse solute permeation and high rejection of feed solute.

CHAPTER 7 – GROUNDWATER DESALINATION FOR IRRIGATION IN EGYPT BY FERTILIZER DRAWN FORWARD OSMOSIS USING AMMONIUM SULPHATE DRAW SOLUTION

7.1 Introduction

Chapter 6 investigated Ammonium Sulphate as a draw solution for FDFO application. This chapter further investigates the draw solution performance using a real brackish Egyptian groundwater sample as feed solution. It must be noted that, this study was conducted at the American University in Cairo, Egypt. Three FO membrane samples were assessed in this study and the best membrane was selected for further testing. The setup used for this investigation is slightly different from that used in the previous chapter. The outcome of this chapter is a publication entitled "Investigating Fertilizer Drawn Forward Osmosis Process for Groundwater Desalination for Irrigation in Egypt".

7.2 Materials and Methods

Again, the experimental investigations in this work were performed using a bench-scale crossflow filtration unit (Figure 7.1 and Figure 7.2). The FO unit consists of a circular FO cell with diameter equal to 40 mm and an effective membrane area of 1.257×10^{-3} m^2 (Figure 7.3). Both the feed loop and the draw loop follow the same water path, as per Figure 7.4. Circular rubber gaskets were used to hold the membrane in place and to give enough depth in each flow channel.

Experiments in this investigation were run at a crossflow rate of 0.22 l/min, which is equal to a crossflow velocity of 12.9 cm/s[3]. The flows were operated in counter-current setting directions using a double headed peristaltic pump (Stenner, model 170DMP5, 25 psi, 1.7 bar, 50 Hz, USA). The temperature both solutions was fixed at 25°C using a temperature water bath and a heater/chiller (Polyscience temperature controller, model 9106A12E)[4].The changes in the DS and FS volumes were recorded in real-time by connecting the DS and FS to digital mass scales which are plugged to a desktop computer for data logging every three minutes. Water flux was estimated from the difference in DS and FS volume, where both fluxes are averaged for accuracy reasons. To consider mass balance, if (ΔFS-ΔDS) exceeded 5 g/d or if noticeable leakage is observed, the experiment is disregarded and repeated. The water flux was calculated from Equation 6.5, previously presented.

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[3] The flowrate of the pump used is not variable.

[4] The same temperature was chosen like the previous investigation done in Chapter 6.

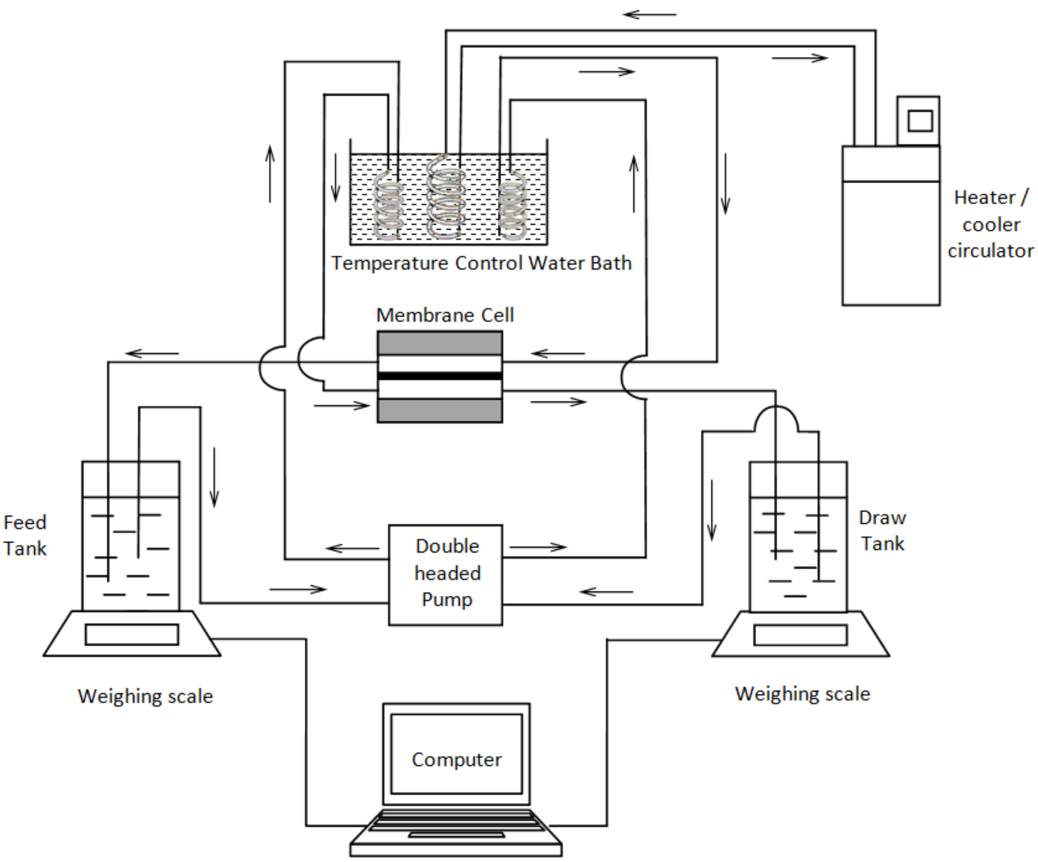

Figure 7.1 - Schematic of setup used (Nasr & Sewilam, 2016a)

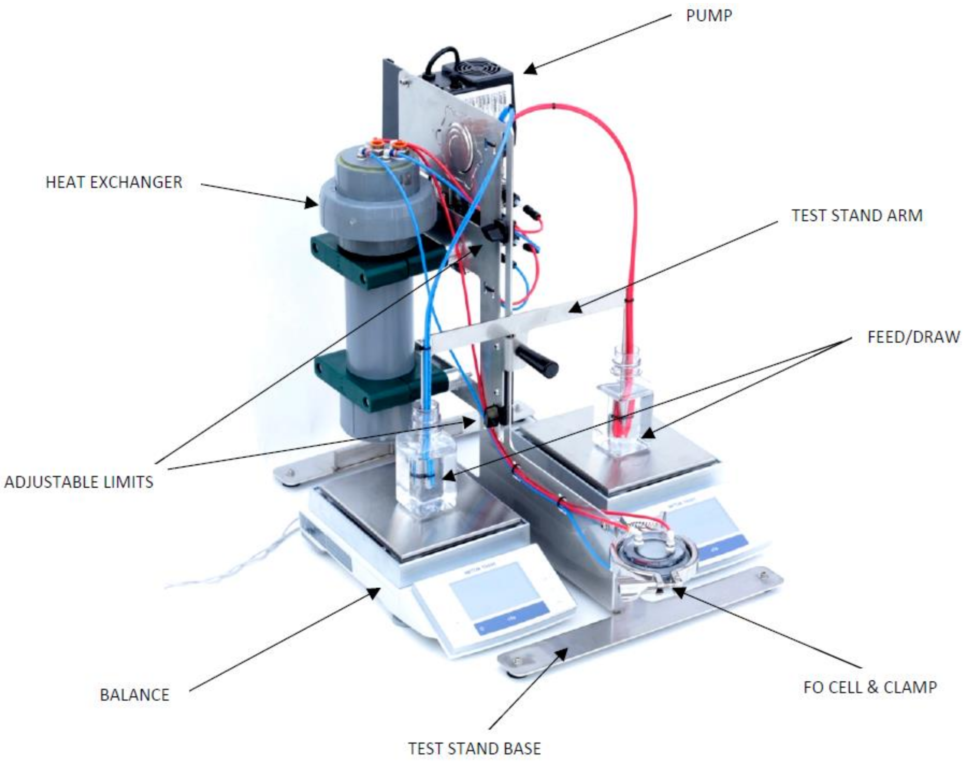

Figure 7.2 - Experimental Setup (Porifera Inc., 2015)

Figure 7.3 - Circular FO cell with an effective membrane area of 1.257 x 10^{-3} m^2

The initial volume of both the DS and FS (V_i) was 2.0 L each. The solutions after passing by the membrane were directed back to their corresponding tanks (Figure 7.2 and Figure 7.4), which led to the continuous dilution of the DS and a continuous increase in the concentration of the FS. This resulted in a continuous decrease in water flux with time due to decline in effective osmotic pressure. However, the water flux was decided from the point at which a stable flux was observed from the plot of flux versus time, which usually happened after around 60 minutes of experiment initiation. All the experiments were run for duration of 24 hours to allow for sufficient diffusion of draw solutes. Both the FS and DS containers were tightly covered using parafilm to avoid evaporation losses during the experiment.

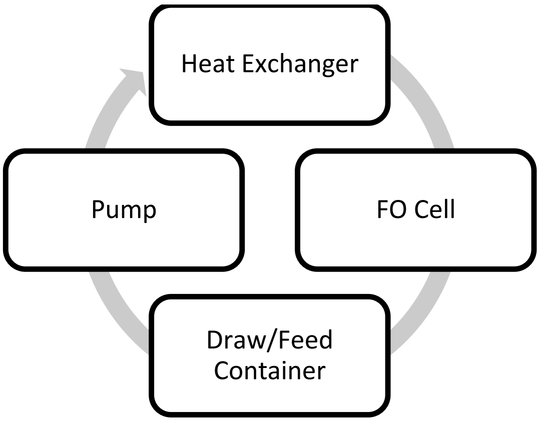

Figure 7.4 -Water flow path through the testing system (Adapted from Porifera Inc., 2015)

7.2.1 Forward Osmosis Membranes

Three different membrane samples were tested using the above described setup. The three membranes tested were:

- CTA from Hydration Technology Innovations (HTI),
- TFC from Woongjin Chemicals, Korea
- Porifera's commercial FO membrane

Table 7.1 summarizes the different membrane properties. SEM images of the first two FO membranes are presented in Figure 7.5. Yet, Porifera had some concerns with respect to publication of its membrane SEM images being proprietary. SEM images of the CTA membrane shown in Figure 7.5 (a) indicate that CTA structure is different from any typical RO membrane. While a typical RO membrane possesses a thin active layer with a thick support layer, CTA membrane has a nested polyester network which gives mechanical support to the membrane. Figure 7.5 (b) shows the TFC membrane structure which comprises a selective active layer over a polysulfone support layer manufactured by phase separation over a fine polyester nonwoven fabric (Yip et al., 2010).

The three membranes were tested for baseline flux using NaCl as DS and DI water as feed. The membrane that exhibited the highest water flux in baseline experiments was selected for the next set of experiments (using the real groundwater as FS). The membrane orientation in this study was FO mode, where FS faces the active layer and the DS faces the porous support layer.

Table 7.1- Membrane properties – as provided by manufacturer and from literature (Yip et al., 2010)

	CTA	**TFC**	**Porifera**
Manufacturer	Hydration Technology Innovations (HTI), Inc.	Woongjin Chemicals, Korea	Porifera Inc.
Model	Cartridge	Hand Casted	Roll-to-roll
Pure Water Permeability Coefficient, A ($Lm^{-2}h^{-1}bar^{-1}$)	1.02±0.03	5.25±0.51	2.2±0.01
Salt permeability coefficient of active layer, B (m/s)	$9.8 * 10^{-7}$	N/A	$1.6 * 10^{-7}$
Total membrane thickness (μm)	93±3	147±16	70±10
Structural Parameter, S (μm)	595±114	N/A	215 ± 30
Material of active layer	Cellulose tri acetate	Polyamide (PA)	Polyamide (PA)
Material of support layer	Polyester mesh embedded	TFC polysulfone	Porous Hydrophilic Polymer

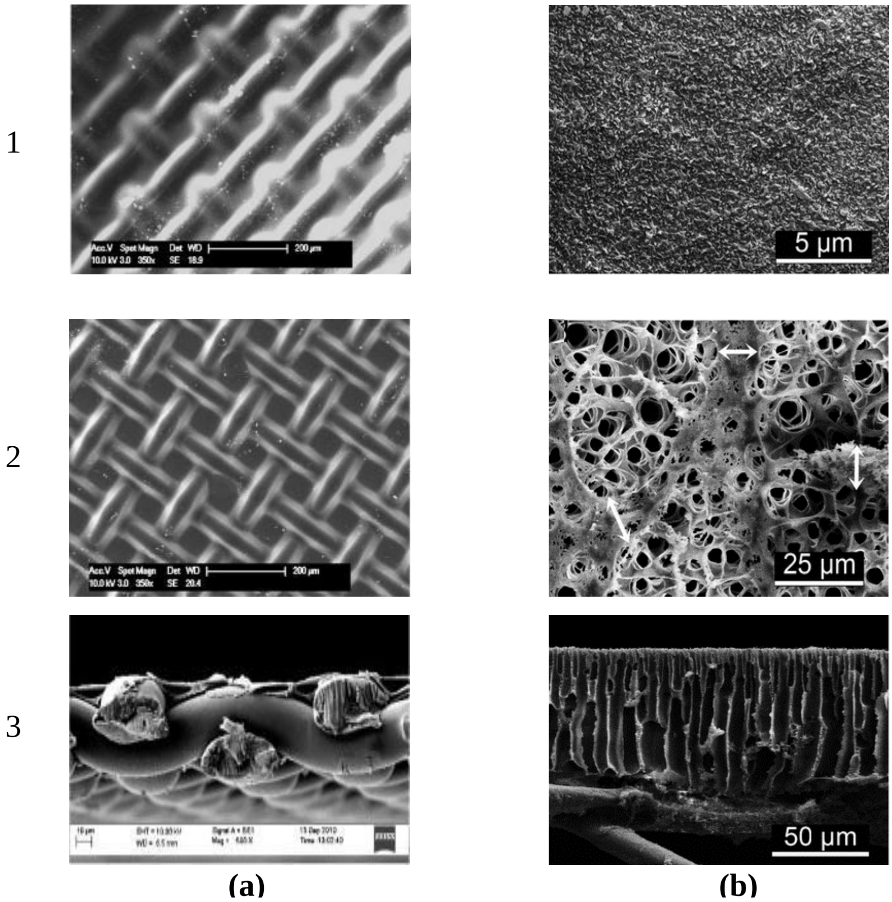

Figure 7.5 - Comparative SEM images of the membranes used (a) CTA, HTI (1: top surface of active layer, 2: bottom surface of support layer, 3: cross section showing woven fabric (Qiu, Setiawan, Wang, Tang, & Fane, 2012; Zhao & Zou, 2011a) (b) TFC, Woongjin (1: top surface of active layer, 2: bottom surface of support layer, 3: cross section) (Yip, Tiraferri, Phillip, Schiffman, & Elimelech, 2010)

7.2.2 Draw solution

An aqueous solution containing ammonium sulphate was chosen as the DS for this investigation. Reason of this selection is elaborated in Chapter 5, which concluded that the selected fertilizer generates osmotic pressure that is much higher than seawater or brackish groundwater, indicating its suitability for use as an osmotic DS (Figure 5.6) (Qiu, Setiawan, Wang, Tang, & Fane, 2012; Zhao & Zou, 2011a).

7.2.3 Feed Solution

A real Egyptian Brackish Groundwater sample was selected for the experiments. Location of the well from which the sample was collected is El Tor, capital of South Sinai (Figure 7.6). Nasr & Sewilam (2015b) state that Sinai is a promising area for FDFO application due to high irrigation water demand, availability of arable lands and ease of brine disposal. Sample was extracted from a deep well at a 150 m depth. Most likely, the extracted water has been obtained from the Nubian Sandstone Aquifer or the Fissured Carbonate Aquifer, both of which have huge exploitable volumes (Abo Soliman & Halim, 2012; M. N. Allam & Allam, 2007; Nashed et al., 2014) emphasizing the sustainability of groundwater in the area.

The groundwater sample is categorized as brackish, as its TDS fall in the range of 1-10 g/l (Figure 2.14) (Freeze & Cherry, 1979; Weert et al., 2009). The sample was pre-treated using ultra-filtration to remove unneeded suspended solids that might damage the FO membrane fabric. The GW sample properties, past ultra-filtration and prior FO process, are presented in Table 7.2. The sample's EC, TDS and SAR are 7.32 mS/cm, 3.66 g/l and 33.9 respectively, classifying it as water that is unsuitable for irrigation (Figure 2.19) and with a remarkably high Sodium Hazard (Fipps, 2003). A water of such quality and high SAR value, if used without proper treatment will lead to sodium toxicity and deterioration of soil structure, which will eventually accelerate soil degradation as well as reduce crop yield (Grattan, 2002).

Table 7.2 - Raw GW sample characteristic (past ultrafiltration) in El Tor, South Sinai (Nasr & Sewilam, 2016a)

Ion	Concentration
Na^+	669.99 mg/l
Cl^-	1041.25 mg/l
NH_4^+	2.1 mg/l
SO_4^{2-}	2224.8 mg/l
Ca^{2+}	564.8 mg/l
Mg^{2+}	215.4 mg/l
K^+	41.73 mg/l
Fe^{3+}	0.036 mg/l
Mn^{2+}	0.016 mg/l
NO_3^-	29.75 mg/l
HCO_3^-	17.08 mg/l
CO_3^{2-}	0 mg/l
EC	7.32 mS/cm
TDS	3.66 g/l
pH	6.5

Figure 7.6 - El Tor, South Sinai, location of extraction well (Google, 2015)

7.2.4 Experimental Plan

Six baseline experiments (BL) were run using different concentrations of NaCl as DS and DI water as FS for each membrane sample. Based on that, the membrane that performed best in terms of flux was selected for further experimentation using ammonium sulphate. Six different concentrations of ammonium sulphate DS were investigated: 0.5, 1, 1.5, 2, 2.5 and 3 M.

The DS was prepared by diluting the salts in distilled water using a magnetic stirrer (Lab Companion, HP-2000) at 250 rpm for at least 15 minutes to ensure that the salt was fully dissolved and consistently mixed. Reagent grade NaCl and $(NH_4)_2SO_4$ were used in this investigation and were supplied by Biostain Ready Reagents, UK.

Like previous experimental investigation carried out in chapter 6, when DI water was used as the FS in the baseline experiments, the RSF and SRSF were determined by measuring TDS using a portable TDS and EC meter (Hach, model 44600 Conductivity / TDS meter). When the FS was GW sample, the draw solute concentration in the FS and feed solute concentration in the DS were determined by inductively coupled spectrometry (Ultima 2 – Jobin Yvon). The concentrations of feed solutes were significantly lower in comparison to that of the DS. Each sample was analyzed a number of times to get reliable results.

Finally, feed ion rejection was measured being an important parameter in FO processes. The forward rejection of the feed solutes was investigated by collecting a DS sample at the end of each experiment and analyzing it for Na^+ and Cl^- ions. Equation 6.4 was used to calculate Na^+ and Cl^- ions Rejection.

7.3 Results and Analysis

7.3.1 Water Flux

Equation 6.5 was used to calculate water flux. Figure 7.7 compares the baseline water flux for the three membranes tested. For these three types, flux and DS concentration can be associated logarithmically, with a correlation coefficient more than 98% indicating goodness of fit.

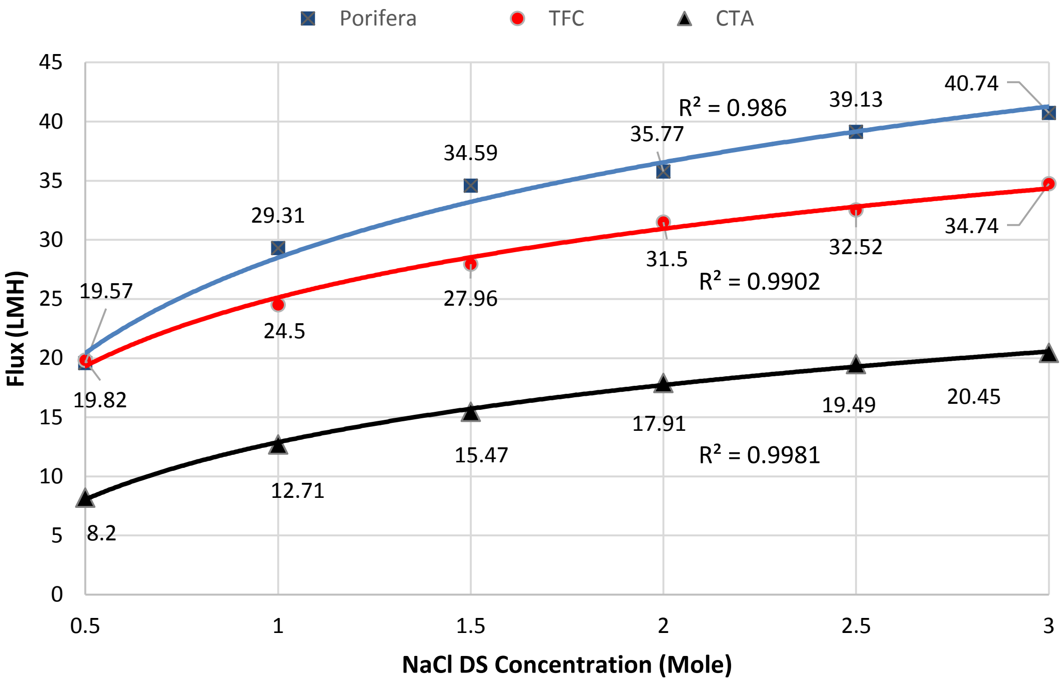

Figure 7.7 - Baseline water Flux comparison for three different types of FO membranes using NaCl as DS and DI as FS (Nasr & Sewilam, 2016a)

Porifera membrane exhibited the highest flux at the same DS concentration compared to other TFC and CTA membrane. For example, at 1 M NaCl DS concentration, Porifera membrane reported 57% and 16% higher flux than that of CTA and TFC membranes respectively. Thus, Porifera membrane proved to perform better in terms of flux. Although Porifera's membrane possesses a moderate Pure Water Permeability Coefficient (A) in comparison to the other two membranes (Table 7.1), its significantly small structural parameter (S) lead to the highest flux. In spite of further increase in DS concentration, rate of water flux increase decreases gradually. The incremental increase in J_w for Porifera membrane for a 0.5 M increase in NaCl DS concentration (projected by the logarithmic correlation) is 8.1, 4.7, 3.3, 2.6 and 2.1 L.m^{-2}h^{-1} respectively.

After each experiment, baseline flux is re-checked to make sure that no scaling took place on the membrane surface, which would affect the following experiment. Figure 7.8 shows flux of baseline experiments for Porifera membrane where DI was used as FS and NaCl with different concentration as DS. As can be seen from Figure 7.8, as DS concentration increases, osmotic pressure increases and thus flux increases.

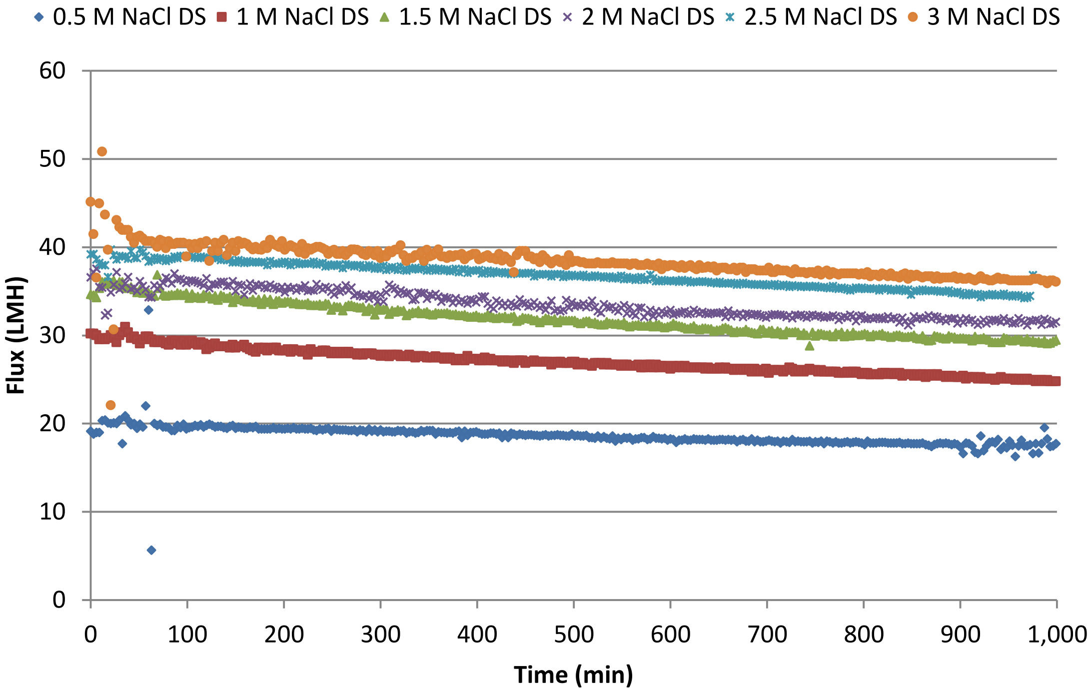

Figure 7.8 - Baseline flux using Porifera membrane (DI as FS and NaCl with different concentration as DS) (Nasr & Sewilam, 2016a)

When $(NH_4)_2SO_4$ was used as the DS, pure water flux increased as molar concentrations of the DS increased. The correlation between DS molar concentration and pure water fluxes was not linear, unlike osmotic pressure where the correlation with DS concentration is somewhat linear up 5.5 M $(NH_4)_2SO_4$ (Figure 5.6). Actually, a logarithmic correlation was inferred between DS concentration and the water flux (Figure 7.9). Other studies reported similar observation (Hancock & Cath, 2009; Seppälä & Lampinen, 2004). The increase in water flux at higher DS concentrations was not proportional to the increased osmotic pressure. Like previously explained in chapter 6, the flattening of the water flux at higher DS concentration is a result of severe DICP effects at high osmotic pressure, as reported in previous studies (Achilli et al., 2010; Lay et al., 2010; McCutcheon et al., 2006; Chien Hsiang Tan & Ng, 2008). While increasing the molar concentration of $(NH_4)_2SO_4$ from 0.5 to 1 M increased water flux by 36%, increasing the molar concentration of $(NH_4)_2SO_4$ from 2.5 to 3 M increased water flux by only 2.2%.

The experimental flux obtained from this study is compared to flux reported from TFC membrane provided by Woongjin (Korea) using same DS and FS. Results are presented in Figure 7.9. Porifera membrane exhibited higher pure flux than that of

Woongjin (Korea) membrane. The difference in flux was clear at higher DS concentration, indicating the severity of DICP at higher osmotic pressure, as discussed previously.

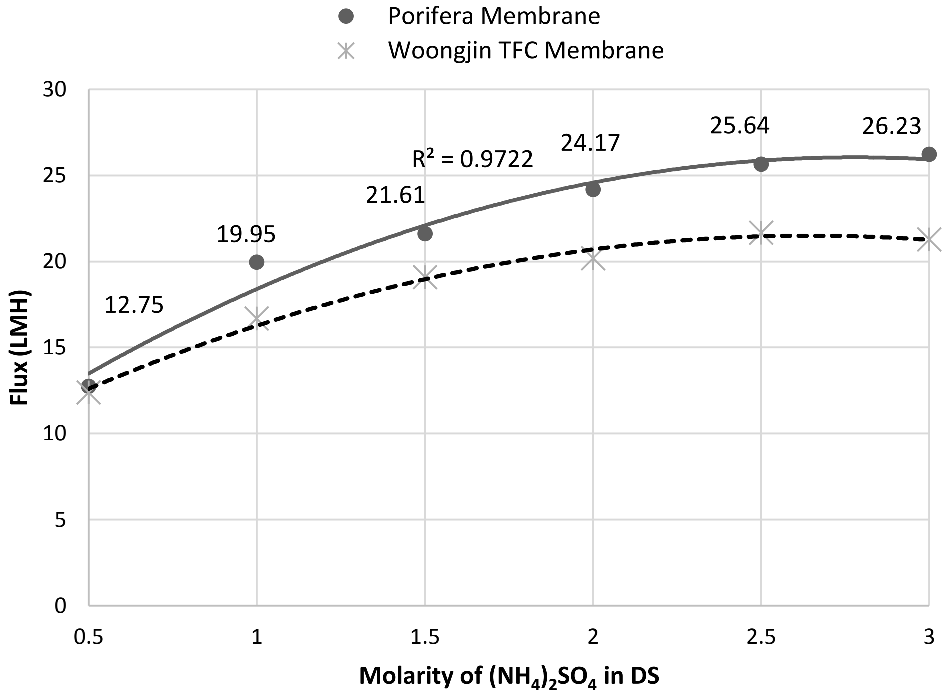

Figure 7.9 – Comparison of pure water flux for $(NH_4)_2SO_4$ DS at different concentrations using different membranes. The solid line indicates flux from Porifera membrane and the dotted line indicates flux from Woongjin TFC membrane (Nasr & Sewilam, 2016a)

7.3.2 Reverse Permeation

SRSF was calculated using Equation 6.3. SRSF results can be summarized in Figure 7.10 below. The general trend of the readings indicates that for all the experiments SRSF was noted to be a small value, which implies high membrane selectivity. All SRSF values ranged between 0 and 0.18 g/l. In comparison, a previous study reports that reverse permeation of urea may reach up to 29.2 g/l (Phuntsho, Shon, Majeed, et al., 2012).

The SRSF value for NH_4^+ ion was noted to be slightly higher than that of SO_4^{2-} ion, especially at flux more than 20 $Lm^{-2}h^{-1}$, which is in agreement with previous investigations (Nasr & Sewilam, 2016b). This phenomenon could probably be justified thermodynamically by factors related to ion exchange mechanism and speciation. While NH_4^+ ion in DS is attracted to the Cl^- ion in FS, SO_4^{2-} ions of DS is attracted to the Na^+ ions of FS. Depending on pH, NH_4^+ ion is in equilibrium with NH_3. As NH_4^+ ion is positively charged, it will have good rejection and high membrane selectivity. Yet, as NH_3 is not charged, it will be poorly rejected. Hence, the measured SRSF of NH_4^+ ion can be artificially high because of the permeation of NH_3.

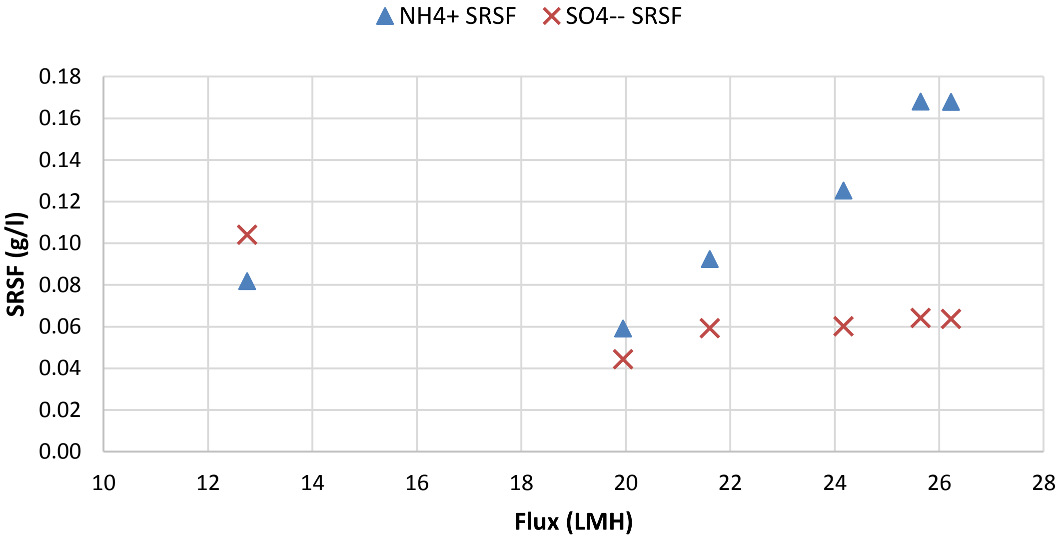

Figure 7.10 - NH4$^+$ and SO_4^{2-} SRSF vs. flux (Nasr & Sewilam, 2016a)

Figure 7.11 shows SRSF as a function of DS concentration. It can be deduced that SRSF is more or less constant regardless of DS concentration, which is in agreement with results from previous chapter. Phillip et al. (2010) supports the illustrated result and confirms that the SRSF is independent bulk draw solution concentration.

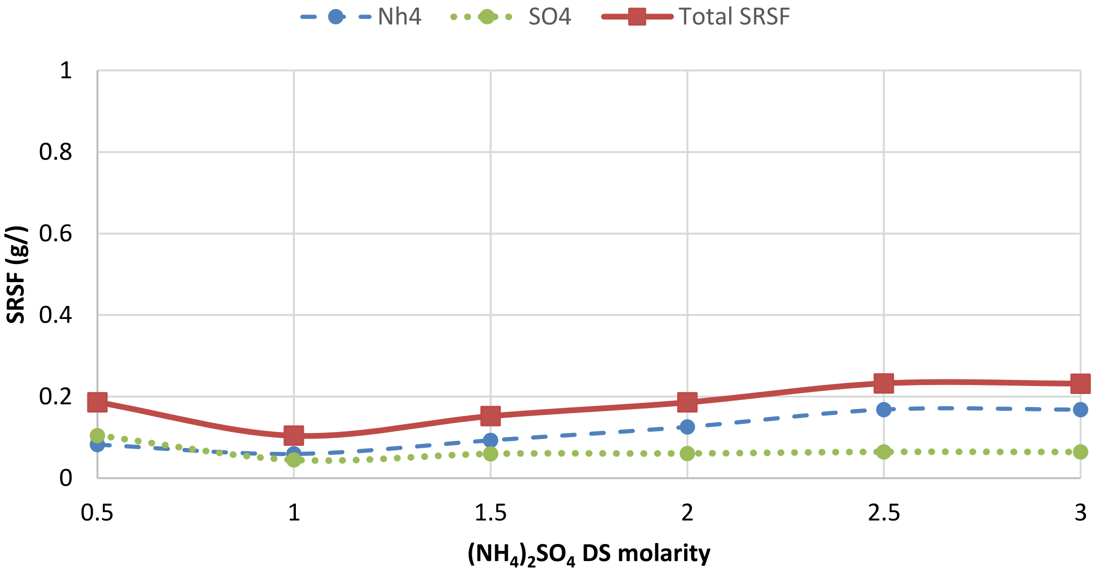

Figure 7.11 - NH_4^+ and SO_4^{2-} SRSF vs. $(NH_4)_2SO_4$ DS molarity (Nasr & Sewilam, 2016a)

7.3.3 Feed Ions Rejection

Equation 6.4 was used to calculate Na^+ and Cl^- ions rejection in this investigation. Feed solutes rejection is illustrated in Figure 7.12. While rejection values of Na^+ ion ranged between 76 and 99%, that of Cl^- ion ranged between 72 and 25%. Typically, rejection increases with the increase in the driving force, which is in direct relation to the molar concentration of the DS. This proved to be true for Na^+ ion but not for Cl^- ion, a phenomenon which required further investigation.

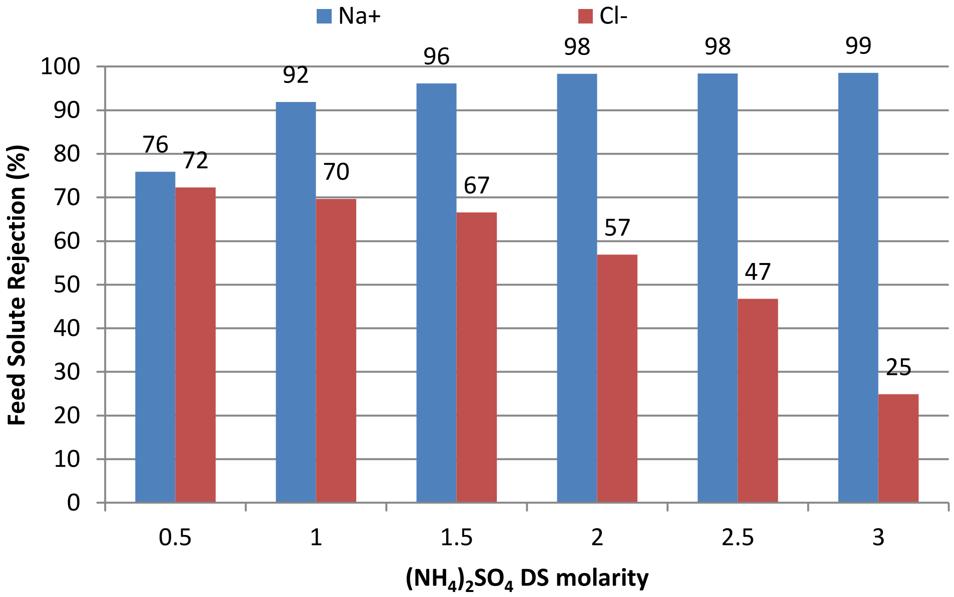

Figure 7.12 - Forward rejection of Na^+ and Cl^- ions at different DS concentrations (Nasr & Sewilam, 2016a)

As can be discoverable from Figure 7.12, the membrane exhibited higher Na^+ ion rejection than for Cl^-, especially at high DS concentrations. Increasing DS concentration lead to increasing Na^+ ion rejection but at the same time lead to decreasing Cl^- ion rejection. This phenomenon could be probably attributed to the membrane surface charge. Originally, this membrane type possesses a negatively charged surface. As DS molarity increases (from 0.5 to 3 M), pH decreases, rendering the solution more acidic. The H^+ ion fully consumes the negative charge on the membrane surface and the surplus H^+ ion leaves the membrane surface positively charged. Thus, it seems that the membrane surface charge reverses from being originally negative to positive, repelling Na^+ ion and attracting Cl^- ion, so more Cl^- ion leave the FS and reaches the DS than does the Na^+ ion.

7.4 Conclusion

This study investigated the performance of Ammonium sulphate as a draw solution in a typical FDFO process to be possibly used to desalinate Egyptian groundwater for irrigation purposes. Three FO membranes were tested for maximum baseline flux. Best membrane was used to desalinate a real brackish groundwater sample using Ammonium sulphate as a draw solution, being a commercial, inexpensive and efficient Egyptian fertilizer. Performance has been assessed by determining the water flux, reverse permeation of draw solutes and the forward rejections of the feed ions.

Porifera's commercial FO membrane proved to be the best membrane with respect to baseline flux due to its small structural parameter (S) in comparison to other tested membranes. It was chosen for further experimentation. Water flux and ammonium sulphate concentration can be associated logarithmically. Additional increase in ammonium sulphate concentration reduces water flux gradually due to increased severity of DICP that occurs at high DS concentration.

SRSF values did not exceed 0.18 g/l for both NH_4^+ and SO_4^{2-} ions, indicating high membrane selectivity. At flux exceeding 20 $Lm^{-2}h^{-1}$, NH_4^+ ion reported higher SRSF values than that of SO_4^{2-} ion. SRSF is almost constant regardless of ammonium sulphate concentration.

While increasing DS concentration lead to increasing Na^+ ion rejection, it caused a significant decline in Cl^- ion rejection. This phenomenon could be probably associated to an ion exchange mechanism and membrane surface charge.

In conclusion, the scheme investigated showed that ammonium sulphate is a competent DS for FDFO application using Porifera's commercial FO membrane demonstrating high osmotic pressure, moderate reverse solute permeation and remarkable rejection of feed solute.

CHAPTER 8 – CONCLUSION AND RECOMMENDATIONS

8.1 Conclusions

The world is facing a water crisis and Egypt is no exception. Agriculture is the prime user of water in Egypt, consuming more than 80% of fresh water available. Although Egypt is a rich-groundwater country, the resource is not efficiently utilized due to poor water quality and high salinity. If a low-cost desalination technology is viable, massive scale desalination for irrigation may possibly be a reality. The effect of such technology on the agricultural sector in Egypt is expected to be outstanding.

Forward Osmosis technology is one of the promising and convenient desalination technologies. Unlike RO, FO desalination is based on the notion of natural osmotic pressure driven by difference in concentration rather than hydraulic pressure. Thus, desalination can be achieved using significantly low energy. FO desalination process is realized when a concentrated DS, generating elevated osmotic pressure, runs through a semi-permeable FO membrane while a FS with a lower osmotic pressure runs on the other side of the membrane. Natural diffusion forces fresh water to leave the FS and to enter the DS, diluting the latter and concentrating the former. The diluted DS is subsequently treated to remove draw solutes to utilize the pure water. One creative application of FO process is fertilizer drawn forward osmosis (FDFO). This application offers uniqueness as separating and recovering of draw solutes is not essential since the draw solutes add value to produced water.

The leverage of FDFO desalination over any other FO application is that when a fertilizer is used as a DS, produced water can be directly applied for fertigation because fertilizers are beneficial for the plants and thus are needed anyway. Yet, FDFO desalination has some limitations that should be considered. Revolutionary draw solutions and efficient FO membranes are getting the attention of most FO water researchers nowadays. In addition, a significant limitation is the high nutrient content in product water, thus meeting irrigation water quality standards becomes a challenge.

Applying FDFO technology in Egypt for augmenting irrigation water by using available brackish groundwater is suggested in this work. As Egypt is a groundwater-rich country, application of FDFO desalination technology would lead to revolutionary platform where brackish groundwater can be efficiently utilized to produce precious nutrient-rich irrigation water. A selection criterion has been outlined to help suggest potential locations for FDFO application maximizing its returns. After investigating Egyptian irrigation schemes and mapping groundwater aquifers in Egypt, the two proposed locations are 1) Nile Valley and Delta region and 2) Red Sea coast in Eastern Desert and Sinai region. It is projected that the impact of the proposed technology on the agricultural segment in Egypt would be significant.

In Nile valley and Delta region, it is suggested to utilize localized irrigation instead of flood irrigation as the former could save up to 40% of the used water. FDFO desalination, using renewable groundwater, coupled with localized irrigation (such as drip irrigation) could possibly cultivate 1 million feddan. Proposed scheme will reduce the pressure on Nile River making more water available for environmental flows leading to a healthy river ecosystem.

For Red Sea coast in Eastern Desert and Sinai region, FDFO desalination is a sustainable solution to help resolve the severe water scarcity problem inhibiting its development. Provision of supplementary irrigation water will help development of new agriculture lands creating new employment opportunities and established communities. Decentralized small-scale farms (less than 2,000 feddan) are suggested in this area, instead of hundreds of thousands of feddan as is common in Delta and Nile valley regions. This will not only minimize water losses, but also will keep the desalinated water at a competitive price.

Choice of a suitable draw solution is one of the key aspects affecting FDFO desalination efficiency. As nitrogenous fertilizers is by far the most dominant category of fertilizers used in Egypt, this study focused only on them. Four nitrogenous Egyptian fertilizers have been closely compared with respect to their availability, economics and performance. The three aspects played a major role in the fertilizer selection. Ammonium Sulpahte was selected to be the most fit fertilizer draw solution exhibiting high osmotic pressure, being non-expensive, non hygroscopic, resistant to valorization, highly soluble in water and containing sulphur which is needed by the plant.

Performance of ammonium sulphate DS was further investigated experimentally using an FO thin film composite (TFC) membrane supplied by Woongjin, Korea. The FS used was synthetic salty water prepared in the lab using different concentrations of NaCl. A bench-scale FO setup was used to run the experiments. The performance was evaluated by testing water flux, reverse permeation and feed ions rejection. It is concluded that there is a logarithmic correlation between flux and ammonium sulphate concentration where any additional increase in ammonium sulphate concentration inhibits water flux due to dilutive internal concentration polarization (DICP) effects. Increasing FS concentration leads to flux decline due to the decline in the differential bulk osmotic pressure. Specific Reverse Solute Flux (SRSF) values at flux less than 10 $Lm^{-2}h^{-1}$ is significantly higher than that for flux more than 10 $Lm^{-2}h^{-1}$. As a result, it is recommended to operate the process at a flux exceeding 10 $Lm^{-2}h^{-1}$ to avoid undesired loss of draw solute by reverse flux. SRSF is approximately constant regardless of ammonium sulphate DS concentration. For the same DS concentration, flux and SRSF are inversely proportional. TFC membrane used in this study displayed high rejection of FS ions for almost all DS concentrations (more than 90%).

To sensibly test the efficiency of the ammonium sulphate draw solution, a real brackish Egyptian groundwater sample was collected, analyzed and used as FS. Being available, three FO membrane samples were assessed in this study and the best membrane was selected for further investigations. In comparison to HTI's Cellulose Triacetate (CTA) and Woongjin TFC membranes, Porifera's commercial membrane proved to be best membrane with respect to baseline flux, where DS was NaCl and FS was DI water. Having the smallest structural parameter (S), internal concentration polarization (ICP) is minimized yielding highest flux. Different concentrations of ammonium sulphate were used as DS using the BGW sample. Like previously, the performance was assessed based on water flux, reverse permeation and feed ions rejection. A logarithmic relation was drawn between water flux and ammonium sulphate concentration. Same relation existed between ammonium sulphate concentration and water flux due to DICP effects. However, in this study, SRSF values did not exceed 0.18 g/l for both NH_4^+ and SO_4^{2-} ions, indicating high membrane selectivity. At flux exceeding 20 $Lm^{-2}h^{-1}$, NH_4^+ ion reported higher SRSF values than that of SO_4^{2-} ion.. Again, SRSF came out to be almost constant irrespective of ammonium sulphate concentration. While increasing DS concentration lead to increasing Na^+ ion rejection, it caused a significant decline in Cl^- ion rejection. This phenomenon could be probably associated to an ion exchange mechanism that is taking place and to the membrane's surface charge reversal.

In conclusion, FDFO is a propitious technology that could possibly alleviate the water scarcity problem in Egypt. Not only is FDFO a sustainable desalination technology, but also it has numerous advantages over conventional desalination technologies, such as RO. Abundant brackish groundwater could be efficiently exploited to produce valuable nutrient-rich irrigation water, being the major fresh water consumer in Egypt. The scheme studied demonstrated that ammonium sulphate is an efficient DS for FDFO process, especially using Porifera's commercial FO membrane exhibiting high osmotic pressure, low reverse solute permeation and remarkable rejection of feed solute.

8.2 Recommendations and Future Works

There are many studies investigating FO process, yet most of these studies are limited to bench-scale investigations, like the study presented here. It is essential that the long-term performance of FDFO desalination technology be examined at a pilot scale level employing state-of-the-art membranes. Although challenging, doing that will help evaluate the potential for commercial scale application of FDFO in Egypt. In addition, a pilot scale will facilitate long-term testing of the process, unlike the experiments carried out here which was run for only 24 hours. Fortunately, the Center of Sustainable Development at the American University in Cairo (AUC) came aware of this need and a pilot scale FO desalination facility is currently being equipped on campus.

Upon completion of the FO desalination facility at AUC, actual irrigation using product water is recommended as a future work. This will elucidate some of the long term issues that were not addressed in this work such as dilution needs, fouling, crop analysis and membrane change frequency. For example, as ammonium sulphate is an acidic form of nitrogen, in the long run limestone should be applied to the soil to neutralize its acidity. The frequency of liming should be studied as this will not only affect the overall cost of the process, but also to avoid exaggerated leaf growth and deterioration of the crop.

Although FO seems to be a promising technology, it is still facing challenges that need further consideration such as CP effects, membrane fouling, reverse permeation, and novel draw solutions. It is worth noting these challenges are inter-related (i.e. one affects the other), as shown in Figure 8.1. For example, a highly porous membrane support layer reduces ICP and a highly selective membrane active layer reduces reverse solute diffusion, which in turn minimizes membrane fouling (Zhao, Zou, Tang, et al., 2012). Furthermore, small molecule size reduces ICP, but at the same time increases both reverse solute diffusion and membrane fouling. Reverse solute diffusion and membrane fouling are directly related. Water flux can be strongly affected by ICP and membrane fouling. Finally ICP, reverse solute diffusion and membrane fouling are basically influenced by FO membrane properties and draw solute (T. Cath et al., 2006). In other words, there is a great need for research and development in the area of novel draw solutions (organic or inorganic) and FO membrane manufacturing to optimize the overall process and mitigate such challenges.

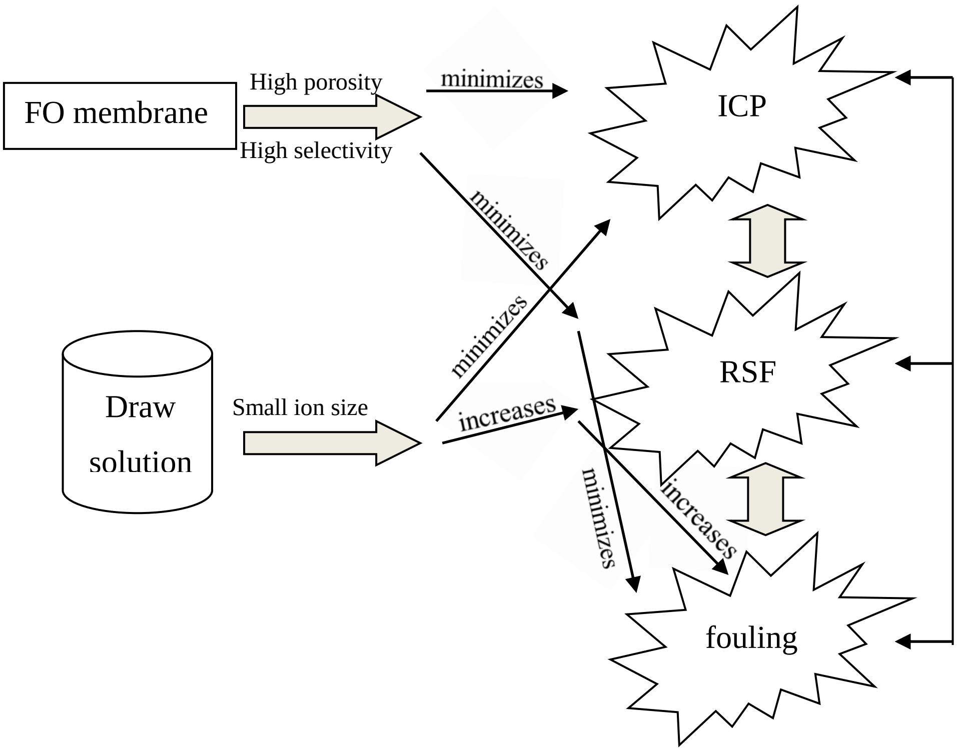

Figure 8.1 – Complex relationship between ICP, membrane fouling and reverse solute flux (adapted from Zhao, Zou, Tang, et al., 2012)

A potential area of research in FO is associated with separation of draw solutes by means of a magnetic field. Nano-scale magnetic particles could possibly be used to amplify the osmotic pressures of the DS. Once the DS containing these particles has been diluted by the fresh water flux from the feed, they can be easily removed from that solution by use of a magnet. This area of research is recently gaining the attention of FO researchers.

Since FDFO desalination is not energy intensive, it holds the potential to be powered by renewable energy, such as wind and solar energy, making it a sustainable environmental friendly desalination technology (with minimum carbon foot print). Renewable energy, especially solar energy, is abundant in most remote communities in Egypt, therefore can be easily utilized for making FDFO desalination a self-powered process. In Egypt, the annual global irradiation is in the range of 6 to 6.5 kWh/m^2/day, which is one of the best worldwide (Salim, 2012).

The energy consumption for the FDFO process has been presented here based on available literature. It is recommended that a comprehensive life cycle analysis for FDFO technology be carried out to investigate the underlying merits and compare it to life cycle analysis of other competing desalination technologies such as RO.

The scope of this study focused on nitrogenous Egyptian fertilizers only. Further studies could be carried out on Phosphorus, Potassium and blended fertilizers available in Egypt. It is worth mentioning that the chemical composition of commercially available blended fertilizers remains proprietary, which needs further investigation in future work.

In this study, a real brackish groundwater sample was collected from only one location in Egypt and was used as a feed solution, as per Chapter 7. In future work, it is recommended to collect numerous samples from different locations in Egypt to better represent Egyptian groundwater and to account for spatial variations. In addition in this study the rejection of only Na+ and Cl- were addressed, even though groundwater contains a variety of major ions such as Ca^{2+}, Mg^{2+}, Fe^{3+} and B^{3+}. It is recommended that future work would incorporate rejection data of all other major ions as they may affect performance of the irrigation water.

FDFO can be easily complemented to reach a “Zero Liquid Discharge” technology, where the process is resource efficient, economic and has no significant hazardous effluent, or discharge, left over. Eventually, the proposed scheme could lead to a technology platform that would supply irrigation water, minimize soil salinity, control fertilizer application and close the irrigation – brackish water – drainage vicious cycle.

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