The Islamic University–Gaza
Research and Postgraduate Affairs
Faculty of Engineering
Master of Civil Engineering
Water Resources Engineering

الجامعـــــــة الإســـلاميـــة ـــ غزة
شئون البحث العلمي والدراسات العليا
كليـــــــــــــة الهنـــدســــــة
ماجستيـــر الهندســـة المدنيـــة
هندســـــة مصـــــادر الميـــــاه

Assessing Forward Osmosis As Potential Alternative Seawater Desalination Technology

تقييم التناضح الأمامي كتقنية محتملة في تحلية مياه البحر

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A Thesis Submitted in Partial Fulfillment of the Requirement for the Degree of Master of Science in Civil-Water Resources Engineering

November / 2016

إقـــــرار

أنا الموقع أدناه مقدم الرسالة التي تحمل العنوان:

تقييم التناضح الأمامي كتقنية محتملة في تحلية مياه البحر

Assessing Forward Osmosis As Potential Alternative Seawater Desalination Technology

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The Islamic University of Gaza

مكتب نائب الرئيس للبحث العلمي والدراسات العليا **هاتف داخلي** 1150

الرقم: ج س غ/35/ :Ref

التاريخ: 2016/11/05 :Date

نتيجة الحكم على أطروحة ماجستير

بناءً على موافقة شئون البحث العلمي والدراسات العليا بالجامعة الإسلامية بغزة على تشكيل لجنة الحكم على أطروحة الباحث/ **محمد شحدة علي الغوطي** لنيل درجة الماجستير في **كلية *الهندسة*** **قسم الهندسة المدنية- هندسة مصادر المياه** وموضوعها:

تقييم التناضح الأمامي كتقنية محتملة في تحلية مياه البحر

Assessing Forward Osmosis As A Potential Alternative Seawater Desalination Technology

وبعد المناقشة التي تمت اليوم الثلاثاء 22 صفر 1438هـ، الموافق2016/11/22م الساعة الحادية عشر صباحاً، اجتمعت لجنة الحكم على الأطروحة والمكونة من:

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وبعد المداولة أوصت اللجنة بمنح الباحث درجة الماجستير في **كلية *الهندسة*/** قسم **الهندسة المدنية- هندسة مصادر المياه** .

واللجنة إذ تمنحه هذه الدرجة فإنها توصيه بتقوى الله ولزوم طاعته وأن يسخر علمه في خدمة دينه ووطنه.

والله ولي التوفيق ،،،

نائب الرئيس لشئون البحث العلمي والدراسات العليا

أ.د. عبدالرؤوف علي المناعمة

Abstract

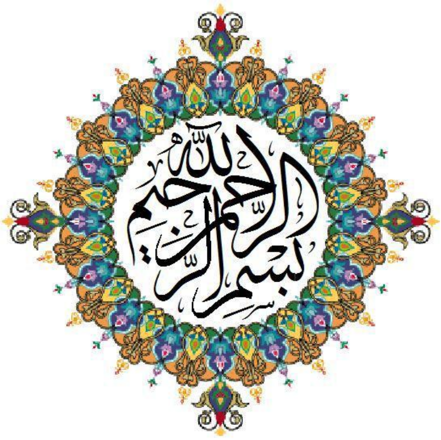
All researches and studies trending to seawater desalination technology, reverse osmosis or nanofiltration, but in this research I tended towards a new technique which is forward osmosis. Forward osmosis (FO) is one of the emerging membrane technologies which has gained renewed interest recently in desalination process, due to its advantages which is less consumption of energy because of low pressure used. The aim of this research makes an effort to investigate the efficiency performance of (FO) technology for extracting water from types of saline waters using as feed solution (FS) and using ammonium bicarbonate (NH_4HCO_3) as draw solution (DS). Two types of saline water were used: Aqueous solution and real water. The performance of tested membrane was measured in terms of flux rate and salt rejection under different operation conditions: feed solution (FS) concentration (2500-37000) mg/l, draw solution (DS) concentration (39,530-197,650) mg/l and applied pressure (0.5) bar. Experimental results showed that, increasing DS concentration reflect positive effects on both water flux and rejection rate because of increase of DS osmotic pressure. In other hand, increasing of the feed concentration reduced the water flux and rejection rate due to less difference in osmotic pressure.

The results demonstrated the performance of FO for synthetic and real water in flux and salt, maximum water flux was 6.6 $L/m^2.h$ for synthetic seawater. In the other hand, for real seawater, results showed that maximum water flux was 4.7 $L/m^2.h$, salt rejection was decreased by time from 97 to 94 %. In this study, heating process performed to removal and recovery ammonium bicarbonate from water.

In conclusion, the results indicated that FO performance was encouraging and proved that FO system could be a powerful desalination unit for desalting different sources of saline waters at different concentration levels.

الملخص

جميع البحوث والدراسات تتجه إلى تحلية مياه البحر باستخدام تكنولوجيا التناضح العكسي أو أغشية النانو، ولكن في هذا البحث اتجهت نحو تقنية جديدة وهي التناضح الأمامي. التناضح الأمامي هي واحدة من التقنيات الناشئة والواعدة التي اكتسبت اهتماما متجددا مؤخرا في عملية تحلية مياه البحر لما لها من مزايا من أهمها قلة استهلاك للطاقة وذلك لقلة الضغط المستخدم. والهدف من هذا البحث هو تقييم أداء تقنية التناضح الأمامي باعتبارها تقنية محتملة في تحلية المياه (المياه الجوفية ومياه البحر). استخدمت نوعين من المياه المالحة: محلول مائي وماء حقيقي. وقد تم قياس الأداء للغشاء من حيث معدل التدفق واسترجاع الأملاح في ظل ظروف تشغيل مختلفة: تراكيز مياه مالحة (2500- 37000) ملغم / لتر، و بيكربونات الأمونيوم بتركيز من (39530- 197650) ملغم / لتر و الضغط (0.5) بار. أظهرت النتائج أن زيادة تركيز بيكربونات الأمونيوم تعكس آثارا إيجابية على كل من تدفق المياه و واسترجاع الأملاح وذلك بسبب زيادة الضغط الاسموزي. من جهة أخرى، زيادة تركيز المياه المالحة تؤدي إلى انخفاض تدفق المياه واسترجاع الأملاح بسبب قلة الفرق في الضغط الاسموزي. وكذلك أظهرت النتائج أداء الغشاء بالنسبة لمياه البحر الاصطناعية والحقيقية ، فكان أقصى تدفق المياه 6.6 لتر / لكل متر مربع في الساعة وذلك مع مياه البحر الاصطناعية. في المقابل، مع مياه البحر الحقيقية، أظهرت النتائج أن الحد الأقصى لتدفق المياه كانت 4.7 لتر / لكل متر مربع في الساعة ، وقد انخفضت نسبة الاسترجاع للأملاح ما بين 97 – 94٪. وتم في هذه الدراسة، استخدام عملية التسخين من أجل إزالة واستنقاذ بيكربونات الأمونيوم من المياه مرة أخرى. وفي الختام، أشارت النتائج إلى أن أداء التناضح الأمامي مشجع وأثبتت أن هذه التقنية يمكن أن تكون وحدة تحلية قوية لتحلية مصادر مختلفة من المياه المالحة في مستويات تركيز مختلفة.



﴿ وَقُلْ رَبِّ زِدْنِي عِلْمًا ﴾

[طه:114]

DEDICATION

To the soul of my father "Allah mercy upon"

To my dear mother " May Allah prolong her age"

To my dear wife, my sons Asem , Mahmood , Amr and my daughter Lareen

To my dear brothers

To my friends and colleagues…

Acknowledgment

First, all praises and glory are due to **ALLAH** for all the bounty and support granted to me. This work would not be done without God‘s endless guidance and support.

I would like to take this opportunity to sincerely thank all individuals who have helped me in this effort. Primarily, I would like to express my sincere gratitude and thanks to my thesis supervisor **Dr. Fahid Rabah**, for his unlimited guidance , encouragement, and continuous support during this research. Also I am grateful to all doctors in the Civil and Environment Departments of the Islamic University.

I gratefully acknowledge financial support from the Middle East Desalination Research Centre (MEDRC), represented by Mrs. **Helen Twist** and the Palestinian Water Authority (PWA), represented by engineer **Ahmed Baraka**, for providing me the information and test results of water which contributed to achieve this research..

I am very thankful to **Prof.Dr. Monther Abd Elateef** and **Mr. Mohammad Matar** from Chemical Department of the Islamic University for their help in order to facilitate the conduct of scientific experiments..

I am very thankful to **Eng. Bashar Moshtaha** from the Municipality of Gaza who gave me assistance in collecting samples of water from various wells.

I would like to thank all those who have assisted, guided and supported me in my study.

Mohammad Shehda Alghouti

TABLE OF CONTENT

ABSTRACT……………………………………………..……………………...…………I

الملخص ……………………………………..……………………..….…..…..………II

Quran………………………………………………………....…………………...III

DEDICATION…………………………….....…………....………..….…..…… IV

ACKNOWLEDGEMENTS……….……………………………...……..…………..…V

TABLE OF CONTENT………………………………………………………..……VI

LIST OF TABLES……………………………………...…..…..…………........X

LIST OF FIGURES……………………………..……………….……..….........XII

LIST OF ABBREVIATIONS ………………..…………….....…....………... XIII

LIST OF UNITES ……………………………………………………………….XIV

CHAPTER ONE: INTRODUCTION………..……………………………...…1

1.1 Background ……………………………………………………...……....…..2

1.2 Problem Statement…………………………………….…………..………..3

1.3 Goal………………………………………….....………..……….........4

1.4 Specific Objectives…………………………….………..………..……..……..4

1.5 Methodology ………………………….…………………………........……….5

1.6 Research Structure …………………….………………………………..……6

CHAPTER TWO: LITERATURE REVIEW………………...………………….…....7

2.1Introduction…………………………..……...……………….……………..8

2.2 Working Principle of FO Membrane……………………………………...8

2.3 Recent Application For FO Membrane……………………..………………..9

2.3.1 Power Generation …………………………………………..……......10

2.3.2 Desalination……………………………..……………...…..…………..10

2.3.3 Wastewater Treatment ………………………..……………..……..……..11

2.3.4 Liquid Food Concentration ………………......................………..…......13

2.3.5 Pharmaceutical Applications ………………..........................…..…..…14

2.3.6 Others ………………..........................…..……………………………....…14

2.3.7 Selection of the membrane orientation in different applications …………15

2.4 Membranes Modules ………………..…..………………..……......…..……..16

2.4.1 Plate and Frame…………....…………………………..……...………..16

2.4.2 Spiral Wound……………………………..……………..………..17

2.4.3 Tubular or Hollow Fibers……………………..…………….……..……....17

2.4.4 Hydration Bags…………………….………..…….…………….…….…..…..….18

2.5 Challenges for FO Membranes.………………………………..…………..…...18

2.5.1 Concentration Polarization (CP)…………..…………………...…..……....18

2.5.1 External Concentration Polarization (ECP)……………..…………….20

2.5.2 Internal Concentration Polarization (ICP) ………………….…….…......20

2.5.2 Membrane Fouling………………………………….....……..........…......22

2.5.2.1 Classification of Membrane Fouling……………….….…...…..….…..23

2.5.2.2 Factors Affecting the Fouling………………………………..….…......23

2.5.2.3 Fouling Removal and Membrane Cleaning…………………………23

2.5.2.3.1 Physical Cleaning ……………………………...……...……..23

2.5.2.3.2 Chemical Cleaning………….………………….....………..24

2.5.2.3.3 Biological Cleaning………..………………...……..……..24

2.5.3 Reverse Solute Flux…………………….……………...……......……..24

2.5.4 Draw Solutes Advancement…………………………...……......…..…..25

2.5.4.1 Types and Classification of Draw Solutes…………...……...……..26

2.5.5 Membrane Development……………………………...……......…..…..26

2.5.5.1 Phase Inversion Formed Cellulosic Membrane………...…..…..…..27

2.5.5.2 Thin Film Composite Membrane………………….…....….………..27

2.5.5.3 Chemically Modified Membrane………...……………………….....28

2.6 Assessment of Membrane Performance…….…………………………….…..29

2.7 Relationship Between the Membrane Challenges……...…………………..…..30

CHAPTER THREE: MARERIALS AND METHODS

CHAPTER THREE: MARERIALS AND METHODS …..………..…….…..…..32

3.1 Materials …………………………………………….………..…...……..…..33

3.1.1 FO Experimental Apparatus………………......…………..…………..……33

3.1.1.1 FO Membrane……………………………….……..…………….……..33

3.1.1.2 CF042D-FO…………………………..…….……………….………..35

3.1.1.3 Facilities …………………………….………...……....………..……..37

3.1.2 Feed Solution(FS)…………………………….……..……...………..…..37

3.1.3 Draw Solution(DS)……………………………….……..……...…………..37

3.1.4 Lab Scale FO Experimental Apparatus………………………………...…..37

3.1.5 Heat Recovery Unit……………………………...…….…….…...…..38

3.1.6 Water Sample ……………………..……………..…..…………………....39
3.1.6.1 Brackish water …………………………………....……………....39
3.1.6. 2 Seawater……………………………………........……….…..40
3.1.7 Research Chemicals…………………….…………………………..40
3.2 Methods……………………………………………..…...…….……..….41
3.2.1 Laboratory tests and analysis ……………...……………..………..…..41
3.2.2 Measurement of FO Performance …..………………...……..…………..42
3.2.3 Experimental Procedures…………………….………..…..……………..43

CHAPTER 4: RESULTS AND DISCUSSION ..…………………...………..44

4.1 General ………………………………………..…………...……...……..45
4.2 First Set of Experiments ……………………..…….………..…….…….45
4.2.1 Membrane performance with DI water for flux and recovery rate…........45
4.2.1.1. Water Flux.………………………………….……….…..……..45
4.2.1.2. Recovery Rate………………………..…………….…..…..…..45
4.2.2 Membrane performance with NaCl Solution for flux and recovery rate….46
4.2.2.1 Effect of DS concentration on flux and recovery rate…………..…..47
4.2.2.1.1 Water Flux……………………………………..……..…47
4.2.2.1.2. Recovery Rate……………………………………...……..48
4.2.3 Membrane performance with NO_3 Solution for flux and recovery rate…...49
4.2.3.1 Effect of DS concentration on flux and recovery rate……………..…49
4.2.3.1.1 Water Flux……………………………………...……..……49
4.2.3.1.2. Recovery Rate…………………………………...……….…..50
4.3 Second Set of Experiments …………………...………………..………..…..51
4.3.1 Membrane Performance With NaCl Solution For Rejection Rate……..…...51
4.3.2 Membrane Performance With NO_3 Solution For Rejection Rate…………...51
4.4 Third Set of Experiments ………………...…………………….……….....52
4.4.1 Membrane Performance in Real Water……………………...……..…….52
4.4.1.1 Effect of DS Concentration on Flux and Recovery Rate…………...…52
4.4.1.2 Effect of Feed Water TDS Concentration on Water Flux……….……54
4.5 Fourth Set of Experiments……………………………..……….…….…..55
4.5.1 Rejection Rate of NO_3……………………………….………..…..….55
4.5.2 Effect of DS Concentrations on NO_3 Rejection Rate…………….…..……55
4.6 Fifth Set of Experiments………………………………………….…….…..56

4.6.1 Membrane Performance With Synthetic Seawater (SSW)…………..……..….56
4.6.1.1 Effect of DS concentrations on water flux and salt rejection ……......….56
4.6.1.2 Effect of Feed Boron Concentration……….………..………………….56
4.6.2 FO membrane performance with real seawater (RSW)...……………..…...…….58
4.6.2.1 Effect of DS concentrations on water flux and salt rejection………..….58
4.6.2.2 Recovery Rate…………………………………………………...……61
4.7 Sixth Set of Experiments…………………………..…………….………..62
4.7.1 removal and recovery process……………………………...……....……62
4.7.1.1 heating process…………………………………………………..…..62
4.7.1.2 heating time……………………………………….…….……….….62
4.7.1.3 removal and recovery efficiency………………………….....…..……62
4.7.2 Comparison between FO and RO……………………………..………...63
CAHPTER (5): CONCLUSIONS AND RECOMMENDATIOS …....……..…..65
6.1 Conclusions…………………………..……………..………………..…..…..66
6.2 Recommendations……………………..……………..…………...……...67
REFERENCES…………………………..……..……………………..…..….**68**
APPENDICES……………………………………………………….....………**80**
Appendix (A) Recent studies on FO membrane fouling …………..……....……..….81
Appendix (B) Summary of draw solutions used for FO desalination ……….....…...83
Appendix (C) Summary of FO membrane development ………………...…..…..85
Appendix (D) Effect of draw solution concentration in brackish and seawater desalination using FO membrane………………………………………...……….89

LIST OF TABLES

Table (3.1): Well sample chemical analysis PWA 2015……………………..……..39
Table (3.2): Measured of chemical and physical properties for seawater samples…39
Table (3.3): Summary of research chemicals ………………..…………..……….…40
Table (3.4): Summary of experimental parameters in FO process …………….....…40
Table (4.1): Relation between the water flux and DS concentration for well samples……………………………………………………………………..….50
Table (4.2): Relation between the NO_3 rejection rate and DS concentration for well samples…..……………………………………………..……….……….....…53
Table (4.3):Analysis of real seawater before and after FO process……..……..…..…59
Table (A.1): Recent studies on FO membrane fouling……………………..…….75
Table (B.1): Summary of draw solutions used for FO desalination………..…..…77
Table (C.1): Summary of notable FO membrane developments…………….....……79
Table (D.1): Performance of FO membrane in water flux for DI water…………….83
Table (D.2): Relation between DS different concentrations and flux for NaCl solutions…………………………….…………………………………….84
Table (D.3): Relation between DS different concentrations and flux for NO_3 solutions………………………………………...……………………...……85
Table (D.4): Relation between DS concentration and rejection rate for 0.085 M NaCl……………………………………………………………………....…86
Table (D.5): Relation between DS concentrations and rejection rate for NO_3…..…87 concentrations…………………………………………………………………88
Table (D.6): Flux rate of FO membrane for Radwan 9……………………..……89
Table (D.7): Flux rate of FO membrane for Aljalaa 14……………………..…..90
Table (D.8): Flux rate of FO membrane for Radwan A3……………………..….91
Table (D.9): Flux rate of FO membrane for Remal 4 Becdar……………..…..……92
Table (D.10): Performance of FO membrane for Radwan 9……………………..93
Table (D.11): Performance of FO membrane for Aljalaa 14…………..……..…94
Table (D.12): Performance of FO membrane for Radwan A3………..……………95
Table (D.13): Performance of FO membrane for Remal 4 Pecdar………..…..……96
Table (D.14): Performance of FO membrane for synthetic seawater…..……...……97
Table (D.15): Performance of FO membrane on flux…………………….…...……98
Table (D.16): Effect of heating process on removal different initial NH_4HCO_3 concentrations…………………………………………………......………..99

LIST OF FIGURES

Figure (1.1): Total capacity installed in the world ……………………………………………1
Figure (1.2): Research methodology steps...………………………………………………4
Figure (2.1): Applications of FO in the fields of water, energy and life science……...7
Figure (2.2): Simplistic desalination or dewatering / concentration process………..…8
Figure (2.3): Basic FO/RO desalination process……………………………………..……9
Figure (2.4): FO/RO desalination plant (100m^3/day) at AlKhaluf, Oman...……..……10
Figure (2.5): Al Najdah desalination plant (200 m^3/day) at Al Najdah in Oman..…11
Figure (2.6): Schematic diagram of an OMBR system …………………………......14
Figure (2.7): Comparison of the permeate flux in PRO and FO modes under membrane fouling as a function of feed concentration ……………………......…....17
Figure (2.8): Schematic diagram of a spiral wound forward osmosis (SWFO) model …………………………………………………………………………………..……..18
Figure (2.9): Morphology of PES hollow fiber substrate..……………..………..…19
Figure (2.10): Illustration of water purification hydration bag ………………….…19
Figure (2.11): Illustration of both internal concentration polarization (ICP) and external concentration polarization (ECP) ………………………………........…21
Figure (2.12): Concentrative ICP and Dilutive ICP across an asymmetric FO membrane ………………………………..…...…………………………...…..…..22
Figure (2.13): Relationships between ICP, membrane fouling, reverse solution diffusion, membrane characteristics and draw solute properties in FO ………..…...32
Figure (3.1): CF042D-FO Membrane Cell.…………………………………...…....34
Figure (3.2): Experimental diagram of FO process …………….....……...….…...35
Figure (3.3): Illustration of flow diagram for draw solution selection ……..…...…36
Figure (3.4): Schematic diagram of FO desalination process for potable water with draw solution recovery system ……………………………………..…....…………37
Figure (3.5): The lab scale experimental system for FO process…………..……….37
Figure (3.6): Schematic of heating process ……..…..……………………..…..……38
Figure (4.1): Effect of NH_4HCO_3 concentrations on the water flux for DI water and different NaCl solution concentrations…………………………………......…….44
Figure (4.2): Effect of NH_4HCO_3 concentrations on the recovery rate of deionized (DI) water and different NaCl solution concentrations.………………..……...…45
Figure (4.3): Effect of NH_4HCO_3 concentrations as draw solution on the flux for different nitrate solution concentrations..……………………...…………………46
Figure (4.4): Effect of feed Nitrate concentration on water flux with different NH_4HCO_3 concentrations...……………………………………………………...…47
Figure (4.5): Effect of DS concentration on recovery rate of nitrate solution concentrations ……………..………………………………………………….....…47
Figure (4.6): Effect of DS concentrations on NaCl rejection for the membrane........48
Figure (4.7): Effect of initial nitrate concentrations on nitrate rejection at different (NH_4HCO_3) concentrations for the membrane…………………………..…..…..49
Figure (4.8a): Effect of NH_4HCO_3 concentrations on water flux for different well samples………………………………………………………..………......……50
Figure (4.8b): Effect of different draw solution concentration on recovery rate for real brackish water with different TDS…………………………………………..…..51
Figure (4.9): Effect of feed TDS concentration on water flux for well samples with NH_4HCO_3 different concentrations.……………………………………………...…51

Figure (4.10): Effect of draw solution concentrations on NO_3 rejection rate with different nitrate and TDS concentrations for real brackish water……………………..52
Figure (4.11): Water flux versus time with different NH_4HCO_3 concentration as DS and 0.6M NaCl as FS …………………………………………………..……..….53
Figure (4.12): Water flux rate with different NH_4HCO_3concentration (at running time 90 minute)……………………………………………………...……....54
Figure (4.13): Effect of draw solution concentration on salt rejection for FO operation ……………………………………………...………..…………..55
Figure (4.14a): Boron concentrations vs. water flux with NH_4HCO_3concentration 2.5M as DS…………………………………………………………………..…..55
Figure (4.14b): Boron concentrations vs. boron rejection rate with NH_4HCO_3 concentration 2.5M as DS and 0.5M NaCl as FS………………………......……56
Figure (4.15): Water flux versus time with different NH_4HCO_3 concentration as DS …………………………………………………………………………...……57
Figure (4.16): Water flux vs. different NH_4HCO_3 concentration as DS and real seawater as FS………………………………………………………………..…57
Figure (4.17): Effect of draw solution concentration on salt rejection for FO operation……………………..……………………………..………………..…..58
Figure (4.18): Effect of operating time on draw solution TDS concentration……………………………………..………………….………..58
Figure (4.19): Effect of different draw solution concentration on recovery rate for synthetic and real seawater……………………………………………………..….59
Figure (4.20): Boron removal efficiency vs. different NH_4HCO_3concentration as DS and real seawater as FS……………………...……………………………...…...60
Figure (4.21): Ammonium bicarbonate removal efficiency during the time……..…60
Figure (4.22): NH_4HCO_3 solution recovery efficiency……………….…….………61

LIST OF ABBREVIATIONS

B	solute permeability coefficient
CA	Cellulose Acetate
C_f	Salt concentration in feed water (mg/l).
C_p	Salt concentration in permeate (mg/l).
CP	Concentration Polarization
D	diffusion coefficient
ECP	External Concentration Polarization
FO	Forward Osmosis
FS	Feed Solution
DS	Draw Solution
HTI	Hydration Technology Innovation
ICP	Internal Concentration Polarization
J_w	Water Flux rate (L/m^2.h)
K	solute resistivity
PWA	Palestinian Water Authority
Q_f	Feed flow rate
Q_p	Permeate flow rate.
R	Rejection rate (%)
RO	Reverse Osmosis
s	structural parameter
TDS	Total Dissolved Solids
TFC	Thin Film Composite
t	membrane thickness
Y	Recovery rate.

Greek

$\pi_{D,b}$	bulk draw osmotic pressure
$\pi_{D,m}$	membrane surface osmotic pressure on the permeate side
$\pi_{F,b}$	bulk feed osmotic pressure
$\pi_{F,m}$	membrane surface osmotic pressure on the feed side
$\pi_{F,i}$	effective osmotic pressure of the feed in AL-DS orientation
$\pi_{D,i}$	effective osmotic pressure of the draw solution in AL-FS orientation)
τ	tortuosity
ε	porosity

LIST OF UNITS

M	Mole(gram per liter)
cm^2	Square centemeter
$(L/m^2.h)$	Liter per square meter per hour
µm	Micrometer
mg/l	Milligrams per Liter
ppm	Part per Million
V	Volume

CHAPTER ONE

INTRODUCTION

CHAPTER (1)

INTRODUCTION

1.1 Background

Water scarcity has become a global risk and one of the most serious concerns for the scientific community as a result of increasing population, continuing industrialization, expanding agricultural activities, increasing inequities between water supply and demand, improper management and degradation of natural water resources, and increasing regional and international conflicts (Rijsberman, 2006). In fact, statistical forecasts and predictions show that two-thirds of the world's population may be subjected to water stressed conditions by the year 2025 which will not only impede the socioeconomic growth but also pose threats to our healthy ecosystems(Karagiannis and Soldatos, 2008).

The Gaza Strip is a highly populated, small area in which the groundwater is the main water source. During the last few decades, groundwater quality has been deteriorated to a limit that the municipal tap water became brackish and unsuitable for human drinking consumption in most parts of the Strip (Aish, 2010).

As shown in Figure (1.1), seawater desalination is the most used solution to address water shortage especially for potable water applications.

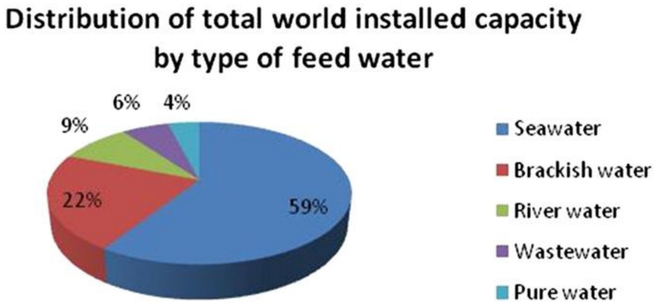


Figure (1.1): Total capacity installed in the world (IDA Desalination Yearbook 2013–2014).(Stewart Burn et al., 2015)

RO processes are used in water treatment processes such as seawater desalination and wastewater reclamation (Liu, M. Wang, D. Wang and Gao, 2009). However, high amount of external hydraulic pressure is required to overcome the osmotic pressure of an aqueous feed solution. This results in a high operating cost (McCutcheon and Elimelech, 2006). Another disadvantage of RO is that the amount of clean water recovered from the process during seawater desalination is relatively low (Wang et al., 2009).

Similar to RO, FO uses a semi-permeable membrane to allow separation of water from dissolved solutes. FO, on the other hand, is an osmotically driven membrane process in which water diffuses through the semi-permeable membrane under an osmotic pressure difference across the membrane (Cath, Childress and Elimelech, 2006).

Forward osmosis (FO) is known as the net movement of water across a semi-permeable membrane driven by a difference in chemical potential across the membrane, i.e., passage of water is from lower concentration side to higher one because the lower the concentration, the higher the water chemical potential. Although the FO phenomenon was observed in 1748, the interests in research on FO and in engineered applications of FO have been increasingly attractive since 2000 (Cath et al, 2006). However, there are still three major challenges of FO in municipal scale seawater desalination: a) fabrication of FO membranes with high water flux and high draw solute rejection; b) being lack of appropriate draw solutions; and c) cost-effective post-treatment on a total system approach (Qin, Danasamy, Lay and Kekre, 2012).

In the recent years, FO technology has received increasing attention from researchers and has been seen as a great opportunity in various fields of water treatment.

1.2 Problem Statement

Reverse osmosis (RO) is currently the most widely used desalination technology for clean water production. However, RO is an energy intensive process because a high hydraulic pressure is required to overcome the osmotic pressure generated by the source water. Other problems in RO, such as significant concentration polarization and membrane fouling, lower the feed water recovery rate. Moreover, the discharge of concentrated brine after RO is a serious environmental issue. In summary, the highly fluctuated oil price، uncertainty of energy cost, issues of water security and brine disposal have led every thirsty country to exploring alternative technologies for clean water production.

Forward osmosis (FO) has been considered as an emerging membrane technology for water reuse and desalination.

One of the promising membrane desalination technology is forward osmosis, this research is initiated to study the potential of this technology in desalination of brackish water and seawater.

1.3 Goal

The main goal of this research ***is to assess the performance of Forward Osmosis membrane as a potential alternative technology for saline water (Brackish & Seawater) desalination.***

1.4 Objectives

The specific objectives of this research are:

- Investigate the efficiency of the separation performance of FO membrane for different concentrating types of feed solution (FS) by using ammonium bicarbonate as draw solution (DS).
- Investigate the effect of ammonium bicarbonate by using it as draw solution with different concentrations on water flux, recovery rate and salt rejection.
- Investigate the efficiency of nitrate removal from brackish water by using FO membrane.
- Investigate the efficiency of heating process for removal and recovery of NH_4HCO_3 with different concentrations.

1.5 Methodology of Research

The methodology of the thesis will be as follows:

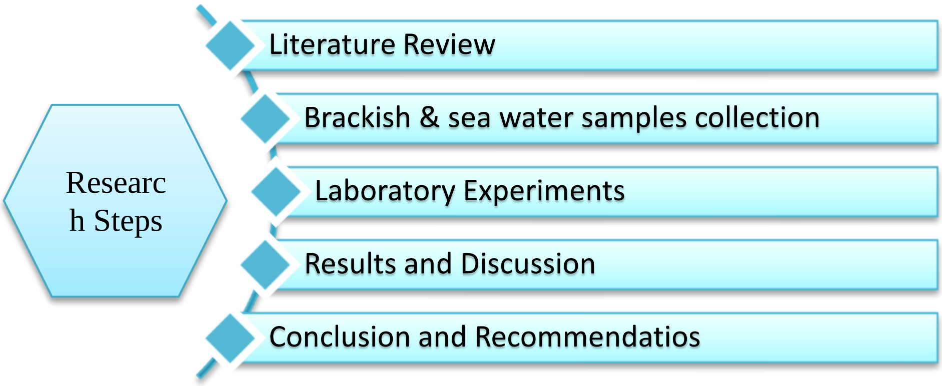


Figure 1.2: Research methodology steps

1.5.1 Literature Review

Survey on published references such as scientific papers, reports and books in the field of this research which may include: Desalination, Forward Osmosis, Reverse Osmosis, applications and its performance with Forward Osmosis technology.

1.5.2 Data Collection

Data gathering from relevant authorities such as Palestinian water authority (PWA), Coastal municipalities water utility (CMWU), Ministries and others .

1.5.3 Brackish & Seawater Samples Collection

Brackish water samples were taken from some wells in Gaza City and seawater samples were taken from the main feed tank of Al Bassa Seawater Desalination Plant, which fed by beach well in Deir El Balah City. After collecting the samples, major chemical analysis were performed for these samples such as (pH, TDS, and other contaminants).

1.5.4 Laboratory Experiments:

Designing and constructing a forward osmosis lab scale system and investigate the effect of operational parameters for efficiency performance of the membrane for desalination synthesized and real saline water.

1.5.5 Results analysis and discussion: Elaborating, analyzing and discussing the results obtained from experimental work.

1.5.6 Conclusions and recommendations The conclusions and recommendations of the study are stated in this chapter of the thesis

1.6 Research Structure

This thesis has been organized into five chapters.

- **Chapter 1 (Introduction)** is an introductory chapter, which provides a general background of the research study, its goal , objectives, methodology and the structure of the thesis.
- **Chapter 2 (literature Review)** Covers a general literature review about desalination technology, membrane classification, performance evaluation and technology of removing TDS and boron.
- **Chapter 3 (Materials and Methods)** describes the materials and methods used in this study for FO process, which contains a detailed description of the experimental setup and procedures. The properties of the brackish and sea water (used in the experiment) obtained from various measurements are presented.
- **Chapter 4 (Results and Discussion)** Presents the results of the use of FO membrane in desalination brackish and seawater , the factor effecting on water flux, recovery rate and rejection rate of TDS , NO_3 and boron
- **Chapter 5 (Conclusion and Recommendations)** summarizes the results and provides the conclusion of this study together with suggestions and some recommendations for future research.

CHAPTER TWO

LITERATURE REVIEW

CHAPTER (2)

LITERATURE REVIEW

2.1 Introduction

With the limitation of fresh water resources, the use of alternative sources like desalination or water reuse is highly studied and developed. RO desalination is a pressure-driven membrane process in which water from a saline feed solution is pushed through a membrane at a hydraulic pressure that exceeds the osmotic pressure of the saline solution. Because of the differences in solubility and diffusivity between water and salt ions, most salt ions are retained by the semi permeable membrane. Although RO is currently the most energy efficient desalination technology, it still requires a great deal of energy to create the high pressures necessary to desalinate seawater (Prante, Ruskowitz, Childress and Achilli, 2013).

In this context, FO is now an emerging separation technology that promises low energy consumption and low fouling issues in comparison to RO process for desalination. FO is a spontaneous process in which water is transported through a semipermeable membrane due to a difference in chemical potential between two solutions. Water will naturally diffuse through the membrane from the fresh water side to dilute the higher saline solution (Phuntsho et al., 2013).

2.2 Working principle of Forward Osmosis

FO is an osmotically driven membrane process using semi-permeable membrane to separate water from dissolved solutes (Cath et al., 2006). In the FO process, the membrane active layer can be placed facing either the feed or the draw solution. Rather than using hydraulic pressure differential (as in RO) for the transportation of water, FO uses the osmotic pressure differential ($\Delta\pi$) across the semi permeable membrane as the effective osmotic driving force (McCutcheon, McGinnis and Elimelech, 2005). No external pressure is applied across the membrane of the two solutions with different π. Osmosis equilibrium is reached when a final hydrostatic pressure difference is reached. This pressure difference is known as the osmosis pressure ($\Delta\pi$). This FO process results in the dilution of the originally concentrated draw solution and the concentration of the originally diluted feed solution (Cath et al., 2006).

FO desalination comprises two stages: first, water is extracted from a saline feed stream into a draw solution and, second, the draw solute is separated from the diluted draw stream to recover the extracted water (Elimelech and Phillip, 2011). In the first stage, the saline feed solution is contacted with a high osmotic pressure draw solution in a membrane module. Driven by the chemical potential gradient, water permeates from the feed solution across the semipermeable membrane into the draw solution.

In the second stage, product water is separated from the draw stream in a closed cycle, thus regenerating the initial draw solution. Various separation processes may be employed to recover water from the draw stream (Stone, Rae, Stewart, and Wilson, 2013). For example, thermolytic draw solutes, such as ammonia–carbon dioxide, may be stripped using low temperature distillation (McCutcheon et al.,2005).

2.3. Recent applications of forward osmosis

FO has been investigated in a wide range of applications, including power generation, seawater/brackish water desalination, wastewater treatment and food processing. All of these applications can be summarized under three general areas: water, energy and life science as illustrated in (Figure 2.1).

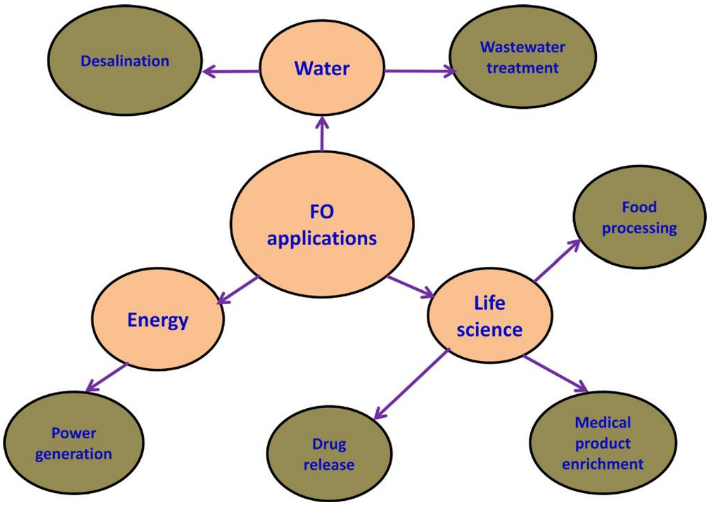


Figure (2.1): Applications of FO in the fields of water, energy and life science (Zhao et al., 2012).

2.3.1. Power generation

Exploiting the osmotic pressure difference of two solutions to generate power is not a new idea. In as early as 1954, the concept of harvesting electric power by mixing fresh and salt water was proposed for the first time [Pattle, 1954]. Unlike conventional energy from fossil fuel sources, salinity-gradient energy or so-called “blue” energy from the mixing of fresh and saltwater in estuaries is renewable and sustainable (Post, Hamelers and Buisman, 2008).

There are three main techniques for the conversion of this salinity-gradient energy, namely PRO, reverse electrodialysis (RED) and vapor compression (Olsson, Wick and Isaacs, 1979). Among them, membrane-based processes such as PRO and RED have gained the most popularity in the past few years (Achilli, Cath and Childress, 2009).

2.3.2. Desalination

To produce desalinated water using a forward osmosis process, there is always at least two steps (the first is FO) with the second step to separate the draw solution / osmotic agent to provide the desalinated water, as simply illustrated in Figure 2.2

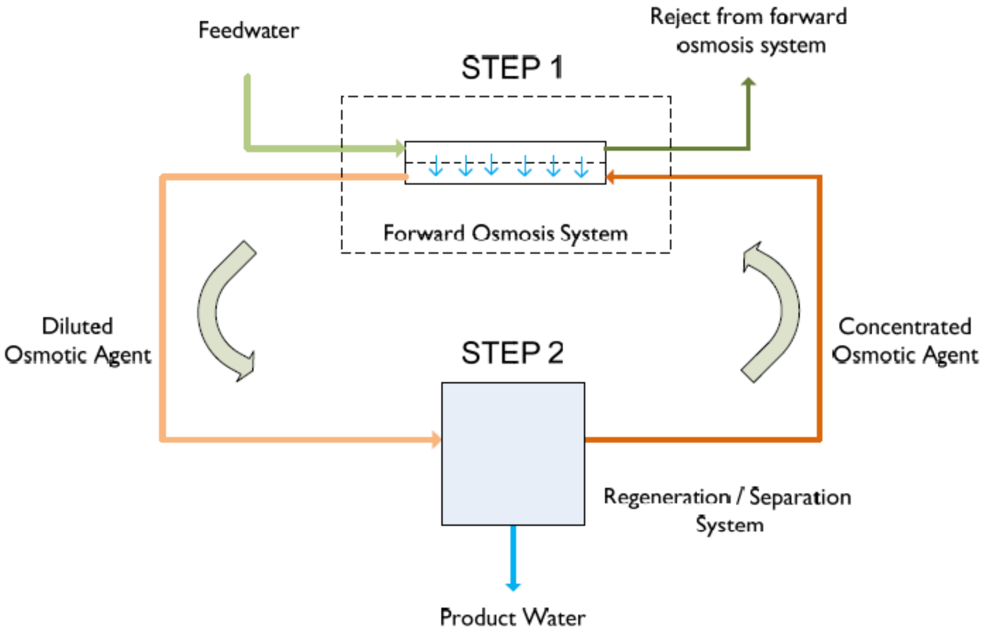


Figure (2.2): Simplistic desalination or dewatering / concentration process(Nicoll, 2013)

4.2.2 Forward osmosis (FO) coupled with reverse osmosis (RO).

The basic concept is shown in Figure 2.3, where there are two steps; the first FO and a second recovery and separation step using RO.

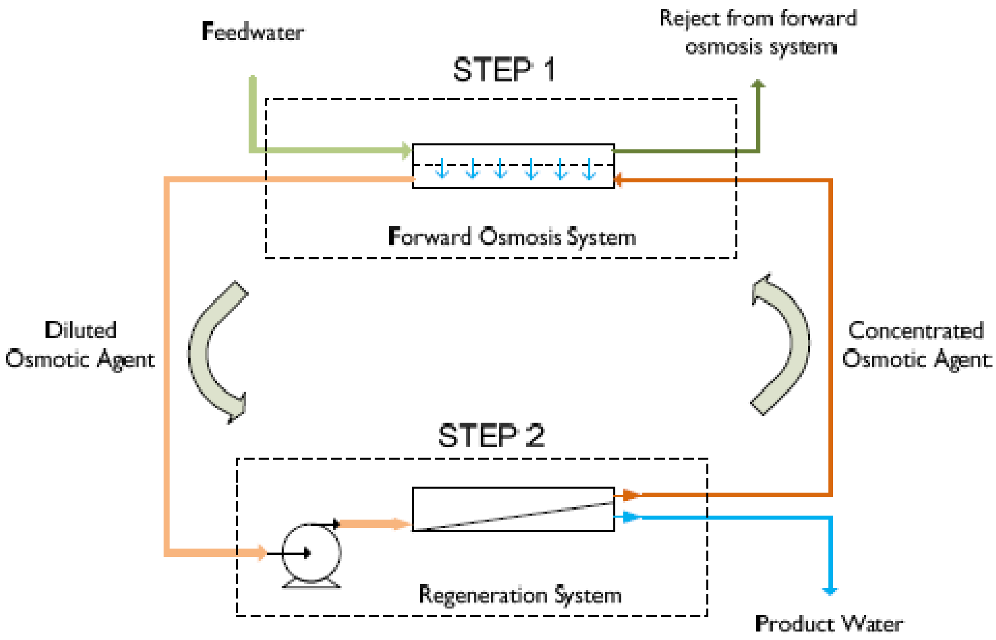


Figure (2.3): Basic FO/RO desalination process. Taken from (Nicoll, 2013)

The RO step is fed with a draw solution, which should be free of all particulates and membrane foulants given the FO step.

It is claimed that the process when used for desalination has a lower energy consumption than a reverse osmosis plant coupled with advanced pre-treatment including ultra-filtration, when operating on difficult feed waters. This is based on the different rates of irreversible performance decline for reverse osmosis depending on the feed water and where the RO step in the FO/RO combination can operate at higher recovery than the RO step alone. (Nicoll, 2013) have reported results from three FO/RO plants located in Gibraltar and Oman (Figure 2.4), two of which operate as commercial desalination plants. Figure 2.4 shows Modern Water's first forward osmosis plant in Oman was the 100 m^3/day at Al Khaluf.

Figure (2.4): FO/RO desalination plant (100m^3/day) at AlKhaluf, Oman. (Nicoll, 2013)

Al Najdah plant is world’s first commercial forward osmosis desalination plant. The site is located approximately 450km south of Muscat in Oman and is in a harsh and hostile environment for plant and equipment as well as the operations staff. In addition, the source water is poor quality and has a TDS of 55,000mg/l making it difficult to treat. Figure 2.5 shows world's first commercial scale forward osmosis plant at Al Najdah in Oman.

Figure (2.5): Al Najdah desalination plant (200 m^3/day) at Al Najdah in Oman. (Nicoll, 2013)

Modern Water is set to build a first forward osmosis (FO) desalination plant with capacity 500 m^3/day in Xugong Island, China.

All FO desalination processes can be classified into two types according to the differences of final water generation methods. One method of FO desalination employs thermolytic draw solutions which can be decomposed into volatile gases (e.g. CO_2 or SO_2) by heating after osmotic dilution. Drinking water can be recovered and the gases can be recycled during the thermal decomposition. In a patent, McGinnis (McGinnis, 2002) described a novel FO method using a combination of draw solutes (i.e. KNO_3 and SO_2) for seawater desalination. This takes advantage of the temperature-dependent solubilities of the solutes: namely the fact that saturated KNO_3precipitates out of the diluted draw solution after cooling. The diluted KNO_3 solution is then fed into another FO unit in which dissolved SO_2 serves as the draw solute. After osmotic dilution, the dissolved SO_2 can be removed by standard means (i.e. heating). (McCutcheon et al., 2005) proposed another novel method using a mixture of CO_2 and NH_3 as the draw solutes for desalination. The resultant highly soluble and thermolytic ammonium bicarbonate (NH_4HCO_3) draw solution can yield high water fluxes and result in high feed water recoveries.

The other type of FO desalination uses water-soluble salts or particles as the draw solutes, and fresh water is generated from the diluted draw solution by other methods. (R.A. Khaydarov and R.R. Khaydarov, 2007) proposed utilizing solar power to produce fresh water from the diluted draw solution after osmotic dilution. (Choi et al.,2009) proposed using a pressure-assisted FO process (i.e. using low hydraulic pressure on the feed side) for seawater desalination, yet no final water generation method was suggested. (Tan and Ng, 2010) investigated seven draw solutes (i.e. NaCl, KCl, $CaCl_2$, $MgCl_2$, $MgSO_4$, Na_2SO_4 and $C_6H_{12}O_6$) for seawater desalination using a hybrid FO–NF system. (Ling et al., 2011) used hydrophilic nanoparticles as the draw solutes for desalination and the nanoparticles could be regenerated by UF . (Zhao, Zou and Mulcahy, 2012) proposed using divalent salts (e.g. Na_2SO_4) as the draw solutes for brackish water desalination because the diluted draw solution could be recovered via NF. (Cath, Hancock, Lundin, Hoppe-Jones, and Drewes, 2010) employed FO as an osmotic dilution process using seawater as the draw solution for impaired water purification in a hybrid FO–RO process. Similar FO–RO desalination systems were proposed to generate both potable water (Bamaga, Yokochi and Beaudry, 2009; Yangali-Quintanilla, Li, Valladares, Li, and Amy, 2011) and the osmotic power of RO brine (Bamaga, Yokochi, Zabara and Babaqi, 2011). In these combined FO–NF or FO–RO processes, FO offers several major benefits, including high quality of drinking water due to the multi-barrier protection, reduced RO fouling because of the pre-treatment by FO, recovery of osmotic energy of RO brine, low energy input and no need for chemical pre-treatment. In fact, the FO process acts as a pre-treatment process (i.e. osmotic dilution) in the second type of FO desalination. To get fresh water, further water recovery methods must be used to desalinate the diluted draw solution.

Further, FO has also been proposed for brine concentration. Desalination brine has become a critical environmental concern in desalination plants, especially for inland communities, where brine discharge sources are not always available. (Tang and Ng, 2008) investigated the effects of membrane structure on FO performance during brine concentration. (Martinetti, Childress and Cath, 2009) found that high recoveries (up to 90%) from concentrated RO brines could be achieved by FO.

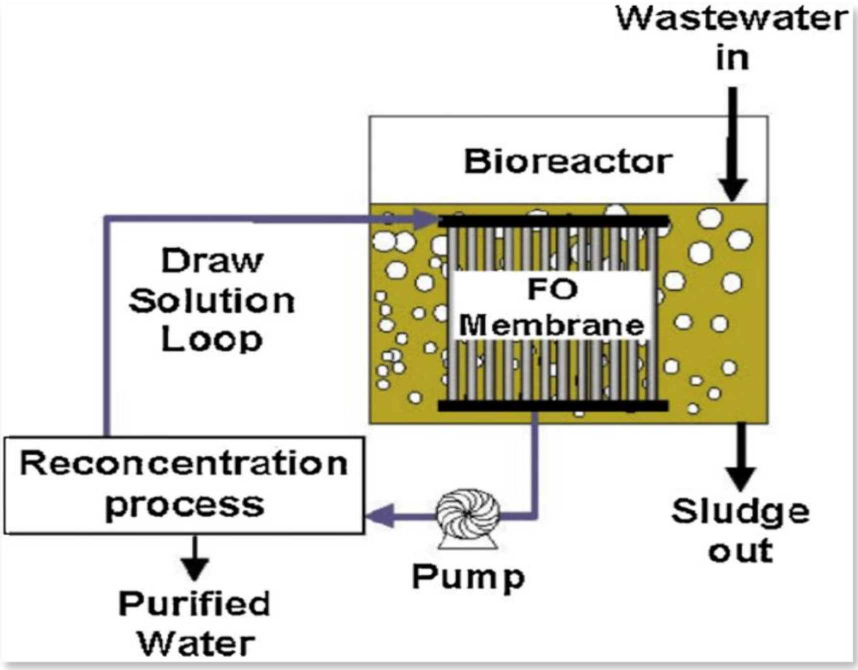
2.3.3. Wastewater treatment and the osmotic membrane bioreactor (OMBR)

Compared to seawater, general wastewater has lower osmotic pressure but much higher fouling propensity. Low fouling tendency is one of the most pronounced advantages of FO. Therefore, FO holds great promise in wastewater treatment. As early as the 1980s, the feasibility of using FO for industrial wastewater treatment was investigated (Votta, Barnett and Anderson, 1974). Seawater was suggested as the draw solution because of its low cost and high availability in coastal areas.

Recently, (Cath, Drewes and Lundin, 2009; Cath et al., 2010) employed a similar idea to produce drinking water using impaired water and saline water sources as the feed and draw solutions in FO, respectively. FO has several benefits for space missions, including high wastewater recovery, low energy cost and minimized resupply can be achieved in. FO membrane contactors can also be used to remove natural steroid hormones from wastewater (Cartinella et al., 2006). Other investigations have been conducted using FO such as for the concentration of anaerobic digester centrate (Holloway, Childress, Dennett and Cath, 2007).

Another promising application of FO for wastewater treatment is in the FO membrane bioreactor, called the osmotic membrane bioreactor (OMBR). The OMBR system is illustrated in Figure 2.6 (Achilli et al., 2009). After osmotic dilution, the diluted draw solution is usually reconcentrated by a post-treatment process (e.g. RO) to produce fresh water. Due to minimized membrane fouling and thus reduced costs via OMBR in wastewater treatment, the commercialization of OMBR may be realized in the future. Recently, Xiao et al. have developed a salt accumulation model to investigate FO performance in OMBR (Xiao et al., 2011).

It is necessary to note that the FO step in wastewater treatment acts as a pretreatment process rather than the ultimate water production process. However, this FO pretreatment step can significantly reduce the membrane fouling, which is one of the most challenging problems in membrane processes for wastewater treatment, resulting in lower treatment costs.



Figure(2.6): Schematic diagram of an OMBR system. Figure taken from [Achilli et al., 2009].

2.3.4. Liquid food concentration

In the food industry, it is often necessary to remove water from liquid food to increase the stability, improve the shelf life and reduce storage and transportation costs. Compared with the conventional evaporative concentration techniques, FO can provide advantages in maintaining the physical properties (e.g. color, taste, aroma and nutrition) of the liquid food without deteriorating its quality (Petrotos and Lazarides, 2001). Therefore, FO has been widely used to concentrate various water-containing foods, including tomato juice (Petrotos, Quantick and Petropaki, 1999), mushrooms (Torringa et al.,2001), fruit juice (Garcia-Castello and McCutcheon, 2011), pears (Park Bin, Reis Brod and Brandini Park, 2002), carrots

(Uddin, Ainsworth and Ibanoglu, 2004), papayas (Garcia, Diaz, Martinez and Casariego, 2010), potatoes (Eren and Kaymak-Ertekin, 2007), apricots (Khoyi and Hesari, 2007), strawberries (Changrue, Orsat, Raghavan and Lyew, 2008), pineapples (Lombard, Oliveira,Fito and Andrés, 2008) and peppers (Ozdemir, Ozen, Dock and Floros, 2008). In these applications, FO acts as the osmotic dehydration process to remove water from the liquid food.

2.3.5. Pharmaceutical applications

In the pharmaceutical industry, FO has two types of applications: osmotic drug delivery and the enrichment of pharmaceutical products (Santus and Baker, 1995; Thombre, Cardinal, DeNoto, Herbig and Smith, 1999; Lin and Ho, 2003). Osmotic drug delivery systems are based on the principle of osmosis. There are many types of osmotic drug delivery systems, including tablets/capsules coated with semipermeable membranes containing micro-pores, polymer drug matrix systems.

The second application area of FO is in the enrichment of pharmaceutical products (e.g. protein and lysozyme). Similar to liquid food, generally these pharmaceutical products are heat sensitive and have large molecule sizes. Therefore, FO can bring some advantages over conventional chemical or thermal concentration methods. (Yang, Wang and Chung, 2009) used FO to enrich lysozyme solutions, and obtained products with high purity and without change or denaturing. (Nayak and Rastogi, 2010) employed FO to concentrate anthocyanin and found that FO had several advantages over thermal concentration in terms of higher stability and lower browning index. (Wang, Teoh, Nugroho and Chung, 2011) investigated an integrated FO–MD (membrane distillation) system for the enrichment of protein solutions. It is worth noting that in the fields of food and pharmaceutical product concentration, the concentrates of FO are the target products, which is quite different from desalination and wastewater treatment. Because there is no need to further separate water.

2.3.6. Others Applications

FO has also been proposed for many other applications. Talaat proposed that FO had the potential to be used for dialysis fluid regeneration (Talaat, 2010). Phuntsho et al. investigated the performance of using fertilizers as the draw solutes for direct fertigation (Phuntsho, Shon, Hong, Lee and Vigneswaran, 2011). The most pronounced benefit revealed by their study was that the diluted draw solution could be used for irrigation directly, without any separation. Additionally, FO-related products, like hydration bags have been commercially used for military, recreational and emergency relief situations (e.g. after earthquake) where reliable drinking water is scarce (Cath et al., 2006).

FO can also play an important role in the production of biomass energy and the protection of the environment (Hoover, Phillip, Tiraferri, Yip and Elimelech, 2011). FO has been proposed to generate biofuels by separating algae biomass (Zou, Gu, Xiao and Tang, 2011). A recent study has integrated FO in a novel way into microbial fuel cells for wastewater treatment, water extraction and bioelectricity generation (Zhang and Brastad, 2011). FO has also been proposed for use in the osmotic dilution of desalination brine before it is discharged into the sea, which will benefit the marine ecological system (Hoover et al., 2011). Employing FO as a means of membrane cleaning to reduce chemical use has been investigated in recent studies (Qin et al., 2010; Ramon, Agnon and Dosoretz, 2010).

2.3.7. Selection of the membrane orientation in different applications

All of the membranes used in FO applications are asymmetric. As a result, there are two membrane orientations, namely the membrane active layer facing the feed solution (denoted as FO mode) and the membrane active layer facing the draw solution (denoted as PRO mode). FO performances can be very different in the two membrane orientations (Gray, McCutcheon and Elimelech, 2006). A recent study has demonstrated that the selection of membrane orientation is primarily dependent on the feed solution component and the degree of concentration. Figure 2.7 shows the water flux decline in PRO and FO modes under membrane fouling as a function of feed concentration. When the feed solution has a higher fouling tendency, the water flux decline in PRO mode can be extremely significant and the isoflux point occurs relatively early (at a lower concentration). This implies that in many of the applications mentioned above wastewater treatment, membrane bioreactors, liquid food or protein concentration, and seawater desalination and brine concentration in which the feed solutions have higher fouling tendencies and/or higher salinities, FO mode may be more favorable. Conversely, PRO mode is preferable when the feed solutions have lower fouling tendencies and/or low salinities (e.g. brackish water desalination), or where intensive concentration is unnecessary (e.g. power generation) (Zhao, Zou, and Mulcahy, 2011).

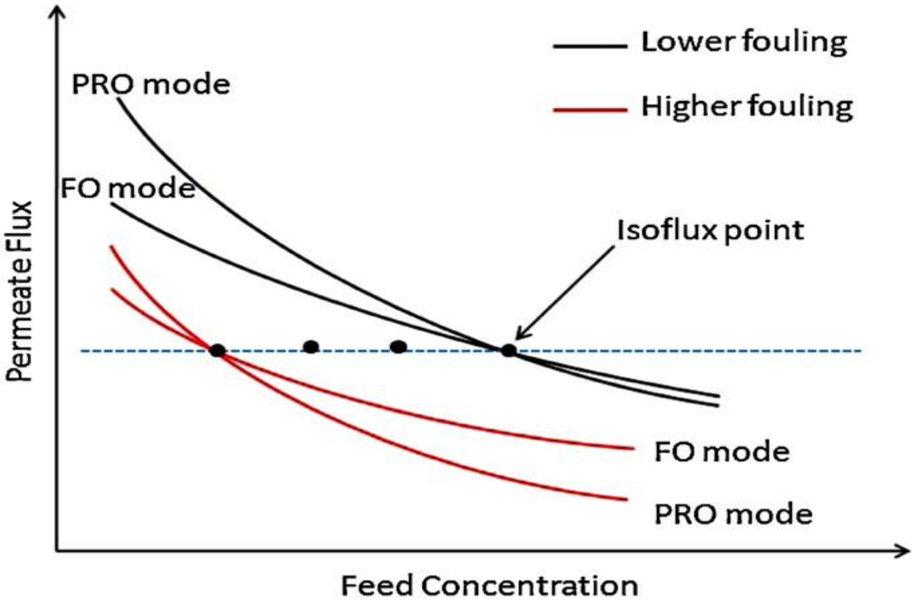


Figure (2.7): Comparison of the permeate flux in PRO and FO modes under membrane fouling as a function of feed concentration. Figure taken from (Zhao et al., 2011).

2.4. Membrane modules and devices

Different module configurations can be used to hold or pack membranes for FO.

2.4.1 Plate-and-frame

The simplest device for packing flat sheet membranes is a plate-and-frame module. Plate-and-frame modules can be constructed in different sizes and shapes ranging from lab-scale devices that hold single, small-size membrane coupons to full scale systems that hold more than 1700 membranes. While the design and construction of large plate-and-frame heat exchangers is well established, the construction of large plate-and-frame membrane modules is more complicated. Two of the main limitations of plate-and-frame elements for membrane applications are lack of adequate membrane support and low packing density.

Lack of adequate membrane support limits operation to low hydraulic pressure and/or operation at similar pressures on both sides of the membrane (requiring relatively high process control).

Low packing density leads to a larger system footprint, higher capital costs, and higher operating costs (labor for membrane replacement). Other limitations of the plate-and-frame configuration include problems with internal and external sealing, difficulty in monitoring membrane integrity, and a limited range of operating conditions (e.g., flow velocities and pressures) (Cath et al., 2006).

2.4. 2 Spiral-wound

The permeate stream flows very slowly in the channel formed by the two glued membranes and its composition and flow velocity are controlled by the properties of the membrane and the operating conditions. Therefore, in its current design, spiral-wound membrane elements cannot be operated in FO mode because the draw solution cannot be forced to flow inside the envelope formed by the membranes.

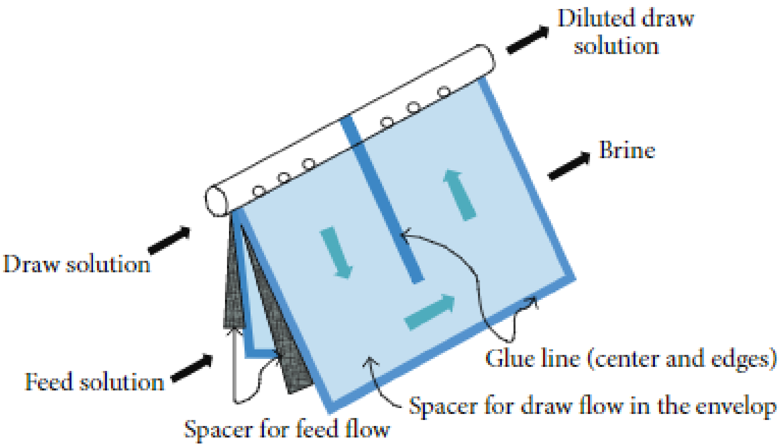


Figure (2.8): Schematic diagram of a spiral wound forward osmosis(SWFO) model showing the direction of water in the module.(Ali et al., 2016)

2.4.3 Tubular or hollow fibers

The use of tubular membranes (tubes or hollow fibers) for continuously operated FO processes is more practical for three main reasons. First, tubular membranes are self-supported. This means they can support high hydraulic pressure without deformation and they can be easily packed in bundles directly inside a holding vessel. Second, it is much simpler to fabricate tubular modules and packing density is relatively high. Third, these modules allow liquids to flow freely on both sides of the membrane a flow pattern necessary for FO.

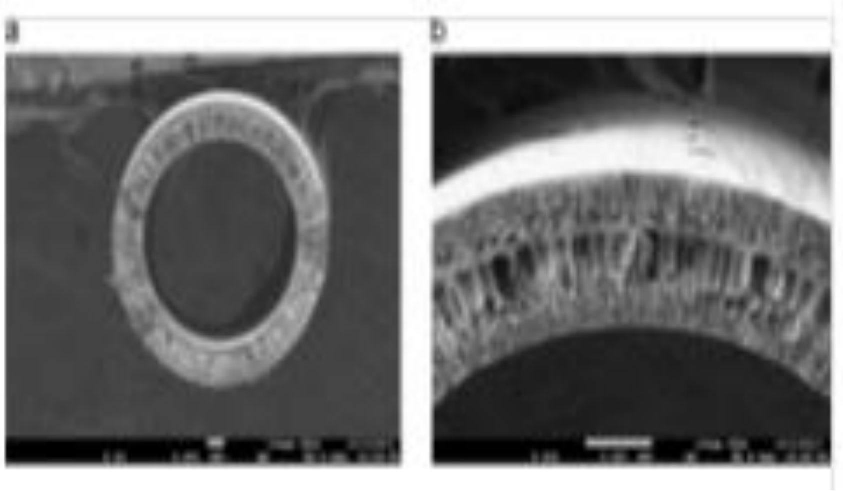


Figure (2.9): Morphology of PES hollow fiber substrate: (a) cross-section at 50; (b) enlarged cross-section at 200.(Fang et al., 2015)

2.4.4. Hydration bags

The hydration bag showed in figure 2.10 is another configuration of flat sheet FO membrane. It is a double lined bag; the internal bag is made of an FO membrane and is filled with draw solution (e.g., flavored sucrose) and the external bag is a sealed plastic bag containing the FO bag and the feed water to be treated.

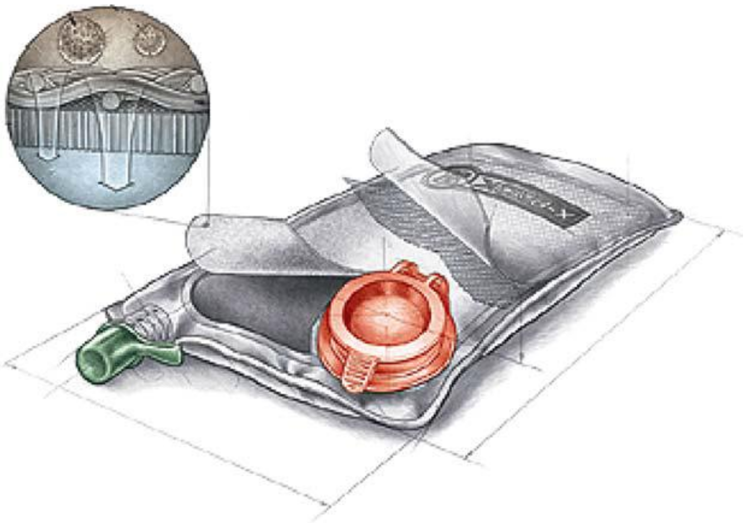


Figure (2.10): Illustration of water purification hydration bag(HTI company).

2.5 Challenges for FO

FO does not operate with hydraulic pressure but with osmotic pressure difference; thereby requires lower energy and is less susceptible to membrane fouling compared to traditional pressure-driven membrane processes like RO. Additionally, FO mostly allows fouling removal by physical cleaning without the need of chemicals (Achilli et al, 2009), higher removal of extensive range of ion contaminants (Zhang et al,2010), and higher water recovery (Martinetti` et al, 2009) over pressure-driven membrane processes. Despite FO possessing these favorable characteristics, there are several challenges faced by FO that limit its application in large scale processes. Some of these limiting factors include concentration polarization, membrane fouling, and reverse solute diffusion, which are governed by factors like membrane orientation (Zhao et al, 2012), inadequate membrane design (Tang et al, 2008), concentration and nature of draw and/or feed solution and operating conditions (temperature of feed/draw solute) (Wong et al, 2012).

2.5.1 Concentration Polarization

Concentration polarization (CP) is a phenomenon arising in all kinds of membrane separation processes, whether the process is pressure driven or osmotically driven. CP develops due to occurrence of concentration difference at the membrane-solution interface arising from selective transfer of species through a semi-permeable membrane (Hoek, Guiver, Nikonenko, Tarabara and Zydney, 2013). In membrane processes that are osmotically driven such as FO and PRO, CP arises due to concentration gradient between draw and feed solutions through an asymmetric FO membrane. CP arising in FO process can be further classified as internal concentration polarization (ICP), which occurs within the membrane support layer, and external concentration polarization (ECP), which exists at the membrane active layer surface.

In FO, the transmembrane osmotic pressure is chiefly responsible for controlling the water flux and recovery. Based on the extensive research conducted on CP, it was found that the occurrence of CP on both sides of FO membrane greatly reduces the effective transmembrane osmotic pressure; therefore, it is one of the major factors that contributes to declining water flux and recovery across the semi-permeable membranes (Gao, Wang, Li and Tang, 2014).

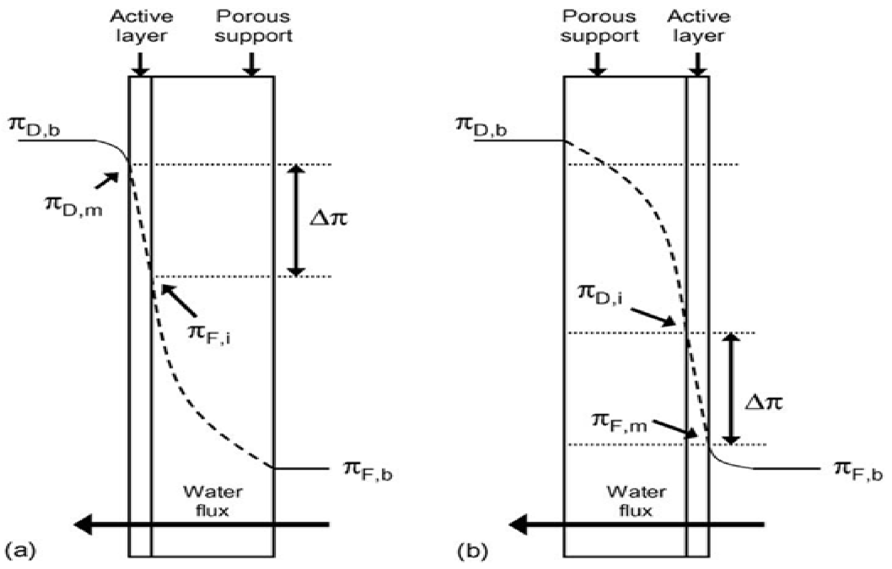


Figure (2.11): Illustration of both internal concentration polarization (ICP) and external concentration polarization (ECP) through an asymmetric FO membrane. ECP exist at the membrane surface while ICP occurs within the porous support.

(a) Active layer against the draw solution (AL-DS); the profile illustrates concentrative ICP and dilutive ECP.

(b) Porous support layer against the draw solution (AL-FS); the profile illustrates dilutive ICP and concentrative ECP.

($\pi_{D,b}$: bulk draw osmotic pressure, $\pi_{D,m}$: membrane surface osmotic pressure on the permeate side, $\pi_{F,b}$: bulk feed osmotic pressure, $\pi_{F,m}$: membrane surface osmotic pressure on the feed side $\pi_{F,i}$: effective osmotic pressure of the feed in AL-DS orientation, $\pi_{D,i}$: effective osmotic pressure of the draw solution in AL-FS orientation)

Two types of CP, namely external concentration polarization (ECP) and internal concentration polarization (ICP) (Cath et al,2006) can take place in FO processes. Generally, ECP exists at the surface of the membrane active layer and ICP occurs within the porous support layer of the membrane.

2.5.1.1 **External Concentration Polarization** (ECP)

ECP is a phenomenon that is common to both FO and RO. ECP occurs at the surface of the active layer of the membrane due to difference in the concentration of the solution at the membrane surface from that of the bulk solution. Unlike pressure-driven membrane process where only concentrative ECP can occur. The modeling results of FO desalination by Sagiv et al. through the coupling of hydrodynamics and mass transfer equations suggest that counter-current FO or allowing the membrane skin to face draw solution provides water flux improvements and decreased the cross transfer of solutes (Sagiv, Zhu, Christofides, Cohen and Semiat, 2014). Concentrative ECP takes place when the dense active faces the feed (FO mode) whereas, dilutive ECP occurs when the dense active layer faces the draw solution (PRO mode) due to diffusion of water from the side of the feed to that of the draw solution (Gao et al., 2014).

The effect of concentrative ECP is a reduced net driving force due to increased osmotic pressure at the membrane active layer interface on the feed side of the membrane. With dilutive ECP, osmotic pressure decreases at the membrane active layer surface on the draw solution side (Zhao et al., 2012). To minimize the accumulation of the rejected solutes on membrane surface, the cross-flow velocity or turbulence or velocity can be increased. Similarly, optimizing the water flux can mitigate the adverse effect of ECP (Cath et al., 2006). As such, ECP has lesser impact on FO performance than ICP.

2.5.1.1 Internal Concentration Polarization (ICP)

Internal concentration polarization (ICP) is a significant problem in FO, being the main cause for the reduced flux (McCutcheon et al,2006;Gray et al,2006).

Figure (2.12) shows two types of ICP occurring in the FO process under different membrane orientation.

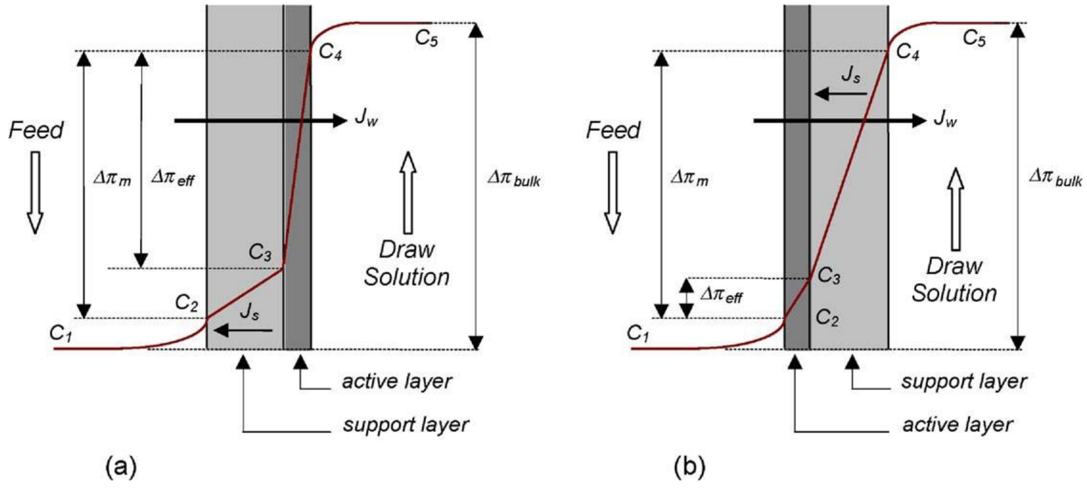


Figure (2.12): (a) Concentrative ICP and (b) Dilutive ICP across an asymmetric FO membrane. (Cath et al,2006).

Concentrative ICP happens when the active layer of the membrane faces the draw solution (AL- DS) (Liu et al,2009). In the AL-DS orientation, shown in Figure 2.12(a), solutes in the feed solution enter the porous support layer and transport to the active layer. Due to the dense active layer, solutes are unable to penetrate through, leading to a build-up of the solutes. The phenomena occur within the porous layer. In comparison to the bulk feed water concentration, C_f, a much higher concentration on the membrane wall, C_3, is formed. The profile in Figure 2.12(a) illustrates the effects of the accumulation; a lower effective osmotic pressure difference $\Delta\pi_{eff}$ across the active layer as compared to the apparent osmotic pressure difference $\Delta\pi_m$, causing a reduced flux.

In the active layer facing feed water (AL-FW) orientation; dilutive ICP occurs within the membrane support layer as water penetrates through the active layer and dilutes the draw solution (McCutcheon et al,2006). As illustrated in Figure 2.12(b), a decline in solute concentration happens from C_5 to C_4. This concentration decrease result in a reduced effective osmotic pressure difference, $\Delta\pi_{eff}$, and thus yielding a lower-than-expected water flux.

As ICP effects occur within the asymmetric membrane's porous support layer, it makes much difficult to control and minimize as it cannot be overcome by changing the hydraulics flow in the membrane unlike ECP (Gray et al., 2006). Since altering the hydrodynamic conditions cannot eliminate ICP, membranes need to be redesigned to suit the operation of FO system.

2.5.1.3 Modelling of ICP

According to classical solution-diffusion theory (Tang et al., 2010, Loeb et al., 1997), effect of respective ICP on the water flux (J_w) can be expressed(Loeb et al., 1997) by:

Concentrative ICP (AL-DS): $$J_w = \frac{1}{K}\left[ln\frac{A\pi_{draw} - J_w + B}{A\pi_{feed} + B}\right] \qquad \text{Equation (2.1)}$$

Dilutive ICP (AL-FS): $$J_w = \frac{1}{K}\left[ln\frac{A\pi_{draw} + B}{A\pi_{feed} + J_w + B}\right] \qquad \text{Equation (2.2)}$$

Where B is the solute permeability coefficient of the membrane, and K is the solute resistivity. K is a measure of solute transport into or out of the membrane support layer and it can reflect the degree of ICP in the support layer. Larger K values mean greater extent of ICP, leading to J_w decline. K is expressed (Liu et al., 2009) as:

$$K = \frac{t\tau}{\varepsilon D} = \frac{s}{D} \qquad \text{Equation (2.3)}$$

Where t is the membrane thickness, τ is the tortuosity, ε is porosity, s is the structural parameter and D being the diffusion coefficient of the draw solution. From equation 5, it is understood that both the membrane properties (the term $\frac{t\tau}{\varepsilon}$ or s) and characteristics of the draw solution (D) is an important intrinsic parameter of a membrane where it influences the ICP in the membrane support (Achilli et al., 2010).

To reduce the dominance of ICP, the only way is to limit flux or lower the solute resistivity, K. According to Elimelech's group (McCutcheon et al., 2006), diffusion coefficient of the draw solution need to be raised in order to lower the K value. This can be done externally by increasing temperature or changing the draw solute. In addition, tailored membrane with a more porous support layer or a smaller thickness can help lower K value.

2.5.2 Membrane fouling

Membrane fouling is significantly associated with all membrane processes and can adversely affect the performance of membranes and decrease the water flux across the membrane. An overview of the recent studies on FO membrane fouling is presented in Table 1 which found in appendix A.

2.5.2.1. Classification of membrane fouling

Similar to membrane fouling in RO (Tang et al., 2011), fouling in FO can be classified into four major groups according to the characteristics of foulants:

- Colloidal fouling – deposition of colloidal particles on the membrane
- Organic fouling – deposition and adsorption of macromolecular organic compounds on the membrane
- Inorganic scaling – precipitation or crystallization of sparingly dissolved inorganic compounds on the membrane; and
- Biofouling – adhesion and accumulation of microorganisms, and development of biofilm on the membrane.

2.5.2.2. Factors affecting the fouling

(1) Operating conditions, such as initial water flux, cross flow velocity, spacer, aeration, and temperature;

(2) Feed water characteristics, such as solution pH, ionic strength, and ionic composition (e.g., divalent cation)

(3) Draw solution composition, such as draw solution concentration and draw solute type

(4) Membrane properties, such as membrane separation and structural properties (i.e., A, B and S values), and membrane surface properties (e.g., hydrophilicity / hydrophobicity, roughness, charge density, surface functional groups); and

(5) Membrane orientation.

It is worthwhile to note that the DS composition and membrane orientation are unique for fouling in FO, while the other three groups are also applicape in pressure driven membrane process (Tang et al., 2011).

2.5.2.3 Fouling removal and membrane cleaning

2.5.2.3.1. Physical cleaning

The physical cleaning methods mainly include membrane surface flushing and membrane backwashing (Mi and Elimelech, 2010). The membrane surface flushing relies on an enhanced shear force (e.g., cross flow) along membrane surface to remove the deposited foulants, while the membrane backwashing is via reversing the water permeation direction and using the permeation drag force to detach and remove the deposited foulants on the membrane(Le-Clech, Chen and Fane, 2006). Both methods have been demonstrated to be effective against the membrane fouling under a variety of conditions.

2.5.2.3.2. Chemical cleaning

Chemical cleaning depends on the chemical reactions to weaken the adhesion force between foulants and membrane. For instance, (Mi et al., 2010) reported that the surface flushing was less effective for polyamide TFC membrane cleaning to the CTA membrane cleaning due to the stronger adhesion between alginate and TFC membrane. Also (Yoon, Baek, Yu and Yoon, 2013) found that the physical cleaning was not effective to recover the water flux when studying the biofouling of FO membranes. Instead, they found that chemical cleaning with chlorine could effectively mitigate the biofouling where membrane should be e highly chlorine resistant.

2.5.2.3.3. Biological cleaning

Biological cleaning has been developed to remove the foulant and recover the water flux. Biological cleaning involves the use of bioactive agents (e.g. enzymatic cleaning or biological predation) for foulant removal (Maartens et al., 1996]. A recent review on MBR cleaning reported three biological cleaning strategies: enzymatic cleaning, energy un coupling and quorum quenching. Briefly, enzymatic cleaning is the most widely used biological method for membrane fouling control (Wang et al., 2014).

2.5.3. Reverse solute flux

In osmotically driven membrane processes, reverse diffusion of the solute from the draw solution through the membrane to the feed solution is also inevitable because of the concentration differences. (Cath et al., 2006) suggested that the reverse diffusion of the draw solute must be considered carefully because it might jeopardize the process. Recent studies have correlated the reverse diffusion of the draw solute to membrane fouling. (Lay et al., 2010) and (Lee et al., 2010) have, respectively, demonstrated that reverse diffusion of the draw solute can enhance the CEOP effect and aggravate FO fouling. (Hancock et al., 2009) and (Cath et al., 2006) have presented the specific reverse solute flux or the fraction of the reverse flux of draw solute to the forward flux of water, as a measure of the selectivity of FO membrane . Apart from permeate flux and salt rejection, specific reverse solute flux is the third evaluation parameter for the FO performance. A higher ratio indicates a lower FO efficiency and a reduction in membrane selectivity. (Phillip, Yong and Elimelech, 2010) has demonstrated that specific reverse solute flux is dependent on the membrane selectivity but is unaffected by the membrane support layer structure and the draw solution concentration.

(Shibuya et al., 2015) reported that the reverse diffusion of permeate water and salt leakage leads to ICP in the porous support layer of commercial. They also evaluated three types of cellulose triacetate (CTA) hollow fiber forward osmosis membranes with diameters of less than 200 lm under various operating conditions i.e. draw solution concentration, cross flow velocity, membrane orientation, and temperature. High water flux-to-reverse salt flux ratios, more than 800 L/mol and higher than those of commercial membranes, were obtained for the CTA HF membranes. In general, reverse solute diffusion is one of the major challenges in FO and it should be fully taken into consideration and should be reduced during the future development of draw solutes and FO membranes.

2.5.4. Draw solutes/solutions advancement

In FO seawater desalination, saline feed water that contains lower solute concentration is sent to a semi-permeable membrane (separating agent). The driving force in this process is naturally created by the difference in osmotic gradient between the feed seawater and the draw solution. The tendency of the solvent to move across the membrane due to this osmotic gradient is what has given FO process an advantage over the conventional RO desalination. The benefits of using FO over RO are largely due to the lower energy cost for external pressure that is needed for RO and lower membrane fouling potential. This is why research in FO should be directed toward the building of highly efficient FO membrane and the development of high-performing draw solutions. Three major requirements should be met by an acceptable FO draw solution: high flux of water, simple recovery with low energy requirement, and minimal reverse solute diffusion (Ge et al., 2013). In addition, the draw solution must be non-toxic, inexpensive, membrane-friendly, and non-responsive to pH changes.

There are three main criteria for selecting a suitable draw solution for FO applications. First, the draw solution should have a relatively high osmotic pressure . Second, the diluted draw solution should be able to be easily and economically reconcentrated and/or recovered . Lastly, the draw solute should exhibit minimized ICP in the FO processes. Furthermore, other factors such as low cost, low reverse solute permeability, zero toxicity, no damage to the membrane, good biofouling-resistance, inertness and stability at or near natural pH should be carefully considered when selecting the draw solute/solution (Cath et al., 2006).

2.5.4.1 Type and classification of draw solute

There are different types of draw solutes that are categorized into organic-based draw solutes, inorganic-based draw solutes, and other compounds including emerging draw solutions such as magnetic nanoparticles (MNPs) and RO brines. These classifications can be sub-classified into ionic (electrolyte) and non-ionic (non-electrolyte) solutions based on whether the solution is made up of charged ions or if it is completely neutrally charged solutes. Some new draw solutions have been suggested recently (Zhao, Chen, Zhao and Lu, 2013). Ge and co-researchers have studied the use of sodium polyacrylate (PAA-Na) polyelectrolytes as FO draw solutes (Ge et al., 2012).

Over the past several decades, a variety of draw solutes/solutions has been investigated in osmotically driven processes. An overview of these draw solutes/solutions with different recovery methods is summarized in Table 2 which found in appendix B.

2.5.5 Membrane development

Since the 1960s, most studies on FO were carried out using RO membranes [84]. However, studies on development of membranes explicitly for FO applications were initiated before 2000. An overview of the recent advancements in FO membrane is presented in Table 3 which found in appendix C.

These newly developed membranes can be categorized into three types based on the fabrication methods: phase inversion-formed cellulosic membranes, thin film composite (TFC) membranes and chemically modified membranes.

2.5.5.1. Phase inversion-formed cellulosic membranes

Cellulose acetate (CA) has been widely used to prepare RO and FO membranes via phase inversion because of its unique advantages. In as early as 1959, (Reid and Breton, 1959) firstly observed that cellulose acetate films allowed much higher salt rejection than other polymers considered. Later, (Loeb and Sourirajan, 1963) had the breakthrough of preparing RO membranes via phase inversion using cellulose acetate polymer. Cellulose acetate has many advantageous characteristics such as:

- Relatively high hydrophilicity that favors high water flux and
- Low fouling propensity,
- Good mechanical strength, wide availability and
- Good resistance to degradation by chlorine and other oxidants.

However, the drawbacks of cellulose acetate (CA) must be fully considered before it is employed for the development of FO membranes. It is known that although cellulose acetate membranes are more hydrophilic and more resistant to chloride degradation compared with TFC polyamide RO membranes, they have poor resistance to hydrolysis and biological attach. In order to minimize the hydrolysis of cellulose acetate membranes, it is necessary to adjust the pH of the feed and draw solutions in the range of 4–6, and to maintain working temperature at not above 35◦ C (Geise et al.,2010).

2.5.5.2. Thin film composite membranes

Presently, commercially available FO membranes from HTI are TFC- membranes with multiple layers. The overall thickness of the first type of HTI^{TM} TFC membrane FO-1 is very thin i.e. approximately 50 lm; whereas, the second one indicated as FO-2, has a thickness greater than 100 lm. Both membranes are asymmetric and CTA based membranes (Zhang et al., 2010; Cath et al., 2006). Mostly FO-1 type membranes have been used for FO studies because they give greater water flux relative to the FO-2 type. On one side of FO-1 membrane, a thin selective layer exists, and there is a support layer on the other side. There is a polyester mesh between the layers to support the membrane mechanically. Similarly, according to the HTI patent, the structure of the FO-2 membrane consists of three layers: a polymeric skin layer (8–18 lm), a porous scaffold layer and a support fabric (Herron, 2008). FO-2 membrane provides a higher salt rejection but lower water flux than the FO-1 type.

2.5.5.3 Chemically modified membranes

chemical modification methods have also been used recently for synthesis of novel FO membranes. For example, synthesizing support layers using novel material such as incorporation of titanium dioxide nanoparticles (Emadzadeh, Lau, Matsuura, Rahbari-Sisakht and Ismail, 2014), carbon nanotubes (Amini, Jahanshahi, and Rahimpour, 2013) or zeolites (Ma et al., 2013) into the membrane have been shown to improve support layer structural features. A bio-inspired hydrophilic polymer (polydopamine or PDA) has been used by Arena et al. to coat and chemically modify the support layers of two commercially available TFC RO membranes to improve their hydrophilicity. The resultant modified membrane reduced ICP and increased hydrophilicity, which enhanced the membrane water flux in FO tests. Improvements in water flux by eight to fifteen times was shown by the modified membranes (Arena, McCloskey, Freeman and McCutcheon, 2011; Arena, Manickam, Reimund, Freeman and McCutcheon, 2014). As a result, the modification method will allow the existing TFC membranes to be used for all engineered osmosis applications. They suggested that the resultant FO membrane could be used in heavy metal removal because of its positively charged property. Recently, their group also developed a type of flat sheet membrane with a positively charged NF-like selective layer on a woven fabric embedded substrate via a similar method (Qiu, Setiawan, Wang, Tang and Fane, 2012).

Obviously, most of the current methods for the preparation of FO membranes are still conventional techniques that have been used for the preparation of pressure-driven membranes (e.g. RO and NF) for several decades. The development of new high performance FO membranes is still in its infancy. Therefore, borrowing the relatively mature methods of preparation of RO or NF membranes is a reasonable and feasible way to proceed. Future studies may further explore more newly developed techniques such as polyelectrolyte dip-coating (Miao, Chen and Gao , 2005; He, Frank, Mulder and Wessling, 2008), layer-by-layer assembly (Saren, Qiu, and Tang, 2011) and UV-photographing (Li, Zhu, Xu, Yi, and Zhu, 2011; Deng, Xu, Chen,Wei, and Zhu, 2011) for the preparation of high performance FO membranes. New membranes with double selective layers, polyelectrolyte multilayers or charged properties may be promising directions for some specific FO applications.

2.6. Assessment of membrane performance

FO performance assessment using the osmotic water and specific reverse solute fluxes will be more practical in the presence of ICP and membrane fouling. The three most important challenges to FO membrane performance are ICP, reverse solute diffusion and membrane fouling. Hence it is important to consider these factors when developing new FO membranes. Until now, not much research has been conducted to account for anti-ICP and antifouling requirements during membrane fabrication. It can be seen from Eqs. (1)–(3) that water flux through FO membrane is dependent on the membrane water and solute permeability, and structural parameter. Hence, evaluation of both K and S is required besides A and B for synthesis of a new FO membrane. Here, ICP is reflected by the solute resistivity (K), which considerably affects the FO water flux. Nevertheless, the effect of ICP in FO is found to very low or even negligible at low solution concentration(Zhao et al., 2011).

In FO the water flux is influenced by the water permeability, and the reverse solute flux is determined by the salt rejection (permeability) of the membrane. There is a strong trade-off between the water permeability and salt rejection (Wei et al., 2011). Generally, a FO membrane with high water permeability also has high salt flux, and vice versa. Therefore, specific reverse solute flux, defined as the ratio of the reverse solute flux to the forward water flux, may be a better parameter to evaluate FO performance (Hancock et al., 2009; Qiu et al., 2012). It will be more reasonable to evaluate the FO performance via the specific reverse solute flux and the osmotic water flux when ICP and membrane fouling are present.

When characterizing a newly developed FO membrane in the future, it is necessary to consider the anti-ICP and anti-fouling properties in addition to the water permeability, the salt rejection (permeability) and the structural parameter. Specific reverse solute flux should also be evaluated. Additionally, good repeatability of fabrication of the FO membrane will be essential before it goes to commercialization (Zhao et al., 2012).

2.7. Relationships between the membrane challenges

The five key challenges in FO have been reviewed and discussed above. In fact, these challenges are not isolated, but closely related to each other. Figure 2.13 illustrates the relationships between ICP, reverse solute diffusion, membrane fouling, the membrane characteristics and the draw solute properties in FO. It can be seen that the membrane support layer should be as porous as possible to reduce ICP, and that the membrane active layer should be highly selective to decrease the reverse solute diffusion.

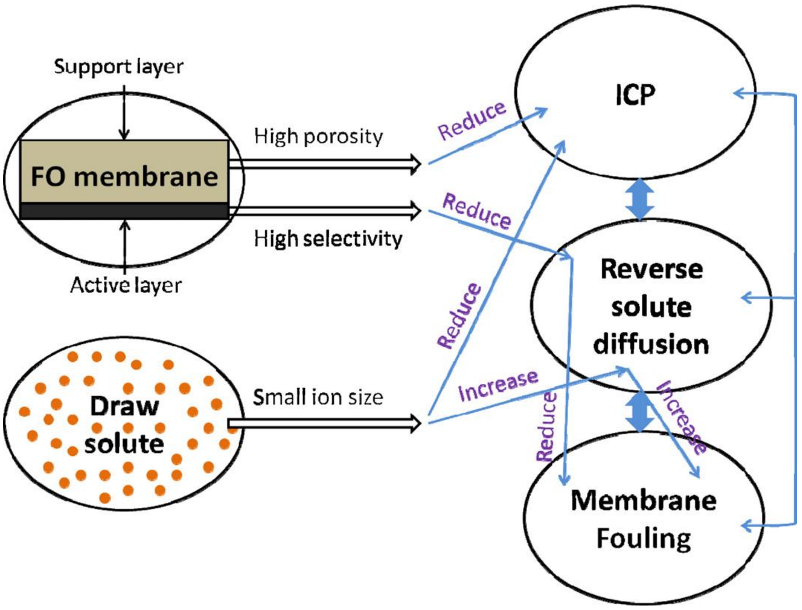


Figure (2.13): Relationships between ICP, membrane fouling, reverse solution diffusion, membrane characteristics and draw solute properties in FO(Zhao et al., 2012).

The minimized reverse solute diffusion can further reduce the membrane fouling. For the draw solute, small ion/molecule size can minimize ICP (Zhao et al., 2011), but it can also increase both the reverse solute diffusion and the membrane fouling. This makes the criteria for favorable draw solutes more critical. Generally, high reverse solute diffusion can cause severe membrane fouling, and vice versa (Lee et al., 2010; Lay et al., 2010). Further, ICP and membrane fouling may result in coupled adverse effects on water flux in FO (Tang et al., 2010). At the same time, ICP, reverse solute diffusion and membrane fouling are fundamentally determined by both the membrane characteristics and the draw solute properties.

2.8. Concluding remarks

Forward osmosis (FO) membrane process as an emerging technology has shown great potential in many applications such as power generation, desalination, wastewater treatment, food processing and dehydration of pharmaceutical products.

Thorough research and publications on FO for desalination, whether as an integrated process or in hybridization with other desalination technologies have been carried out, but to advance from experimental studies to actual commercial and economically viable implementations, the development of new and durable high performing draw solutes and membranes is essential to attain sustainable FO applications. breakthroughs in the development of both novel FO membranes and draw solutes. The membranes should have the characteristics of high water permeability and selectivity, minimized ICP. The desirable draw solutes should be able to induce high osmotic pressure, be regenerated/or recycled easily and economically, and minimize ICP. Additionally, the draw solutes must have zero toxicity and be compatible with the FO membranes. A desirable draw solute plays a key role in the popularity of FO applications. Further development of draw solutes will allow a wider application of FO in various practical fields.

Simultaneously, both draw solute properties and membrane characteristics essentially determine ICP, membrane fouling and reverse solute diffusion. Finally, the advancement of hybridized FO systems and incorporation of renewable energy into FO desalination for draw solution recovery and water production would enhance the sustainable applications of FO.

CHAPTER THREE

MATERIALS
AND
METHODS

CHAPTER (3)
MATERIALS AND METHODS

3.1 Materials

3.1.1 FO Experimental Apparatus

3.1.1.1 FO membrane

A flat sheet FO membrane module was used in this study. The flat sheet membrane module was YMAIM4205 FO-FS module made up of flat sheet thin film composite (TFC) with embedded polyester FO membranes (Aquaporin, Ole Maaløes Vej 3 / 2200 Copenhagen N / Denmark). The number 4205 refers to the effective membrane area 42cm^2 and the membrane is sealed in a protective plastic bag with 5 pieces. Membrane thickness 110µm ±15µm. Operating conditions of the membrane exposed to temperatures between 5-50^{o}C, as well as the rate of pH between 2-11. Membrane was operated with the feed water against the active rejection layer. The active side is marked by a label on the bag and can also be identified by the cut-off corner. If this corner is located on the lower right then the active side is facing up. The membrane can be stored at room temperature but preferably stored at 4^{o}C.

3.1.1.2 CF042D

A CF042D-FO membrane Cell (Sterlitech Corporation, Kent, WA, U.S.A.) was used as FO cell. The cell was illustrated in Figure (3.1).

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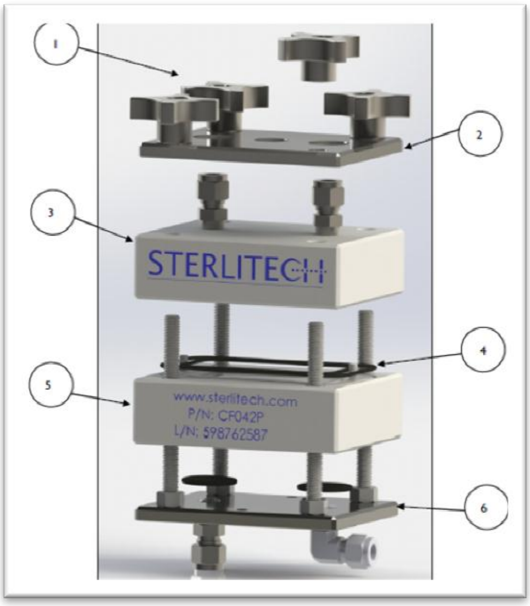
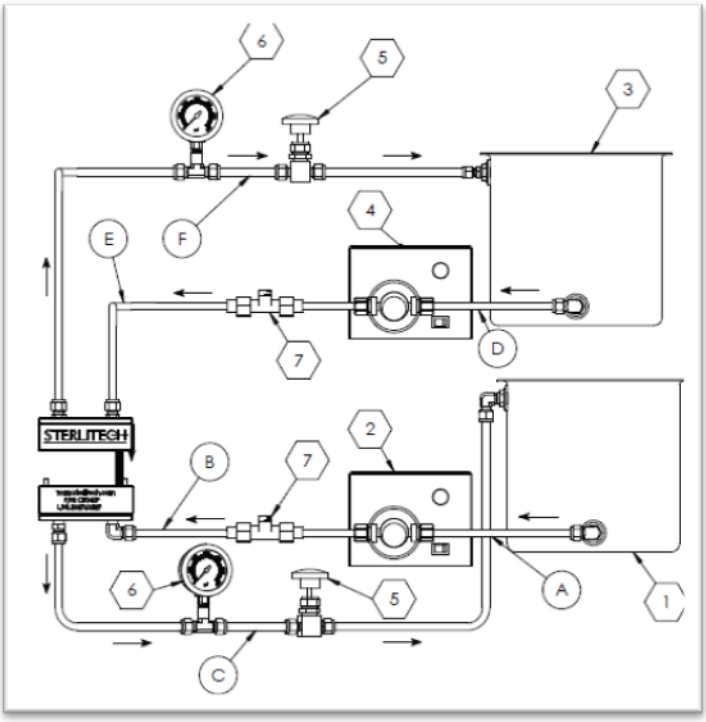


Legend:
1) Top knobs
2) Top plate
3) Cell Top
4) O-rings
5) Cell Bottom
6) Bottom plate with screws

Figure (3.1): CF042D-FO Membrane Cell

3.1.1.3 Facilities

The facilities used in the experiment consist of: pumps, tanks, pipes, valves, pressure gauges. Figure 3.2 shows the experimental diagram.



Legend:
1) Feed tank
2) Feed pump
3) Draw solution tank
4) Draw solution pump
5) Pressure control valve
6) pressure gauge
7) flow meter
A. Feed tank to the feed pump
B. Pump outlet to the feed inlet of the cell body
C. Feed outlet of the cell body to the concentrate collection tank/feed tank
D. Draw solution tank to the draw solution pump
E. Draw solution pump outlet to the draw solution inlet of the cell body
F. Draw solution outlet of the cell body to the draw solution collection tank

Figure (3.2): Experimental diagram of FO process

3.1.2 Feed solution (FS)

Real brackish water with different concentration of total dissolved solids [TDS], real sea water and solid sodium chloride (NaCl) which molecular weight 58.44 g. was diluted in deionized water to be a solution of sodium chloride. Each solution was measured electrical conductivity value by EC meter before and after the experiment of each batch.

3.1.3 Draw solution (DS)

Solid ammonium bicarbonate (NH_4HCO_3) which molecular weight 79.06 g. was used to prepare the draw solution was diluted in deionized water and used as draw solution (DS).

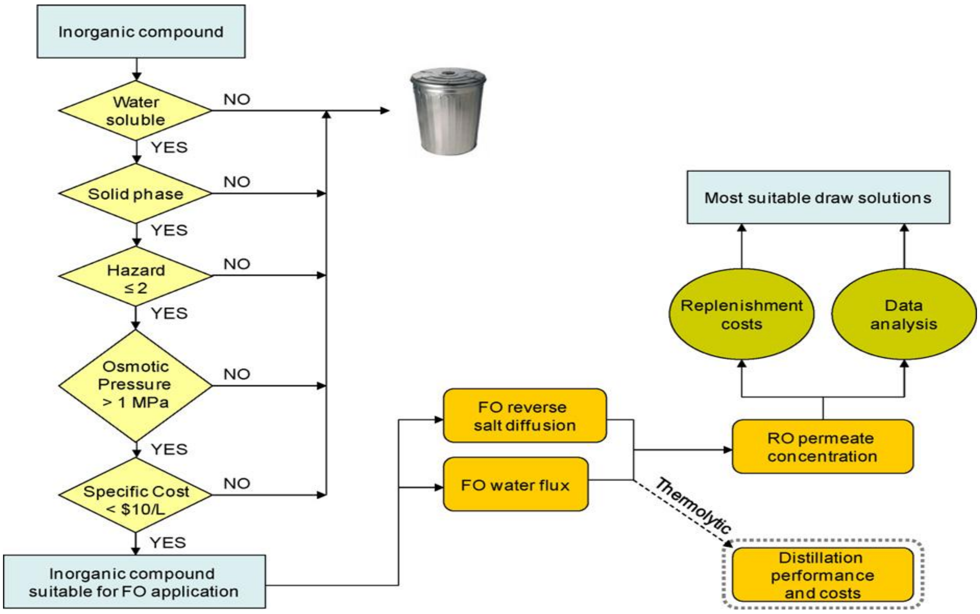


Figure (3.3): Illustration of flow diagram for draw solution selection. (Achilli et al., 2010)

Ammonium bicarbonate (NH_4HCO_3) has several characteristics. It has high solubility, low cost, easily recoverable in the reconcentration or recovery system, high osmotic pressure potential and non-toxic, it be used as high grade food fermentation agent. share with baking soda be used in bread, biscuit, battercakes, etc. Ammonium bicarbonate has cheap price and available in Gaza. Easily to extract from water by heating to a moderate temperature, can be obtained by heating using solar energy (solar heater).

Upon moderate heating (60^oC), ammonium bicarbonate decompose into ammonia and carbon dioxide gases that can be separated by heating process. Separated gases can then be used to regenerate the draw solution.

3.1.4. Lab-scale FO experiments

The schematic diagram of FO system configuration is shown in Figure 3.4 Brackish water/ seawater contacts one side of the FO membrane in a forward osmosis unit as the feed solution. A draw solution with high osmotic pressure contacts the other side of the FO membrane. The specially designed cross-flow membrane cell has symmetric channels on both sides of the membrane, each channel with dimensions of 2, 40, and 10mm for height, length and width, respectively. The temperature of FS and DS was fixed at 25 °C and two diaphragm pump (DP) were used to circulate feed solution (FS) and draw solution (DS) by fixing at 10 Psi (0.7 bar). The draw and feed solutions flowed co-currently in each channel on both sides of the membrane. During the operation, both the feed solution and draw solution were recirculated at 500 mL min^{-1}. The water flux ($l/m^2.h$) is calculated by the change in weight of the feed or draw solution. Figure (3.5) shows the image of lab - scale system for FO process.

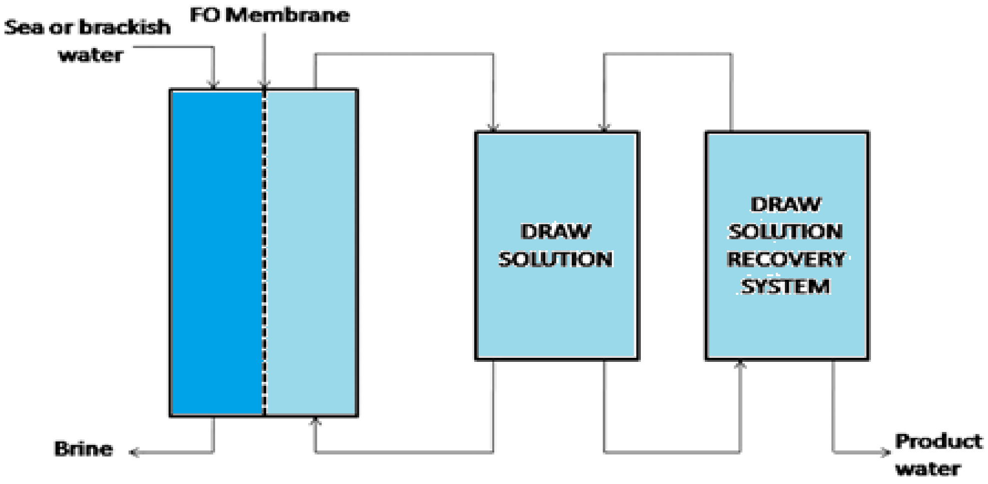


Figure (3.4): Schematic diagram of FO desalination process for potable water with draw solution recovery system.

Figure (3.5): The lab scale experimental system for FO process

3.1.5 Heat Recovery Unit

Ammonium bicarbonate (NH_4HCO_3)was removed from diluted draw solution by heating process at temperature 65 °C up to 5 hrs. Water bath with heater and thermostat ,flask filled with ammonium bicarbonate with various concentration, air blower was setting in heating process to activate the separation process of ammonium bicarbonate. condenser was set at the top of the flask to reduce water loss. The NH_3 and CO_2 were separated from the diluted draw solution and flowed into an adsorption flask containing deionized water to regenerate the draw solution. Ammonium bicarbonate concentrations of 0.1 M , 0.25 M, 0.5M and 0.75 M (7,900 mg/l - 19,750 mg/l 39,500 mg/l - 59,250 mg/l) was prepared by dissolving ammonium bicarbonate powder in deionized water in 1 L volumetric flask. Experimental equipment for thermal process shown in Figure (3.6).

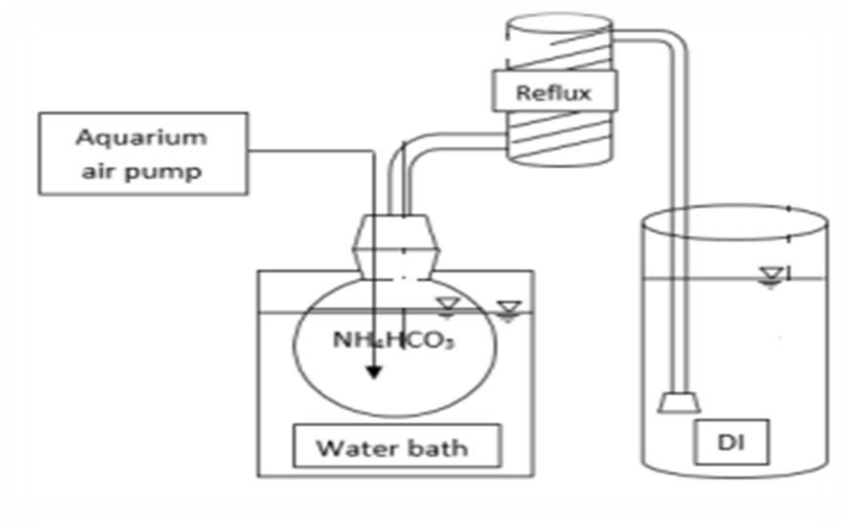


Figure (3.6): Schematic of heating process

3.1.6 Water Sample

3.1.6.1 Brackish water

Water samples were collected from different municipal wells in Gaza city. The water samples were collected based on PWA chemical tests results in 2015. Table (3.1) shows the selected wells and chemical analysis.

Table (3.1): Well sample chemical analysis (PWA, 2015)

Well Name Parameter	Rimal (3)	Rimal (4) PECDAR	Alshaikh Radwan(3)	Alshaikh Radwan (9)	Aljalaa
EC (μΩ/cm)	26000	24500	13910	3650	**7530**
TDS (mg/L)	16120	15190	8624	2263	**4669**
pH	7.2	7.3	7.76	7.44	**7.3**
Ca (mg/L)	598	724	768	172	**300**
Mg (mg/L)	583	615	401	119	**238**
Na (mg/L)	4390	4000	1662	382	**840**
K (mg/L)	110	9.6	15	4	**6.8**
Cl (mg/L)	8698	7946	4809	1005	**2222**
NO_3 (mg/L)	79	111	193	81	**69**
SO_4 (mg/L)	1119	870	403	46	**102**
Alkalinity (mg/L)	227	231	187	205	**198**
Hardness (mg/L)	3896	4345	3570	918	**1730**

3.1.6.2 Seawater

seawater samples were obtained from the main feed tank of Al Bassa Seawater Desalination Plant which is fed by a beach well in Deir El Balah city. Analyzed for different parameters as shown in Table (3.2).

Table(3.2): Measured of chemical and physical properties for seawater samples

Parameter	Unit	Concentration
pH	-	8.1
Conductivity	mS/cm	59
TDS	mg/l	37760
Cl	mg/l	20279
Na	mg/l	11780
Ca	mg/l	480
Mg	mg/l	1448
S	mg/l	2958
K	mg/l	445
B	mg/l	4.55

3.1.7 Research Chemicals

Chemicals for the research were mainly used for the preparation of the synthetic water and titration, listed in Table (3.3).

Table (3.3): Summary of research chemicals

Item	Description	Notes
Chemicals	- Sodium chloride: (NaCl), with purity 99.5%, - Ammonium Bicarbonate: (NH_4HCO_3), with purity 99.2%, - Hydrochloric acid: (HCl). - Sodium hydroxide: (NaOH). - Boric acid: (H_3BO_3), with purity 99%,	**Used as Feed Solution** **Used as Draw Solution** **For titration** **For synthetic water preparation**
Other materials	Deionized water which brought from the IUG labs.	**For simulated water samples preparation**

Effects of different operating parameters were investigated to quantify the performance of FO membrane for NaCl, nitrate and boron removal in the synthetic water samples as shown in Table (3.4).

Table (3.4): Summary of experimental parameters in FO process.

Experimental parameter	Ranges
NaCl concentration (mg/L)	5000 - 35000
NO_3 concentration (mg/L)	50 - 200
Boron concentration (mg/L)	3, 5 and 7

3.2 Experimental Methods

3.2.1 Laboratory tests and analysis

3.2.1. 1 Conductivity

The electrical conductivity (EC) of the solution was measured using conductivity meter (Microprocessor conductivity meter BODDS-307wW. To get TDS value we multiply EC by (0.64).

3.2.1.2 pH

The pH was measured with (pH/ORP/ISE Graphic LCD pH Bench top Meter , HANNA instrument) pH meter.

3.2.1.3 Nitrate Measurement

Standard method 4500-NO_3 nitrogen (nitrate) method was used in nitrate measurement. nitrate concentration was determined by CT-2600 Spectrophotometer

3.2.2 Measurement of FO performance

3.2.2.1 water flux

FO performance of membrane was evaluated with a cross-flow FO setup at room temperature. An effective membrane area, A_m of 42 cm^2. The water flux of the FO membranes was determined by measuring the weight changes of the feed solution. Water flux, J_W can thus be determined (Zhao et al., 2012).

$$J_W = \frac{\Delta\, weight}{water\ density \times effective\ membrane\ area \times \Delta time} \qquad (3-1)$$

Where :

J_W Water flux

Δ weight changes of draw solution weight

Δ time is the measured time interval.

3.2.2.2 Recovery Rate

Recovery rate is calculated using equation (3-2).

$$Y = \frac{Q_P}{Q_f} \times 100 \qquad (3-2)$$

Where:
Y: recovery rate.
Q_P: permeate flow rate.
Q_f : feed flow rate.

3.2.2.3 Rejection rate

Rejection rate is one of the most important characteristics of the membrane. It has the same meaning of removal efficiency that it represents the ability of membrane to reject salts from feed water. Rejection rate depends on the feed water characteristics, membrane characteristics. Rejection rate was measured using equation (3-3).

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \qquad (3-3)$$

Where:
R: Rejection rate (%)
C_p: Salt concentration in permeate (mg/l).
C_f: Salt concentration in feed water (mg/l).

3.3 FO experimental procedure

1- The lab scale of FO membrane desalination system was fixed as shown in figure (3.5).

2- FO flat sheet TFC membrane gathered in the membrane cell.

3- Prepare the samples for FS & DS in order to do the required experiments and measured pH, conductivity , concentration, weight and volume for each sample.

4- The pressure controlled on 0.5 bar, which recommended from the manufacturer.

5- Turn on the system for 180 minutes for each experiment.

6- After each test the following data recorded:

- Permeate flow water.

- Concentration for feed and draw solution (pH, conductivity, TDS).

- Volume and weight for feed and draw solutions.

7- TDS & NO_3 and B concentrations were measured at the labs. Flux rate, recovery rate and rejection rate were calculated.

8- The membrane was cleaning After 24-h FO permeation with deionized water for cleaning at a cross-flow rate for 20 min , then use another water sample and doing another experiment.

CHAPTER FOUR
RESULTS
AND
DISCUSSION

CHAPTER (4)
RESULTS AND DISCUSSION

4.1 General

This chapter discuss the characteristics of the desalinated water that is produced by using FO membrane. The characteristics of water flux, recovery rate and salt rejection were also investigated.

4.2 First Set of Experiments

In this set of experiments, the performance of FO membrane was measured for each experiment by using deionized (DI) water for water flux and recovery rate. The process was repeated using different concentrations of NaCl solution (0.085M - 0.17M - 0.25M or 5,000 - 10,000 - 15,000 mg/l) and NO_3 solution with different concentrations (50 - 100 – 150- 200 mg/l) as feed solution (FS). Each experiment was carried out with different ammonium bicarbonate (NH_4HCO_3) concentrations as draw solution (DS) from (0.5 to 1.5M or 39,530 to 118,600 mg/l) and applied constant pressure of 0.5 bar. Details of flux and recovery rate of DI water and NaCl solution are listed below:

4.2.1 Effect of DS concentrations

4.2.1.1. Deionized (DI) : Water Flux

Water flux is a key performance parameter for FO membrane and it decreases with FO operation because of the decreased osmotic pressure due to draw solution dilution/feed solution concentration and reverse salt flux.

Using DI water, the water flux rate of the FO membrane was measured under different NH_4HCO_3 concentrations as draw solution (DS) from (0.5 to 1.5M) by applied pressure of 0.5 bar. The obtained permeate flux values for examined membrane and their dependence on the DS concentrations are presented in Figure (4.1). The relationship between the water flux and the DS concentrations is logarithmical relation with high correlation coefficient ($R^2 = 0.99$), from Figure (4.1) it is clear that increasing of DS concentration leads to increasing the flux. It is clearly noticeable that the DI water flux rate ranges between 4.65 to 10.44 L/m^2.hr.

4.2.1.2 NaCl Solutions

4.2.1.2.1 FO with NaCl Solutions (0.085M - 0.17M - 0.25M)

In this section, the performance of FO membrane for water flux and recovery rate using synthetic brackish water were measured. Synthetic water is prepared with NaCl solution with different concentrations (0.085M - 0.17M - 0.25M) used as FS and NH_4HCO_3 solution with different concentration varied between (0.5–1.5M) used as DS with applied constant pressure of 0.5 bar.

Water flux of the FO membrane was evaluated using synthetic saline water (NaCl feed solution) with concentrations ranging from 0.085M to 0.25M. Four series of different concentrations of NH_4HCO_3 as draw solution (DS) varied from 0.5 to 1.5M were tested for each experiment on FO membrane to compare their results with the results of another run using real brackish water that has a various TDS concentrations ranging from 2500 to 16000 mg/l.

The results were summarized in Figure (4.1) show that the water flux increases with the increase of draw solution concentration.

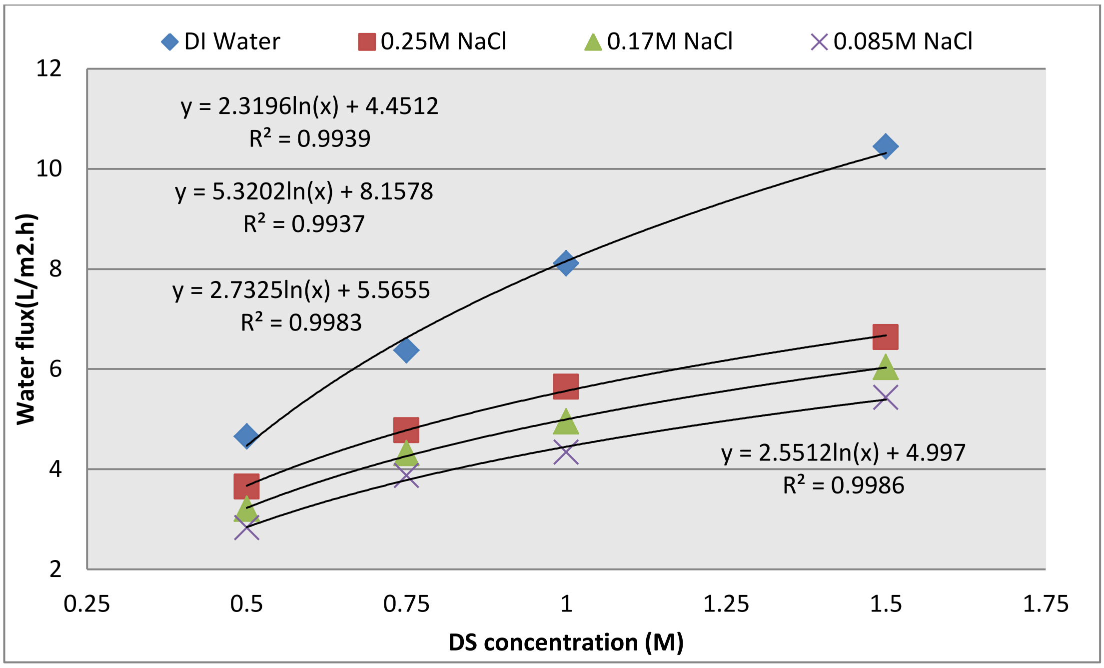


Figure (4.1): Effect of NH_4HCO_3 concentrations on the water flux for DI water and different NaCl solution concentrations.

It was observed from figure (4.1), that there is a logarithmic relationship between water flux and DS concentration with high correlation coefficient (R^2= 0.99). It is noticed that water flux for DI water is higher than that of the NaCl solutions. An increasing of water flux for DI water comparing with NaCl solution, for example, when draw solution concentration 0.5 M, the flux rate was 4.65 L/m^2.h with deionized water, while with the same draw solution concentration flux rate was 3.56 L/m^2.h for 0.085 M NaCl solution concentration. This increasing in flux due to the increases in draw solution osmotic pressure.

(Hemiri, Sharif, and Hussein, 2009) proposed that FO performance for water flux reach 8 L/m^2.h by using NH_4HCO_3 as draw solution with concentration 80,000 mg/l and NaCl solution as feed solution with concentration 2,500 mg/l.

4.2.1.3 Recovery Rate

The recovery rate is the ratio of the permeate flow rate of draw side to the flow rate from feed side. Figure (4.2) shows the relationship between the recovery rate and draw solution concentrations for deionized (DI) water and NaCl solutions. It is noticed that the recovery rate increase with the increase of the DS concentration.

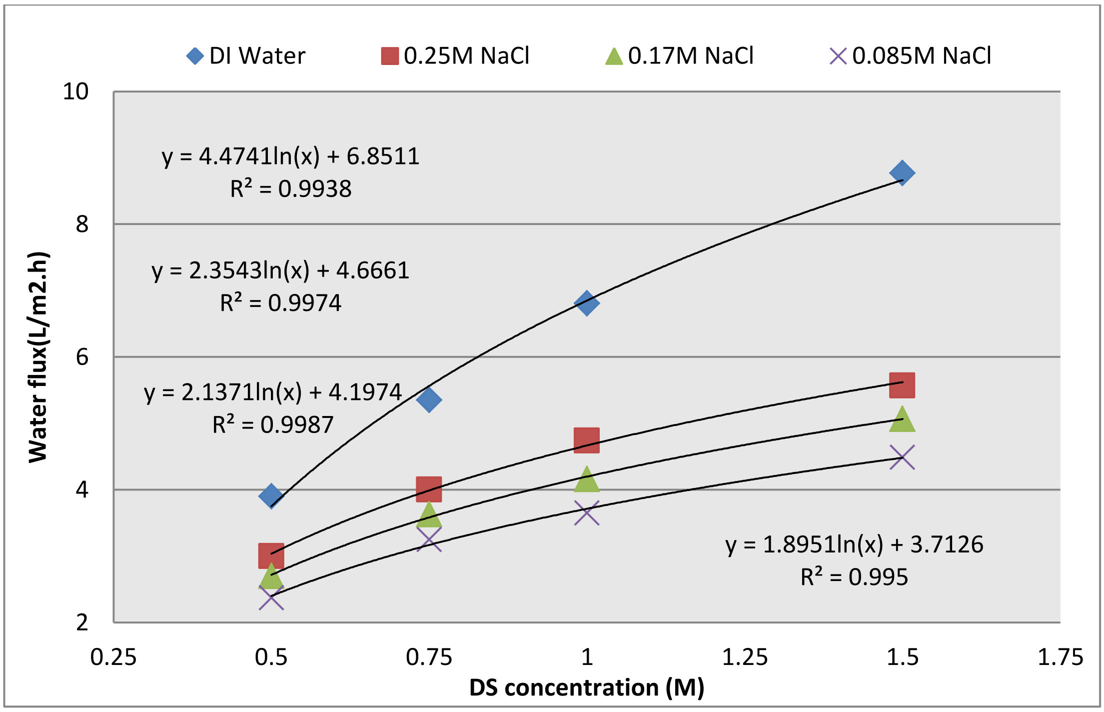


Figure (4.2): Effect of NH_4HCO_3 concentrations on the recovery rate of deionized (DI) water and different NaCl solution concentrations.

4.2.2 Membrane performance with NO_3 Solution for flux and recovery rate

Different concentrations of nitrate solution were prepared, varied between 50 to 200 mg/L. The flux rates of the solutions were measured at different NH_4HCO_3 concentration used as draw solution (DS); in order to investigate the effect of these concentrations on water flux and recovery rate for nitrate solution.

4.2.2.1 Effect of DS concentration on water flux and recovery rate

4.2.2.1.1 Water Flux

The results showed that the water flux rate increase logarithmically by the increase of the DS concentrations as shown in Figure (4.3).

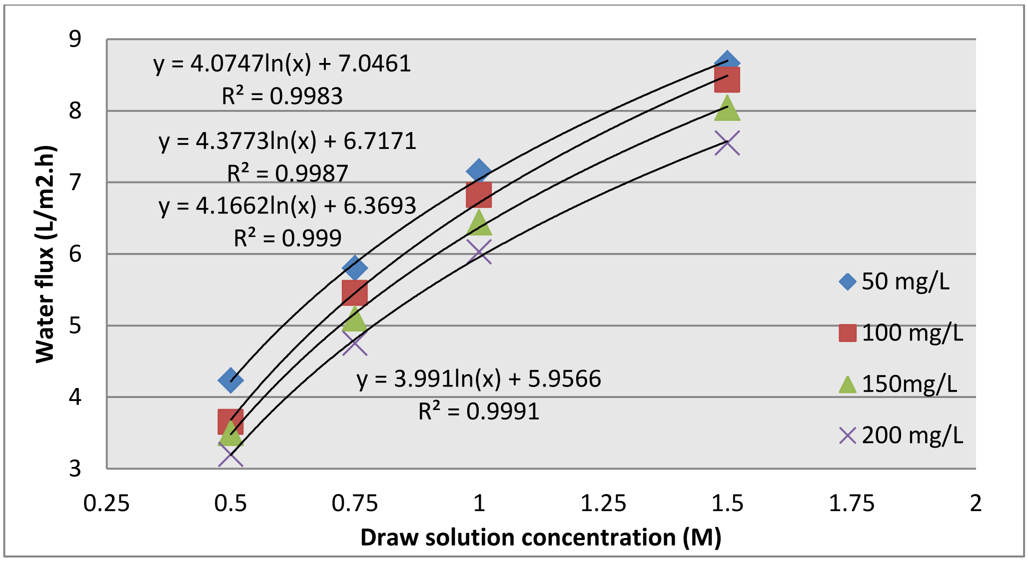


Figure (4.3): Effect of NH_4HCO_3 concentrations as draw solution on the flux for different nitrate solution concentrations.

It is clear from Figure 4.3 illustrate the relationship between initial Nitrate concentration and water flux. The results show that the water flux increase when the nitrate concentration decrease and DS concentration increase. In Figure 4.4 it is observed the effect of initial nitrate concentration on the water flux by the membrane. It is observed that when the nitrate concentration increase the flux rate decrease.

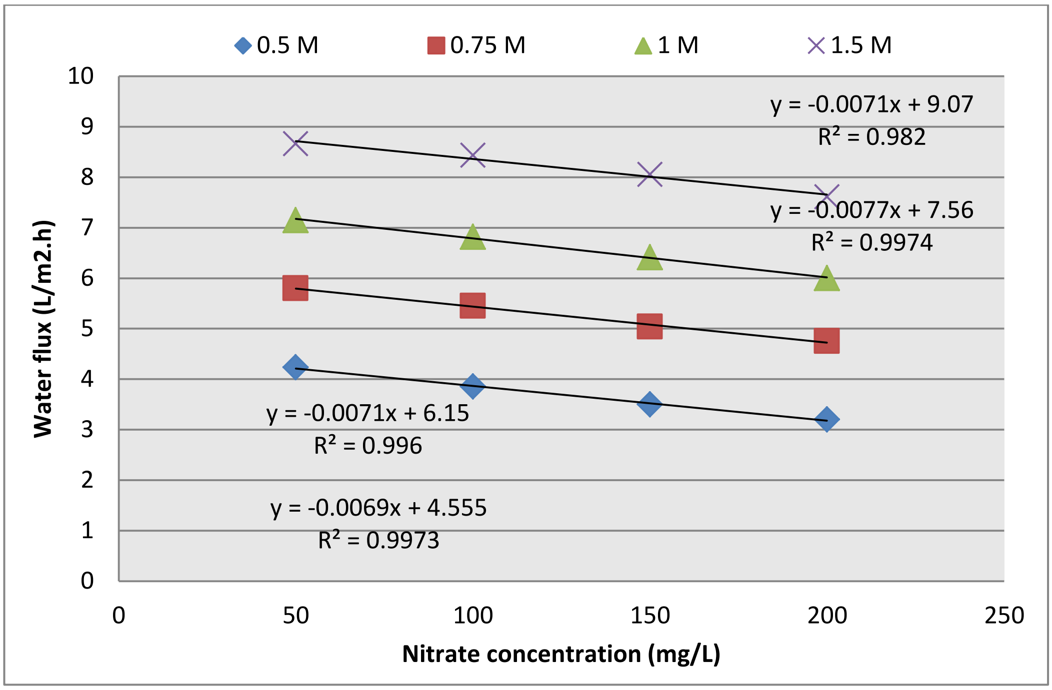


Figure (4.4): Effect of feed Nitrate concentration on water flux with different NH_4HCO_3 concentrations.

4.2.3.1.2 Recovery Rate

Figure (4.5) shows the relationship between the recovery rate and draw solution concentrations. It is noticed that the recovery rate increase with the increase of DS concentration.

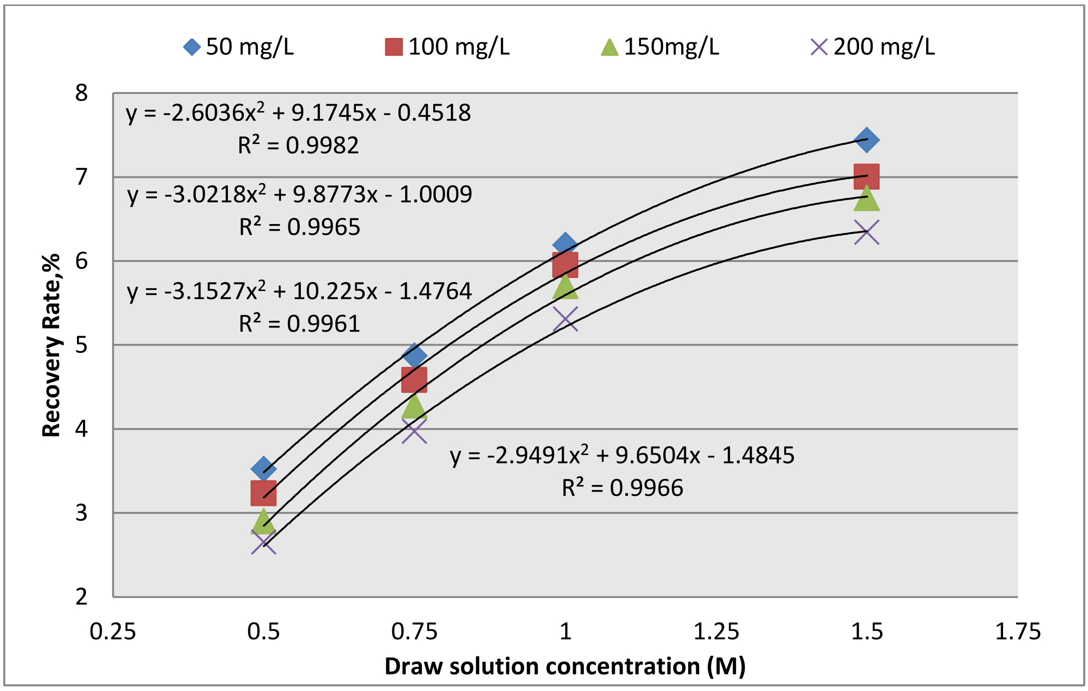


Figure (4.5): Effect of DS concentration on recovery rate of nitrate solution concentrations.

4.3 Second Set of Experiments

In this set, we investigate the performance characteristics of FO membrane using ion rejection for different NaCl and Nitrate solution concentrations by using different DS concentrations.

4.3.1 Membrane performance with NaCl Solution for rejection rate

The rejection rate of NaCl solution with concentrate 0.085M (5000mg/l) for the membrane was investigated with different DS concentrations as shown in Figure (4. 6). The results show that the rejection rate decrease with an increase of DS concentrations (exponential relation with R^2=0.98). The salt rejection was slightly decrease to 98.75%.

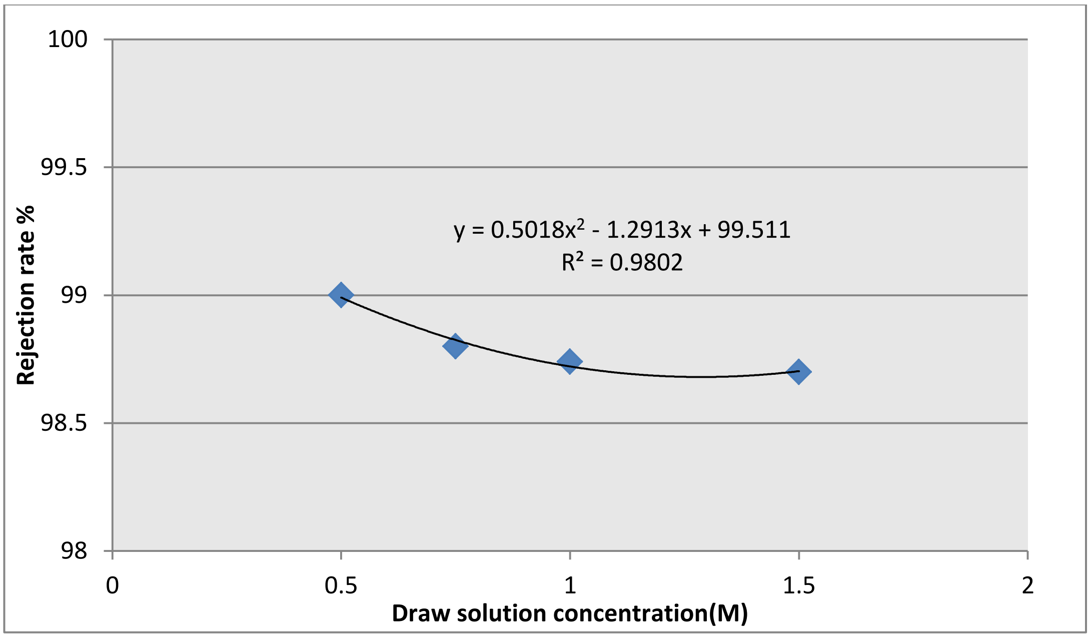


Figure (4.6): Effect of DS concentrations on NaCl rejection for the membrane

4.3.2 Membrane performance with Nitrate Solution for rejection rate

The Nitrate removal of solutions at different NH_4HCO_3 solutions concentrations were measured. The results summarized in Figure (4.7) show the relation between nitrate rejection at different NH_4HCO_3 solutions concentrations as DS and different nitrate concentrations.

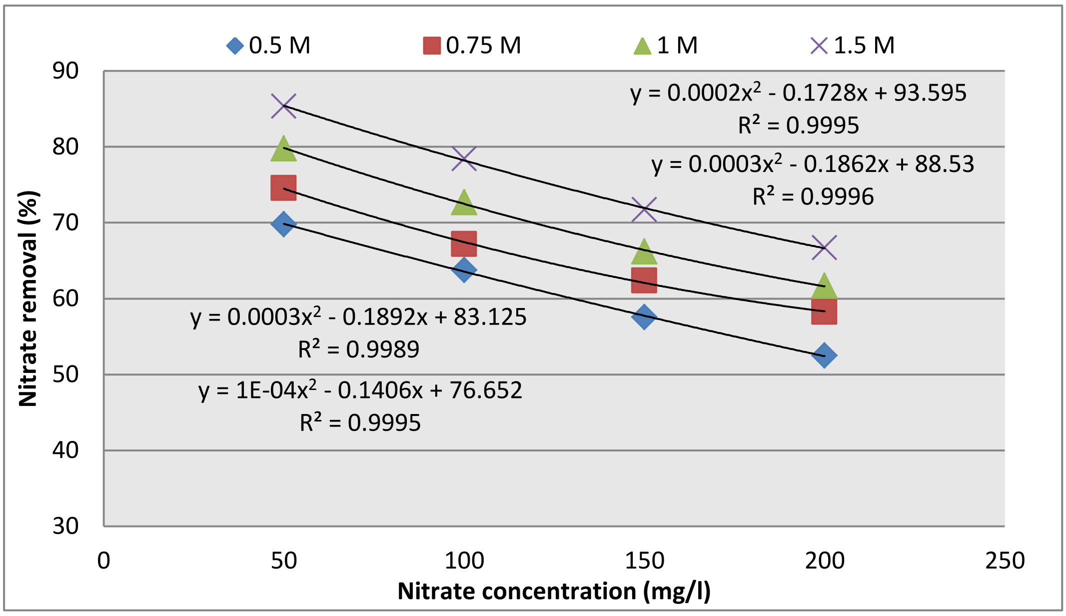


Figure (4.7): Effect of initial nitrate concentrations on nitrate rejection at different (NH_4HCO_3) concentrations for the membrane.

4.4 Third Set of Experiments

In this set, FO membrane water flux and recovery rate were evaluated using real brackish water with different TDS concentrations as feed solution. Ammonium bicarbonate solution using as draw solution with different concentrations.

4.4.1 Membrane Performance in Real Water

In this section, the performance of FO membrane for water flux, recovery rate and nitrate removal of real brackish water were evaluated and compared with aqueous solution. Four well samples were collected from different places from Gaza City. TDS concentration of the samples varied in the range of 2500-16000 mg/L and Nitrate varied from 70 - 200 mg/l. DS concentration varied between (0.5 to 1.5M) with applied constant pressure of 0.5 bar.

4.4.1.1 Effect of DS concentration on flux and recovery rate

Figures (4.8a,b) illustrate the effect of the NH_4HCO_3 solution concentration as DS on the flux and recovery rate using four random samples selected from water wells (Radwan9, Aljalaa14, Radwan A3, Remal 4 Becdar). The TDS concentration in these samples ranges between (2500-16000) ppm and the nitrate concentration in these sample ranges between (70-200) ppm.

As observed in Figures (4.8a,b) the flux and recovery rate is directly proportional to the DS concentration as in the case of the aqueous solution observed in section 4.2. The maximum flux and recovery rate observed at 1.5 M in Radwan 9 well, and minimum flux at 0.5M in Remal 4 Becdar well. It was observed that Radwan 9 well sample contains the lowest TDS concentration its 2428 ppm, and Remal 4 Becdar well sample contains highest TDS concentration (15200 ppm). Therefore, the TDS concentration has influenced the flux rate as discussed in section 4.4.1.2.

Table (4.1) shows the water flux of well samples at different NH_4HCO_3 concentration as (DS) for all the four well samples. The maximum flux was 6.63 L/m^2.hr with recovery rate 5.6% obtained at Radwan 9 well using DS concentration 1.5 M. The minimum flux was 2.35 L/m^2.hr with recovery rate 2 %, obtained at Remal 4 Becdar well using DS concentration 0.5 M.

Table (4.1): Relation between the water flux and DS concentration for well samples

Well Name	**TDS**	**NO_3**	**DS Concentration (M)**			
	(mg/l)	**(mg/l)**	**0.5**	**0.75**	**1**	**1.5**
			Flux Rate (L/m^2.h)			
Radwan9	2428	81	3.35	4.34	5.42	**6.63**
Aljalaa14	4786	69	3.00	3.94	4.95	**6.02**
Radwan A3	8650	193	2.72	3.67	4.52	**5.43**
Remal 4 Becdar	15200	111	2.35	3.26	4.13	**5.0**

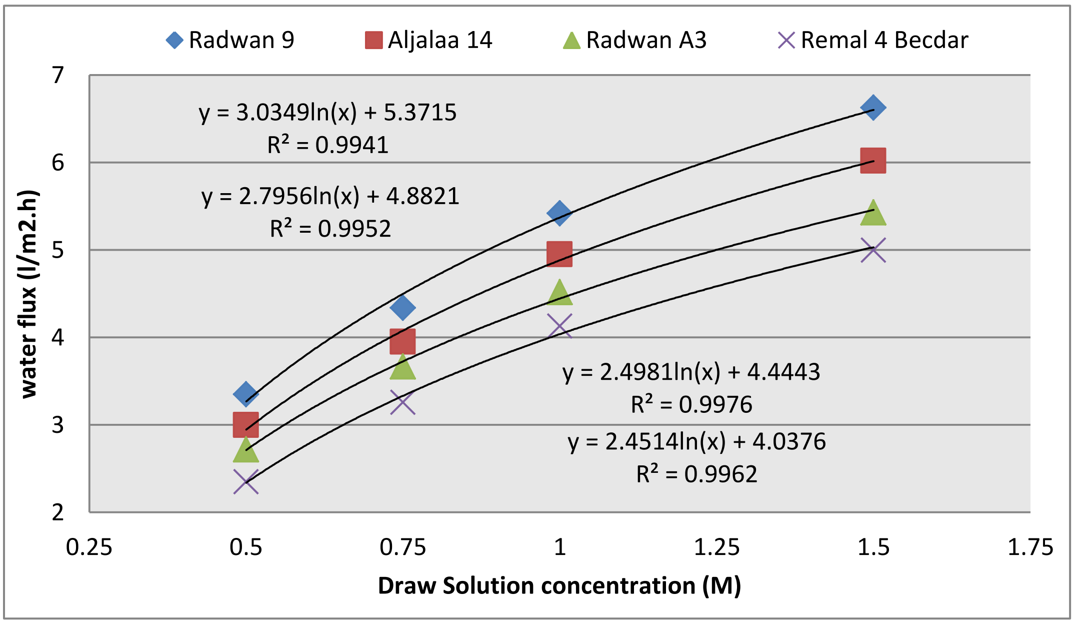


Figure (4.8a): Effect of NH_4HCO_3 concentrations on water flux for different well samples

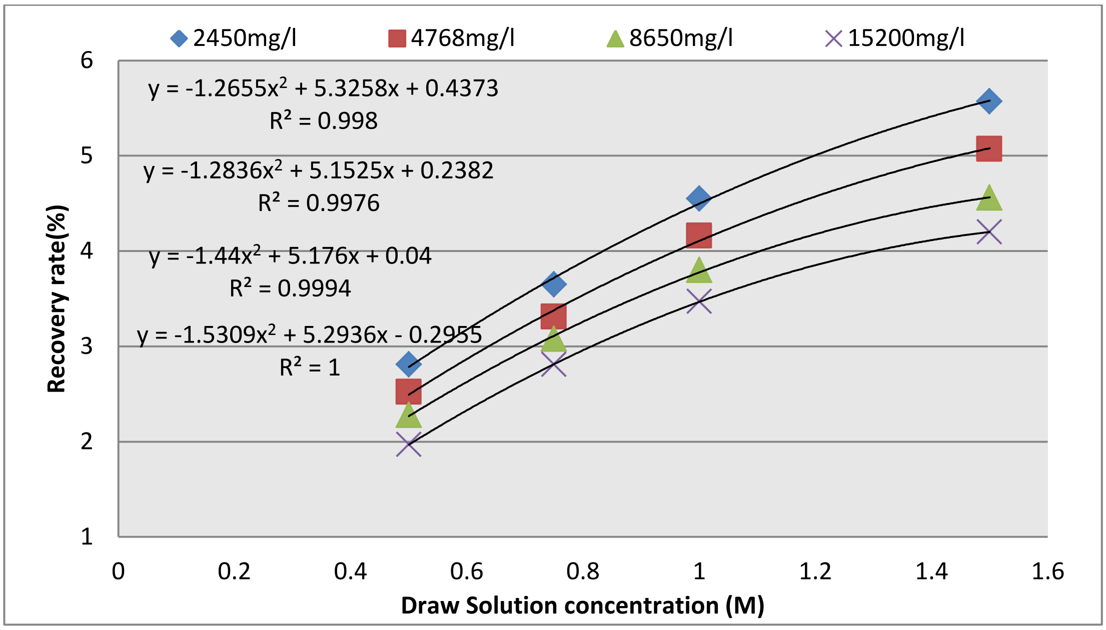


Figure (4.8b): Effect of different draw solution concentration on recovery rate for real brackish water with different TDS.

4.4.1.2 Effect of feed water TDS Concentration on Water Flux

Figure (4.9) shows the relation between feed water TDS concentration and flux rate. The results show that while the TDS concentration increases the flux rate decreases.

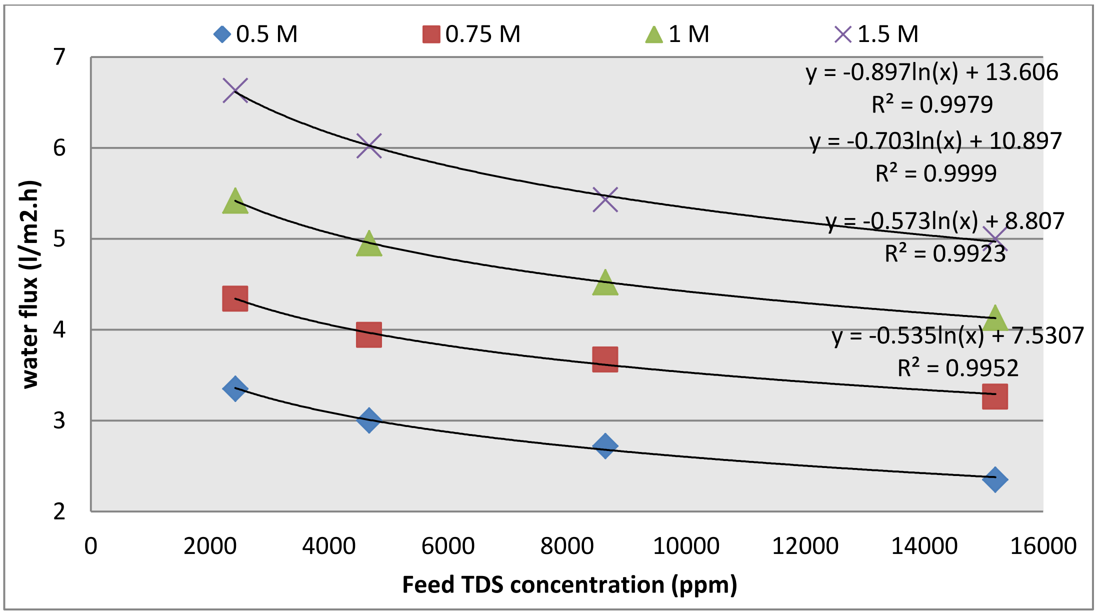


Figure (4.9): Effect of feed TDS concentration on water flux for well samples with NH_4HCO_3 different concentrations.

4.5 Fourth set of experiments

4.5.1 Rejection Rate of NO_3

4.5.1.1 Effect of DS concentrations on NO_3 rejection rate

The result showed that the rejection rate increase by the increase of the DS concentrations as shown in Figure (4.10) illustrated the effect of DS concentrations on NO_3 rejection using FO membrane. It can be noticed that the nitrate rejection rate is directly proportional to the DS concentration.

For example, at draw solution concentration 1.5M the result of Radwan 9 well sample indicated that the nitrate rejection 65.61%, While with the same concentration the result reach 63.7% for Remal 4 because the TDS concentration plays an important role.

Table (4.2): Relation between the NO_3 rejection rate and DS concentration for well samples

Well Name	**TDS**	**NO_3**	**DS Concentration (M)**			
And ID	**(mg/l)**	**(mg/l)**	**0.5**	**0.75**	**1**	**1.5**
			Rejection Rate (%)			
Radwan9	2428	81	60.60	65.1	69.70	**75.70**
Aljalaa14	4786	69	57.90	61.14	65.70	**70.42**
Radwan A3	8650	193	52.45	56.45	61.66	**65.61**
Remal 4 Becdar	15200	111	49.68	54.23	59.90	**63.72**

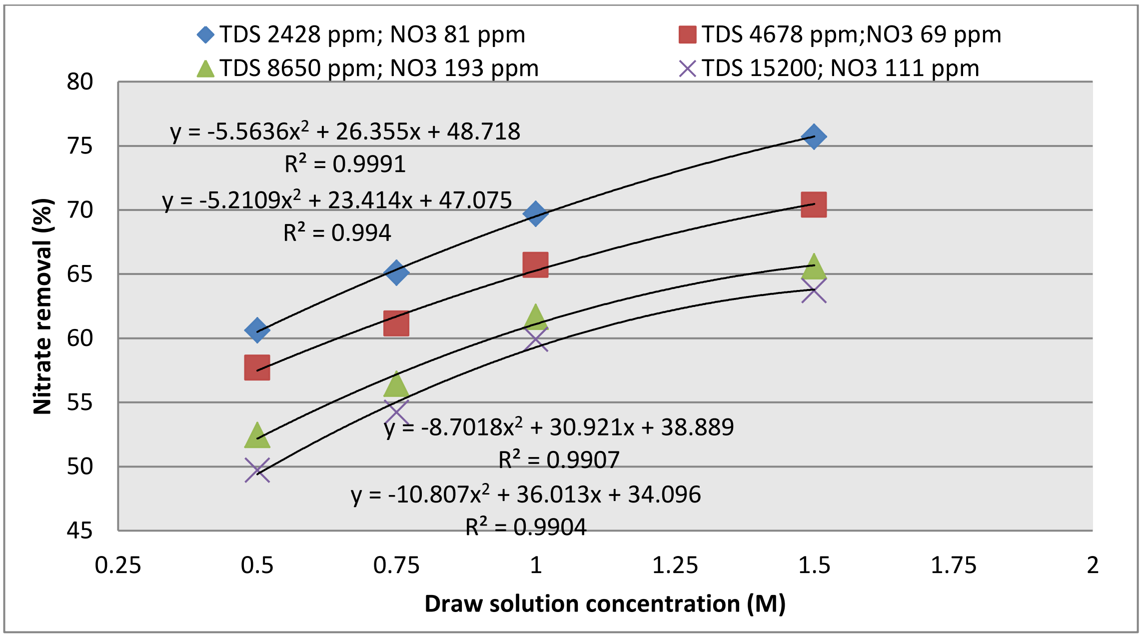


Figure (4.10): Effect of draw solution concentrations on NO_3 rejection rate with different nitrate and TDS concentrations for real brackish water .

4.6 Fifth set of experiments

4.6.1 FO membrane performance with synthetic seawater (SSW)

4.6.1.1 Effect of DS concentrations on water flux and salt rejection

The performance of FO process using synthetic seawater (NaCl solution 0.5M or 35064 mg/l) as FS and ammonium bicarbonate draw solute as DS was investigated in this set. The run experiments conducted to compare results with the results of another run using real seawater that has a concentration of (37760 mg/l). Figure 4.11 represents water flux as time till 6.58 L/m^2.hr at 90 min., then decreased gradually to 3.34 L/m^{2}hr after 3 hrs. The water flux found to be inversely proportional to the running time. The water flux decreased with the running time because the DS concentration got diluted during the experiment. Accordingly, the osmotic pressure is reduced over the time, taking into consideration that the internal concentration polarization (ICP) will influence the water flux.

The behavior of flux decline with time was illustrated by (Zhao et al.,2012) and (Gray et al.,2006), they demonstrated that coupled adverse effects of internal concentration polarization (ICP) and membrane fouling can reduce the osmotic water flux and increased mass transfer resistance as the feed water became more concentrated due to water permeation from FS to DS.

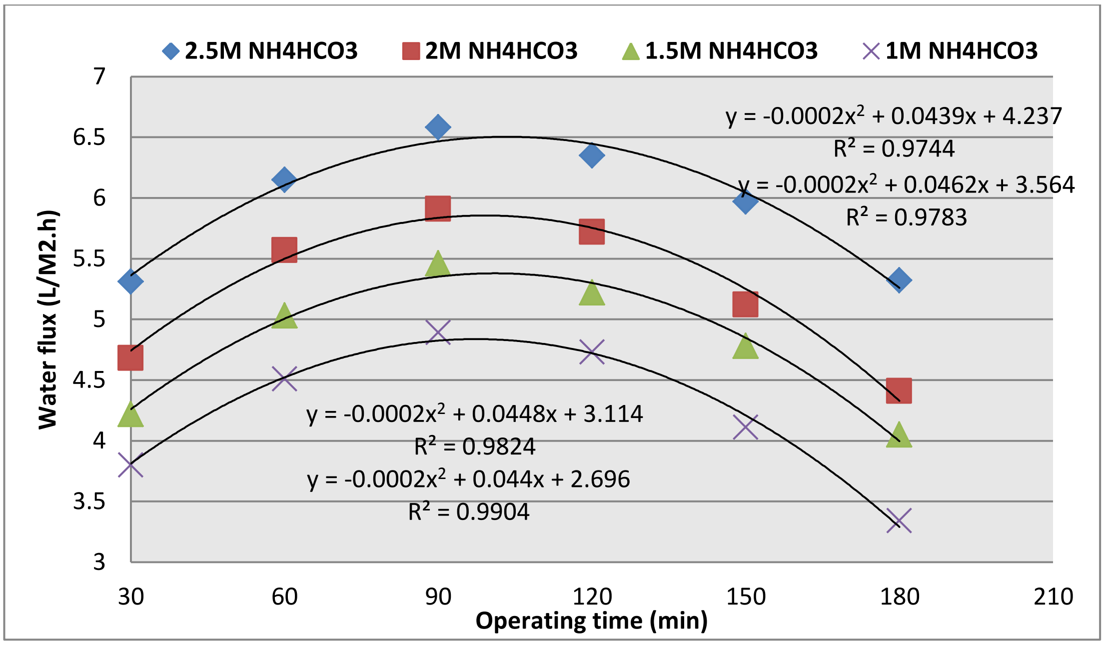


Figure (4.11): Water flux versus time with different NH_4HCO_3 concentration as DS and 0.5M NaCl as FS .

(Qin et al, 2013) proposed that The water flux with synthetic seawater (0.5 M NaCl) as feed solution and 2.5 M NH_4HCO_3 as draw solution was 5.7 L/m^2.h. (McCutcheon et al.,2005) obtained water flux of 13.5 L/m^2.h. using (0.5 M NaCl) as feed and 6M NH_4HCO_3 as draw solution at 50ºC.

The results shown and summarized in Figure 4.12 showed that the water flux increase linearly with the increase of DS concentration with high correlation (R^2=0.99). It is observed that the DS concentration increased the flux rate increase, The reason for this is due to the increase in the osmotic driving force between FS and DS. By decreasing DS concentration the water flux decreased gradually to 6.58, 5.91 5.46 and 4.89 L/m^2.h at 2.5, 2,1.5 and 1 M NH_4HCO_3.

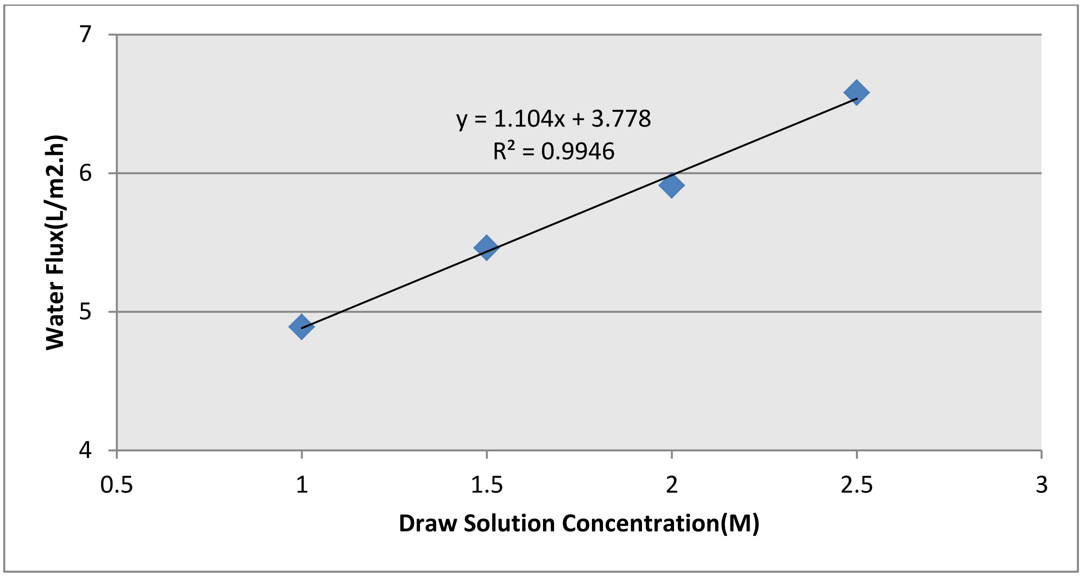
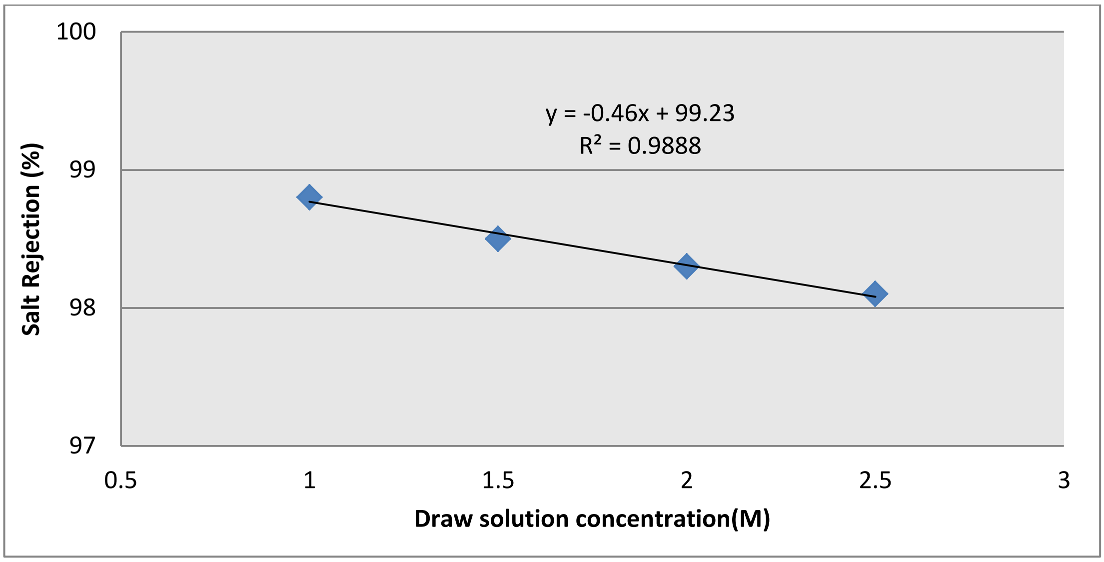


Figure (4.12): Water flux rate with different NH_4HCO_3concentration (at running time 90 minute).

Figure 4.13 demonstrates the effect of DS concentration on salt rejection. It is appeared that, after 3 hours permeation time, the salt rejection was decreased gradually by time from 98.8 at 1 hr to 98.1% at 3 hrs.



Figures (4.13): Effect of draw solution concentration on salt rejection for FO operation

4.6.1.2 Effect of feed boron concentration

The effect of feed boron concentration (3,5 and 7 mg/l) was investigated under the operational conditions such as (2.5M NH_4HCO_3 as draw solution concentration, flow rate 0.5 L/min., applied pressure of 0.5 bar).

From the obtained results, it can be seen that the values of residual boron concentrations increase when the feed boron concentrations increase.

As observed in Figures (4.14a,b) the water flux and rejection rate is inversely proportional to the initial boron concentration .

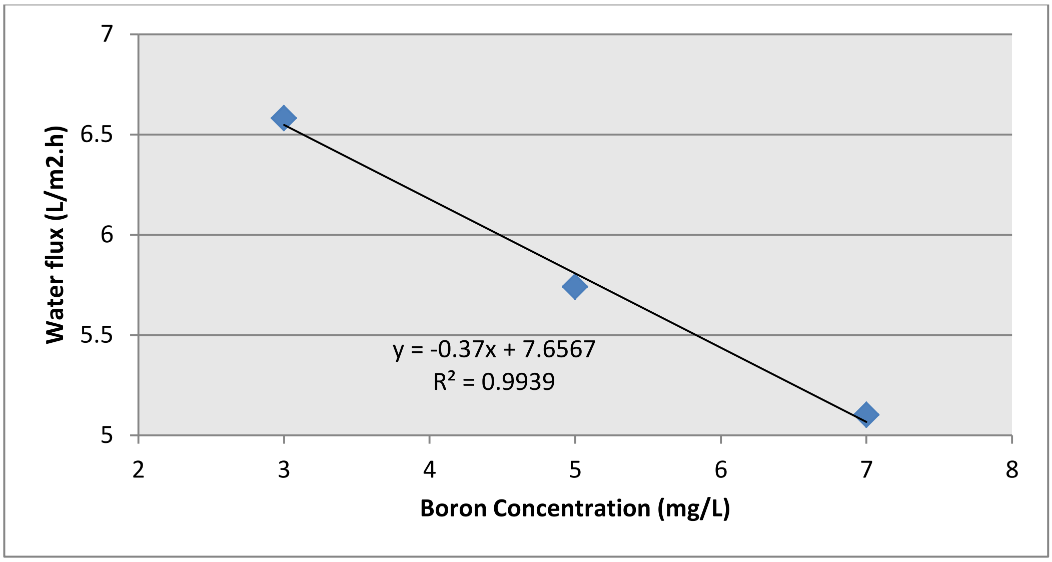


Figure (4.14a): Boron concentrations vs. water flux with NH_4HCO_3concentration 2.5M as DS.

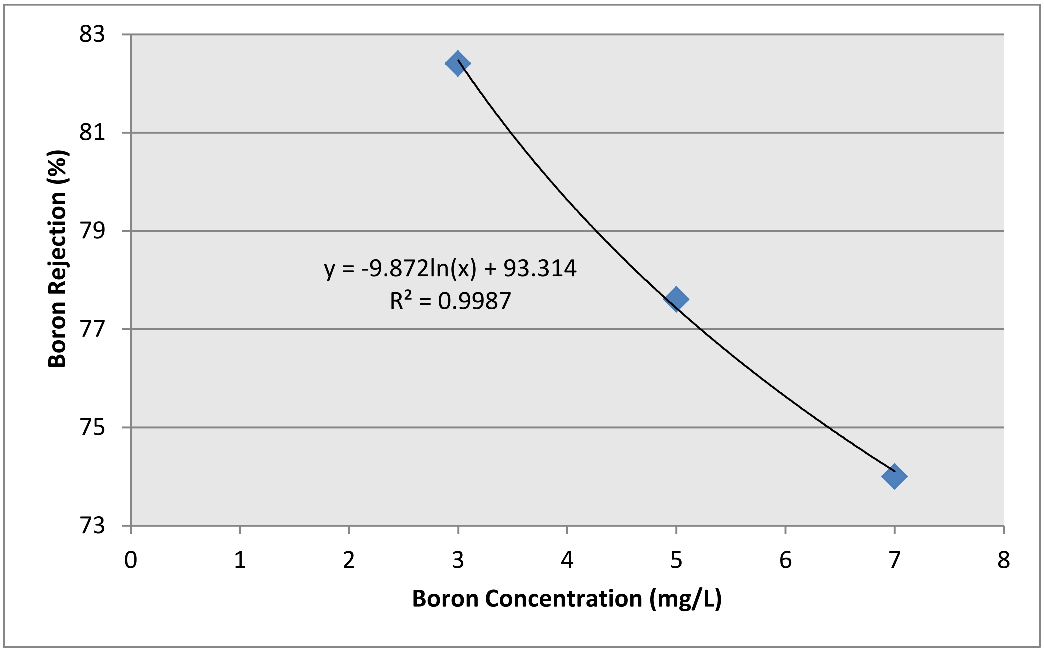


Figure (4.14b): Boron concentrations vs. boron rejection rate with NH_4HCO_3 concentration 2.5M as DS and 0.5M NaCl as FS.

(Qin et al, 2013) proposed that boron rejection with synthetic seawater (0.5 M NaCl) as feed solution and 2.5 M NH_4HCO_3 as draw solution was 85% and boron rejection with real seawater with the same DS concentration was n56%.

4.6.2 FO membrane performance with real seawater (RSW)

4.6.1.1 Effect of DS concentrations on water flux and salt rejection

The performance of FO process using real seawater as FS and brackish water as DS by addition of ammonium bicarbonate draw solute to increase the osmotic driving force. Figure 4.15 represents water flux as a function of permeation time. It was found that the water flux was increased with time till 4.71 L/m^{2}hr at 1.5 hr then decreased gradually to 3.94 L/m^{2}hr after 3 hrs. with DS concentration 2.5M.

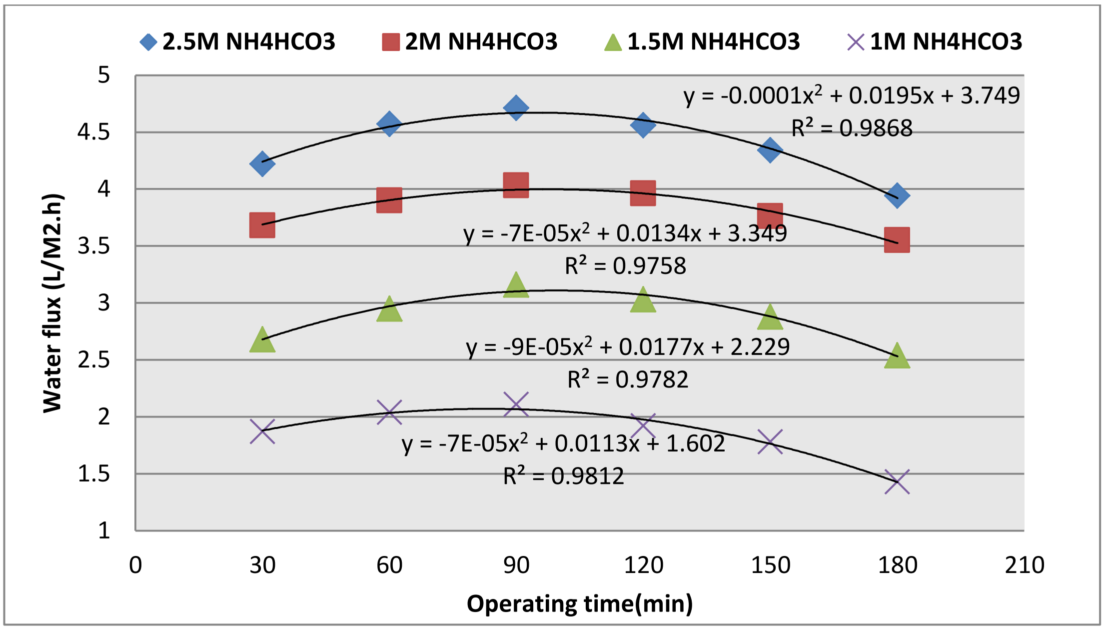


Figure (4.15): Water flux versus time with different NH_4HCO_3 concentration as DS.

The results shown and summarized in Figure 4.16 showed that the water flux increase linearly with the increase of DS concentration with high correlation (R^2=0.99). It is observed that the DS concentration increased the flux rate increase, The reason for this is due to the increase in the osmotic driving force between FS and DS. By decreasing DS concentration the water flux decreased gradually to 4.83, 4.03 3.16 and 2.11 L/m^2.h at 2.5, 2,1.5 and 1 M, respectively.

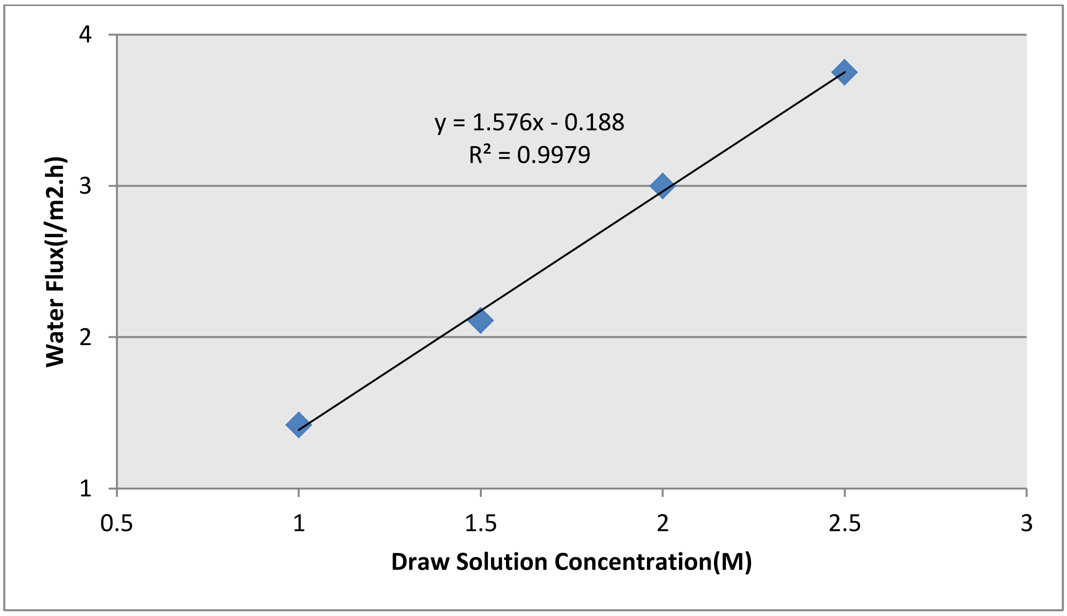
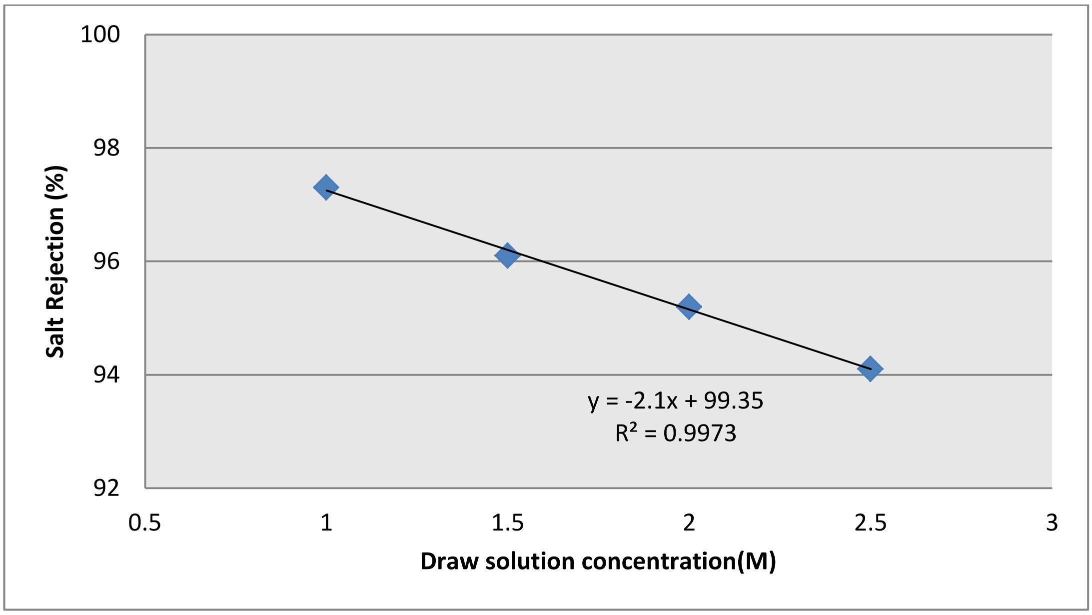


Figure (4.16): Water flux vs. different NH_4HCO_3 concentration as DS and real seawater as FS.

Figure 4.17 demonstrates the effect of DS concentration on salt rejection. It is appeared that, after 3 hrs permeation time, the salt rejection was decreased gradually by time from 97.3 at 1 hr to 94.1% at 3 hrs.



Figures (4.17): Effect of draw solution concentration on salt rejection for FO operation

Figure 4.18 shows DS salinity as a function of FO operating time; as expected from dilution effect, the TDS of DS was decreased sharply from 57344 to 33835 mg/L after 1 hr and then decreased gradually to 14354 mg/L at 3 hrs. This can be attributed to the high osmotic driving force in the beginning of the operation which leads to high water flux and fast DS dilution.

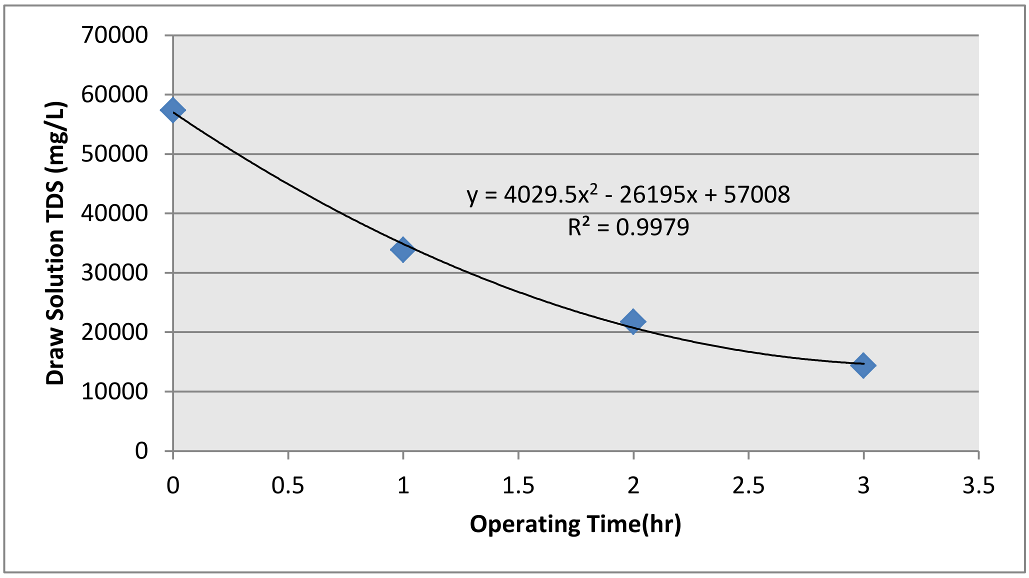


Figure (4.18): Effect of operating time on draw solution TDS concentration.

Table 4.3:Analysis of real seawater before and after FO process

Time (hr) Parameter	0	3
FS TDS (mg/L)	37760	40320
DS TDS (mg/L)	57344	14354

4.6.2.2 Recovery Rate

Figure (4.19) shows the relationship between the recovery rate and draw solution concentrations. It is noticed that the recovery rate increase linearly with the concentration for the two types of synthetic and real seawater.

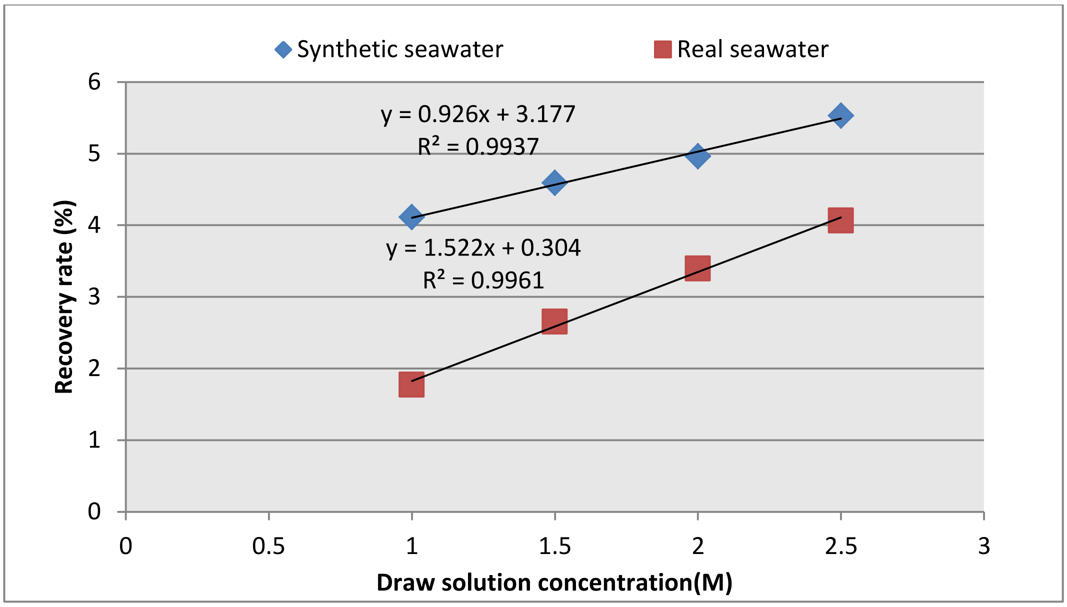


Figure (4.19): Effect of different draw solution concentration on recovery rate for synthetic and real seawater.

4.6.2.3 Boron removal for real seawater

Rejection rate of boron increase linearly with the increase of DS concentration showed in Figure (4.20).

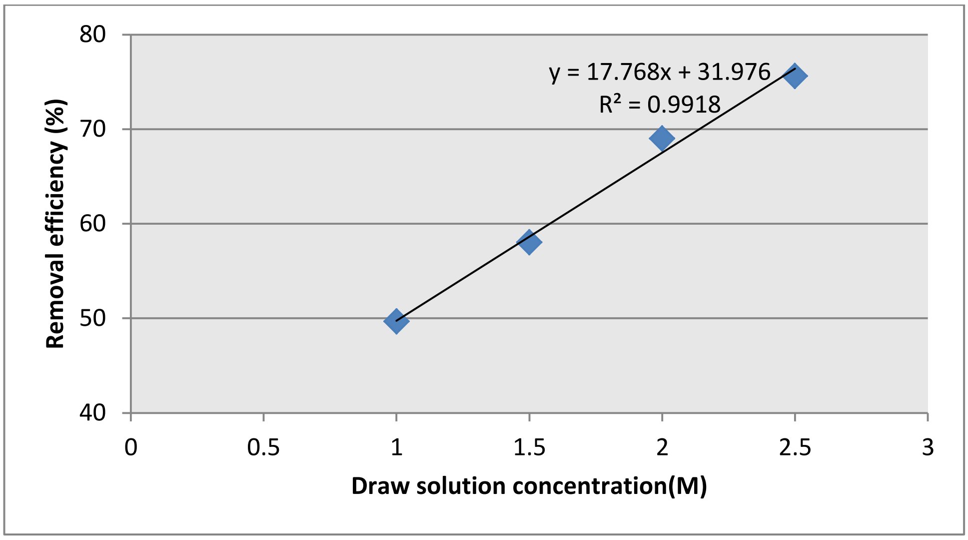


Figure (4.20): Boron removal efficiency vs. different NH_4HCO_3concentration as DS and real seawater as FS.

4.7 Sixth set of experiments

4.7.1Removal & Recovery process

4.7.1.1 Heating process

The results illustrated in Figure (4.21) indicated that ammonium bicarbonate (NH_4HCO_3) can be removed by heating and bubbling together. Temperature is one of the factors effecting on NH_4HCO_3 solubility. The removal efficiency increases when both heating to (60°C) and air bubbling were applied together.

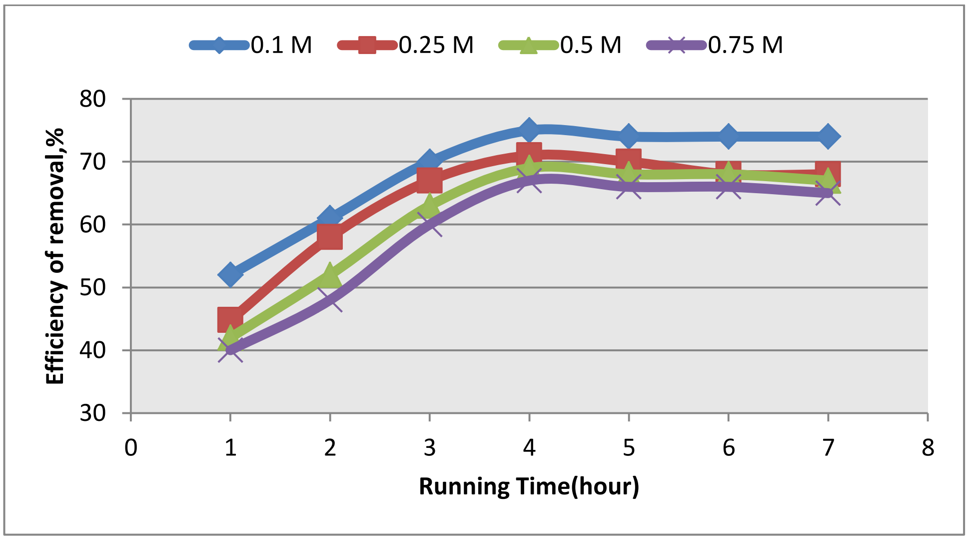


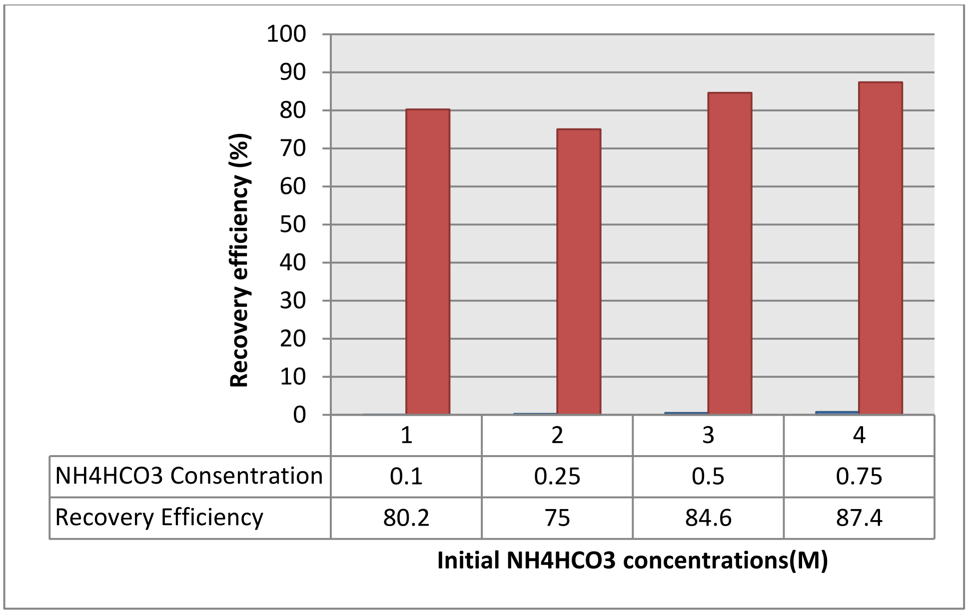
Figure (4.21) Ammonium bicarbonate removal efficiency during the time

4.7.1.2 Time for heating

Heating can effectively remove ammonium bicarbonate from the solution and additional air bubbling was required. Figure (4.21) indicates that the ammonium bicarbonate removal efficiency increase from 40-50% during the first hour to 70-80% at end of the fourth hour. The concentration was relatively constant after that time.

4.7.1.3 Removal and recovery efficiency

Ammonium bicarbonate is decomposed to ammonia (NH_3) and carbon dioxide (CO_2) gas when heated. After heating and air blower, It was found that the ammonium bicarbonate removal efficiency of the system after 4 hours is in the range between 70 -80 %, (average 75 %). NH_3 and CO_2 are gas which can be recovered and dissolved to ammonium bicarbonate again. Recovery efficiency was 75 - 87% showed that in (Figure 4.22).



	1	2	3	4
NH4HCO3 Consentration	0.1	0.25	0.5	0.75
Recovery Efficiency	80.2	75	84.6	87.4

Figure (4.22) NH_4HCO_3 solution recovery efficiency

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

CHAPTER (5)

CONCLUSION AND RECOMMENDATIONS

5.1: Conclusion

The following conclusions could be drawn from the present research:

1- The water flux that is obtained from forward osmosis (FO) membrane can be increased with decreasing the concentration of feed solution and increasing solute concentration of draw solution.

2- FO membrane showed good results for flux rates. When DS concentration was 0.5 M the flux rate was 3.56 $L/m^2.h$, while when DS concentration was increased to 1.5 M the flux rate was 6.63 $L/m^2.h$ for feed concentration 0.085M NaCl. For 200mg/l NO_3 concentration when DS concentration was 0.5M flux rate was 3.2 $L/m^2.h$, while when DS concentration was increased to 1.5 M flux rate was 7.62 $L/m^2.h$.

3- FO membrane showed best results for NaCl removal from aqueous solution, the rejection rate was around 99% for feed concentration 0.085M NaCl (5000 mg/L) and constant pressure of 0.5 bar.

4- FO membrane showed the results for nitrate removal in aqueous water. For 200mg/l NO_3 concentration when DS concentration was 0.5M rejection rate was 52% , while when DS concentration was increased to 1.5 M rejection rate was 67%.

5- The efficiency of nitrate rejection rate was inversely proportional with feed TDS concentration, as well as the nitrate rejection rate using FO membrane reached 47% in real brackish water with TDS 15200 .

6- FO membrane showed low water flux values in seawater desalination it decreased gradually to 4.83, 4.03, 3.16 and 2.11 $L/m^2.h$ at 2.5, 2,1.5 and 1 M.

7- Results demonstrated the efficiency of ammonium bicarbonate removal and recovery by heating at 60^oC and air bubbling, e.g., when heated 0.5M NH_4HCO_3 concentration for 5 hours the removal efficiency reached 80%.

8- We faced a problem for getting a good lab scale FO membrane system with high efficiency in order to obtain the best results.

5.2. Recommendations

1- The results presented in this study lay the foundation and groundwork for further research analysis. Adopting these experimental findings on the suggested parameters that influence on rejection ions in the FO process, it is recommended for further research to be conducted especially to study the FO performance in terms of recovery ratio, TDS, heavy metal rejection and separation of draw solution

2- It is recommended to investigate different types of commercially available DS and FO membrane elements.

3- Other associated factors including: pH, membrane configurations, flow modes and operating pressure are highly recommended for future consideration.

4- Development of draw solution recovery systems is highly recommended as the subject of future research.

5- Test the cost effective criteria for FO against RO to be used in commercial and large scale.

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APPENDESICES

APPENDIX (A)

Table (A.1): Recent studies on FO membrane fouling.(Akther et al. / Chemical Engineering Journal 281 (2015) 502–522)

Fouling type	Mitigation measure	Findings
Organic fouling [71]	Physical cleaning (hydrodynamics control strategies)	Minor fouling of support layer resulting from impact of organic and particulate matter with seawater/brine as draw solution and DI water as feed; formation of less compact fouling layer on the surface of the membrane; the use of spacer in the feed channel and pulsed flow easily eradicated the foulants from the membrane surface
Organic fouling (Alginate) [72]	Hydraulic cleaning	Alginate fouling was reversible, up to 98%, through a short time physical cleaning
Inorganic fouling (Gypsum scaling) [73]	Hydraulic cleaning	Water flux recovery of 90% and 75% was obtained for CA and PA membranes, respectively, by rinsing membranes in water; PA membrane requires chemical cleaning to almost recover initial water flux
Organic fouling [74]	Hydraulic cleaning	Removal of natural organic matter including biopolymers; organic fouling was removed by 98% using water flushing
Combined organic and colloidal fouling (alginate, humic acid, and bovine serum albumin as organic model foulants; silica colloids as inorganic model foulants) [66]	Physical cleaning (hydrodynamics control strategies)	Reverse draw solute flux into the feed solution influenced both colloidal and organic fouling causing accelerated cake enhanced osmotic pressure (CEOP); reverse diffusion of dextrose was insignificant compared to sodium chloride due to much bigger hydrated radius of dextrose compared to sodium chloride
Inorganic fouling (scaling) [75,76]	Physical cleaning	Reverse diffusion of diammonium phosphate (DAP) from the draw solution to the feed solution caused significant scaling; main contributors to membrane scaling were phosphates of magnesium, magnesium ammonium, and calcium; physical cleaning was effective for permeate flux recovery

Table(A.1):(continued)

Fouling type	Mitigation measure	Finding
Combined organic and inorganic fouling (Alginate and gypsum as model foulants [77]	Physical cleaning (rinsing the membrane surface with pure water and continuously introducing air bubbles)	Synergistic effect between gypsum scaling and alginate fouling resulted in faster water flux reduction; scaling mechanism changed from bulk crystallization to heterogeneous/surface crystallization in the presence of alginate; recovery of initial water flux after combined fouling would still require chemical cleaning
Combined organic–colloidal fouling (Alginate, silica colloids, and their mixture as model foulants) [78]	Physical cleaning (hydrodynamics control strategies)	Combined fouling resulted in a faster flux decline than the individual foulants because of the synergistic effect of alginate and silica colloids; applied hydraulic pressure on the feed side resulted in higher fouling propensity and lower fouling reversibility of combined organic–colloidal fouling; single foulants were removed easily under all conditions
Biofouling [80]	Spacer thickness	The impact of biofouling on membrane flux was diminished by thicker spacers; biofilm spatial distribution changed with feed spacer thickness
Inorganic fouling (scaling) [81]	Physical cleaning (change in working temperature)	Higher operating temperature significantly enhanced initial permeate fluxes and water recoveries but caused more serious water flux decline and membrane scaling in brackish water desalination; foulants crystallization on the membrane surfaces became more compact as the temperature was increased from 25 to 45 C
Biofouling [69]	Graphene oxide surface functionalization	Inactivation of bacteria (E. coli) by 65% after the contact time of 1 h
Biofouling [70]	Ag/TiO2-coating	The bacterial growth on the Ag/TiO2-coated membrane was found to be almost 11 times less, compared to the uncoated membrane

APPENDIX (B)

Table(B.1): Summary of draw solutions used for FO desalination.

year	Research group	Draw solute/solution	Recovery method	Advantages and disadvantages	Reference
1965	Batchelder	SO_2	Heated gas stripping operation	Easy but requires heat energy, harmful	[Batchelder,1965]
1965	Glew	Mixture of water with SO2 or aliphatic alcohols	Heating/distillation	Easy but requires heat energy, harmful	[Glew,1965]
1972	Frank	Aluminum sulfate	Precipitation with calcium hydroxide	No energy required, but toxic reaction products	[Frank,1972]
1975	Kravath and Davis	Glucose	Not required	For emergency water supply only	[Kravath et al,1975]
1976	Kessler & Moody	Nutrient solution	Not required	For emergency water supply only	[Kessler et al,1976]
1989	Stache	Fructose	Not required	For emergency water supply only	[Stache,1989]
1992	Yaeli	Glucose	RO	Requires electrical energy	[Yaeli,1992]
2002	McGinnis	KNO_3 and SO_2	Cooling and heating	Requires energy, complicated, harmful	[Me,2002]
2005-2007	Elimelech And coworkers	NH_4HCO_3	Moderate heating up to 60 °C	High water flux, requires heating, bad smell of ammonia in the product water	[18,83,84]
2007	Adham	Magnetic nanoparticles	Use of a canister separator	Easy separation but low osmotic pressure	[Ahdam et al,2007]
2007	Adham	Dendrimers	UF/adjusting pH	High osmotic pressure, UF requires energy, pH-controlled removal is necessary	[Ahdam et al,2007]
2007	Adham	Albumin	Heating	Inefficient separation	[Ahdam et al,2007]
2010	Chung	2-Methylimidazole-based organic compounds	FO–MD	High osmotic pressure but high ICP	[Yen et al,2010]
2010-2011	Chung	Magnetic nanoparticles	Using magnetic field	Easy separation, susceptible to nanoparticle aggregation	[Ge et al,2010, Ling et al,2010]
2011	Wang	Polymer hydrogels	Pressure and thermal stimuli	High water recovery, not suitable for practical applications, microbial contamination is possible	[Li et al,2011;, Li et al,2011]
2011	Chung	Super hydrophilic nanoparticles	UF	Multiple UF stages required for pure water recovery	[Ling et al,2012]
2012	Chung	Polyacrylic acid sodium salts (PAA–Na) active layer	UF	High solubility and osmotic pressure, recovery only by pressure-driven process	[Ge et al,2012]

Table (B.1): (continued)

Year	Research group	Draw solute/solution	Recovery method	Advantages and disadvantages	Reference
2012	Chung	Surface-dissociated nanoparticle	Integrated electric field-nanofiltration system	High osmotic pressure, NF requires energy	(Ling et al,2012)
2013	Stone	Hexavalent phosphazene salts	Not reported	Pure water recovery requires further research, Hydrolysis of membrane is possible	(Stone et al,2013)
2013	Stone	Switchable polarity solvent (SPS)	Heating with nitrogen bubbling	Energy efficient, but degrades the cellulose acetate membrane, poor water quality	(Stone et al,2013)
2013	Alnaizy	Copper sulfate	Metathesis precipitation	No energy required, can be only used for brackish water desalination, toxic reaction products, costly consumables	(Alnaizy et al,2013)
2013	Alnaizy	Magnesium sulfate	Metathesis precipitation	No energy required, toxic reaction products, costly consumables	(Alnaizy et al,2013)
2013	Ou	Thermo-sensitive polyelectrolytes	Hot UF	Low energy requirement, but low flux and poor water recovery	(Ou et al,2013)
2013	Cai	Semi-IPN hydrogels	Heating	Low energy requirement, but low water flux	(Cai et al,2013)
2014	Na	Citrate-coated magnetic nanoparticles (cit-MNPs)	Not reported	Pure water recovery requires further research	(Na et al,2014]
2014	Zhao	Poly(sodiumstyrene-4-sulfonate-co-n-isopropylacrylamide) (PSSS–PNIPAM)	Membrane distillation (MD)	Feasible with seawater, but energy required	(Zhao et al,2014)
2014	Sato	Dimethyl ether	Exposure to air	Energy-efficient, volatile osmotic agent	(Sato et al,2014)
2014	Ge	Ferric and cobaltous hydroacid complexes	NF	High water flux, energy required for regeneration	(Ge et al,2014)
2015	Zhang	Electric-responsive polymer hydrogels	Electric field	Requires electrical energy	(Zhang et al,2015)
2015	Zhao	Poly(amidoamine) terminated with sodium carboxylategroups (PAMAM-COONa)	MD	High water flux, energy required for regeneration	(Zhao et al,2015)
2015	Tian	Poly (sodium 4-styrenesulfonate) (PSS)	Low pressure-UF	Cost-effective, but UF required	(Tian et al,2015)
2015	Haratanto	Thermo-responsive microgels	Centrifugation at 40°C	High water recovery, high flux, but heating involved	(Hartanto et al,2015)

APPENDIX (C)

Table (C.1): Summary of notable FO membrane developments .

year	membrane	material	Preparation	Feed solution (draw solution)	Water flux in FO mode (L/m^{2}h)	Reference
2007	NF hollow fiber membrane	Polybenzimidazole (PBI)	Dry-jet wet phase inversion	DI water (2.0 M MgSO4)	5.65	[Wang et al,2007]
2009	NF hollow fiber membrane with thin wall	Polybenzimidazole (PBI)	Phase inversion, chemical cross-linking by p-xylylene	DI water (5.0 M MgSO4)	20	[Wang et al,2009]
2009	Dual-layer NF hollow fiber membrane	Polybenzimidazole-polyethersulfone (PBI-PES)	Co-extrusion	DI water (5.0 M MgCl2)	24.2	[Yang et al,2009]
2010	Hollow fiber	Polyethersulfone (PES) hollow fiber substrate, polyamide active layer	Dry-jet wet spinning method, interfacial polymerization	DI water (0.50 M NaCl)	5 (#A–FO) 14 (#B–FO)	[Wang et al,2010]
2010	Hollow fiber	Polyethersulfone (PES) hollow fiber substrate, polyamide active layer	Dry-jet wet spinning method, interfacial polymerization	0.59 M NaCl (2 M NaCl)	12.4	[Chou et al,2010]
2010	Double-skinned flat sheet	Cellulose acetate	Phase inversion, thermal annealing at 85°C for 15 min	DI water (5 M MgCl2)	48.2	[Wang et al,2010]
2010	Flat sheet TFC	Polysulfone (PSf) support, polyamide active layer	Phase inversion, interfacial polymerization	DI water (1.5 M NaCl)	>18	[Yip et al,2010]
2010	Hollow fiber NF	Cellulose acetate	Dry-jet wet-spinning process	DI water (2 M MgCl2)	5	[Su et al,2010]
2010	Double dense-layer	Cellulose acetate	Phase inversion	DI water (2.5 M NaCl)	6	[Zhang et al,2010]
2011	Flat sheet composite	Cellulose acetate on nylon fabric support	Phase inversion in water	35 g/L NaCl (150 g/L MgSO4)	1.3	[Sairam et al,2011]
2011	Flat Sheet	PAN substrate	Layer-by-layer (LbL) assembly method	Distilled water (0.1 M MgCl2)	15	[Saren et al,2011]
2011	Positively charged hollow fiber	PAI substrate, treated by PEI	Chemical modification	Pure water (0.5 M MgCl2)	8.36	[Setiawan et al,2011]
2011	Flat sheet TFC	PES-sulfonated polymer substrate, polyamide active layer	Phase inversion, interfacial polymerization	Seawater (2 M NaCl)	13.5	[Widjojo et al,2011]
2011	Flat sheet TFC	Porous polysulfone substrates, polyamide active layer	Phase inversion, interfacial polymerization	10 mM NaCl (2 M NaCl)	18.1	[Wei et al,2011]

Table (C.1): (continued)

year	membrane	material	Preparation	Feed solution (draw solution)	Water flux in FO mode (L/m^2h)	Reference
2011	Nanoporous flat sheet	PES cast on PET fabric	Phase inversion	**DI water** (3 M NaCl)	30	[Yu et al,2011]
2011	Flat sheet	Cellulose ester	Phase inversion	Seawater (1.5 M NaCl)	5	[S. Zhang et al,2011]
2011	Flat sheet TFC	PES nano-fiber support, polyamide active layer	Electrospinning, interfacial polymerization	-	-	[X. Song et al,2011]
2011	Flat sheet TFC	PSf nano-fiber support, polyamide active layer	Electrospinning, interfacial polymerization	-	-	[N. N. Bui et al,2011]
2011	Chemically cross-linked flat sheet	PAN substrate	Layer-by-layer (LbL) assembly with chemical crosslinking	DI water (3 M MgCl2)	30	[C. Qiu et al,2011]
2012	Molecularly designed cellulose ester	Cellulose ester	Phase inversion	DI water (2 M NaCl)	1-14.9	[R.C. Ong et al,2012]
2012	Flat sheet TFC	Sulphonated poly(ether ketone) (SPEK) substrate, polyamide active layer	Wet phase inversion, interfacial polymerization	Model seawater (2 M NaCl)	17	[G. Han et al,2012]
2012	Flat sheet TFC	PSf support, polyamide active layer with fine-tuned nanoparticles	Non-solvent (water)-induced phase separation, interfacial polymerization, surface functionalization	-	-	[A. Tiraferri et al,2012]
2012	Dual-layer hollow fiber	PAI/PES dual-layer substrate, (polyethyleneimine) PEI polyelectrolyte cross-linking	Dry-jet wet spinning, chemical cross-linking	DI water (0.5 M MgCl2)	20.6	[L. Setiawan et al,2012]
2012	Antifouling NF-like hollow fiber	PAI substrate, PEI polyelectrolyte cross-linking, polystyrene sulfonate sodium salt (PSS) deposition	Dry-jet wet spinning, chemical cross-linking, PSS deposition	2000 ppm Na2SO4 (0.5 M Na2SO4)	12	[L. Setiawan et al,2012]
2012	Macrovoid-free TFC hollow fiber	PES hollow fiber support, polyamide active layer	Phase inversion, interfacial polymerization	Water (1 M NaCl)	25	[P. Sukitpaneenit et al,2012]
2012	Zeolite-polyamide thin film nanocomposite	PSf support, polyamide rejection layer incorporated with NaY zeolite nanoparticles	Phase inversion, interfacial polymerization	10 mM NaCl or DI water (0.5, 1.0 or 2.0 M NaCl)	Variable depending on the amount of zeolite nanoparticles	[N. Ma et al,2012]

Table (C.1): (continued)

year	membrane	material	Preparation	Feed solution (draw solution)	Water flux in FO mode (L/m^{2}h)	Reference
2012	Double-skinned and cross-linked layer-by-layer	PAN substrate	Layer-by-layer (LbL) assembly method, chemical cross-linking	DI water (1 M NaCl)	30	[S. Qi et al,2012]
2012	Flat sheet NF-like membrane	Torlon polyamide-imide (PAI) material substrate, PEI for post-treatment	Phase inversion, chemical post-treatment	DI water (0.5 M MgCl2)	16.3-11.47	[C. Qiu et al,2012]
2013	Flat sheet membrane with modified PES substrate	PES/multiwalled carbon nanotube (MWCNT) substrate, polyamide active layer	Carboxylated MWCNTs Dispersion within PES via solution blending, phase inversion process, interfacial polymerization	-	-	[Y. Wang et al,2012]
2013	Thin-film nanocomposite (TFN)	PSf support, polyamide rejection layer, amine functionalized multi-walled carbon nanotubes (F-MWCNTs) as additives in 1,3-phenylendiamine (MPD) solution	Phase inversion, interfacial polymerization	10 mM NaCl (2 M NaCl)	40 (with 0.1 F-MWCNT wt/ MPD vol%)	[M. Amini et al,2013]
2013	Dual-layer hollow fiber	PBI/POSS outer layer, PAN/PVP inner layer	Phase inversion, dual-layer hollow fiber spinning, thermal annealing	DI water (2 M MgCl2)	12 (with 0.5% POSS)	[F. J. Fu et al,2013]
2013	Flat sheet membrane with modified PES substrate	PES/multiwalled carbon nanotube (MWCNT) substrate, polyamide active layer	Carboxylated MWCNTs Dispersion within PES via solution blending, phase inversion process, interfacial polymerization	-	-	[Y. Wang et al,2012]
2013	Thin-film nanocomposite (TFN)	PSf support, polyamide rejection layer, amine functionalized multi-walled carbon nanotubes (F-MWCNTs) as additives in 1,3-phenylendiamine (MPD) solution	Phase inversion, interfacial polymerization	10 mM NaCl (2 M NaCl)	40 (with 0.1 F-MWCNT wt/ MPD vol%)	[M. Amini et al,2013]
2013	Dual-layer hollow fiber	PBI/POSS outer layer, PAN/PVP inner layer	Phase inversion, dual-layer hollow fiber spinning, thermal annealing	DI water (2 M MgCl2)	12 (with 0.5% POSS)	[F. J. Fu et al,2013]
2013	Flat sheet TFC	Carboxylated polysulfone (CPSf) substrate, polyamide active layer	Phase inversion, lithiation procedure, interfacial polymerization	DI water (1 M MgCl2)	18	[Y. H. Cho et al,2013]
2013	Functionalized multi-walled carbon nanotube (MWCNT) immobilized hollow fiber	PAI hollow fiber substrate immobilized with MWCNT and chemically treated with PEI solution	Phase inversion, vacuum filtration, chemical post-treatment	DI water (0.5 M MgCl2)	~13	[K. Goh et al,2013]
2013	Polyamide TFC	Polyvinylidene fluoride (PVDF) nanofiber substrate, polyamide active layer	Electrosipinning, interfacial polymerization	DI water (1 M NaCl)	11.6–28	[M. Tian et al,2013]

Table (C.1): (continued)

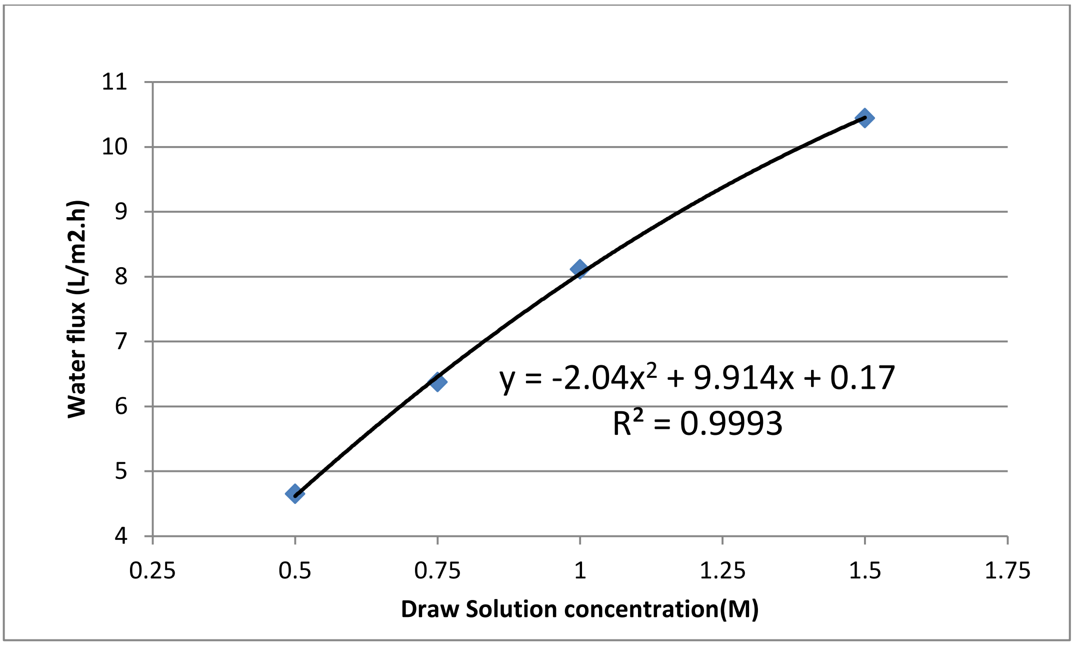
year	membrane	material	Preparation	Feed solution (draw solution)	Water flux in FO mode (L/m^{2}h)	Reference
2013	Flat sheet TFC	Sulfonated polyphenylene sulfone (sPPSU) substrate, polyamide active layer	Direct synthesis route with various content of sulfonated units, interfacial polymerization	DI water (3 M NaCl)	10	[N. Widjojo et al,2013]
2013	Thin-film inorganic (TFI) membrane	Microporous silica xerogels immobilized onto a stainless steel mesh (SSM) substrated	Layer-by-layer (LbL) deposition	DI water (2 M NaCl)	59.8	[S.You et al,2013]
2014	Poly (vinyl) alcohol coated RO membranes	Polysulfone support layer of RO membranes (seawater SW 30-XLE and brackish water BW 30, Dow Water & Process Solutions) coated with poly (vinyl) alcohol (PVA)	PVA crosslinking using maleic acid or glutaraldehyde	DI water (0.05 M, 0.5 M, 1 M, and 1.5 M NaCl)	<0.6	[A. Saraf et al,2014]
2014	Nanofiber thin film composite (NTFC)	Hydrophilic cross-linked PVA nanofiber support, polyamide active layer	Electrospinning, chemical cross-linkage, interfacial polymerization	DI water (0.5 M NaCl)	27.24	[J. M. C. Puguan et al,2014]
2014	Flat sheet TFC	RO membranes (SW 30-XLE and BW 30, Dow Water & Process Solutions) support layers modified with polydopamine (PDA)	Dopamine polymerization	Pure water (2 M NH4CO3)	7 (BW 30) 11 (SW 30-XLE)	[J. T. Arena et al,2014]
2014	TFC hollow fiber	Polyethersulfone hollow fiber substrate, polyamide active layer chemically treated with cetyltrimethyl ammonium chloride (CTAC)	Interfacial polymerization, chemical cross-linking	DI water (2 M NaCl)	5.32	[Q. Jia et al,2014]
2014	Thin-film nanocomposite (TFN)	PSf support, polyamide active layer containing silica nanoparticles	Phase inversion, interfacial polymerization	10 mM NaCl (2 M NaCl)	22 ± 2 (0.1 wt/vol.% silica loading)	[N. Niksifat et al,2014]
2014	TFC tri-bore hollow fiber	Tri-bore Matrimid support, Polyamide active layer on inner surface	Dry-jet wet-spinning process using a specially designed tri-bore spinneret with blossom geometry	Pure water (2 M NaCl)	11.8	[L. Luo et al,2014]
2014	Flat sheet TFC	(PSf)–titanium dioxide (TiO2) nanocomposite substrate, polyamide active layer	Phase inversion, interfacial polymerization	10 mM NaCl (2 M NaCl)	40 (0.75 TiO2 loading)	[D. Emadzadeh et al,2014]
2014	Flat sheet TFC	Polysulfone (PSf) and sulfonated poly (phenylene oxide) (SPPO) substrate, polyamide active layer	Phase inversion, interfacial polymerization	DI water (2 M NaCl)	39	[Z. Zhou et al,2014]
2015	Flat sheet TFC	Silica–polysulfone substrate, polyamide active layer	Phase inversion, interfacial polymerization	DI water (1 M NaCl)	~28	[X. Liu et al,2015]

Appendix (D)

1. Deionized Water

Table D.1 Performance of FO membrane in water flux for DI water

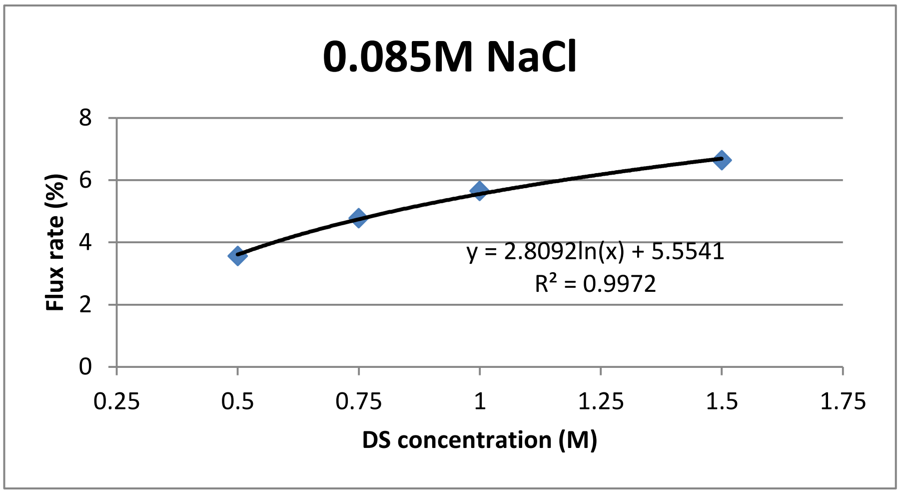
Draw solution concentration (M)	$J_v(L/m^2.h)$
0.50	**4.65**
0.75	**6.37**
1.00	**8.11**
1.50	**10.44**

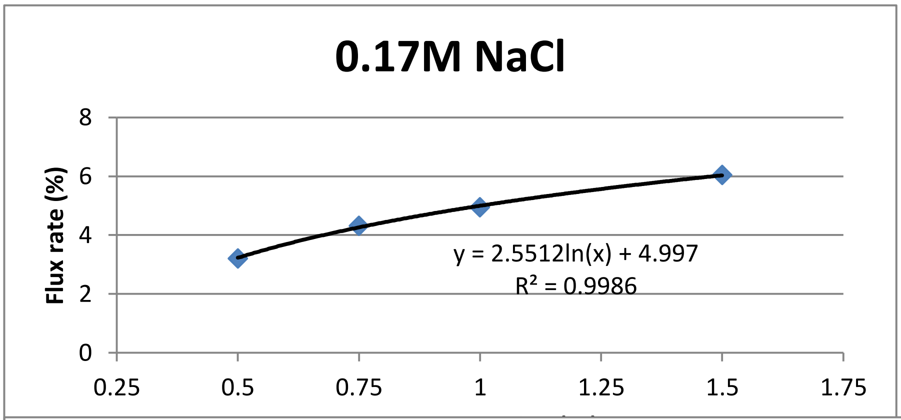


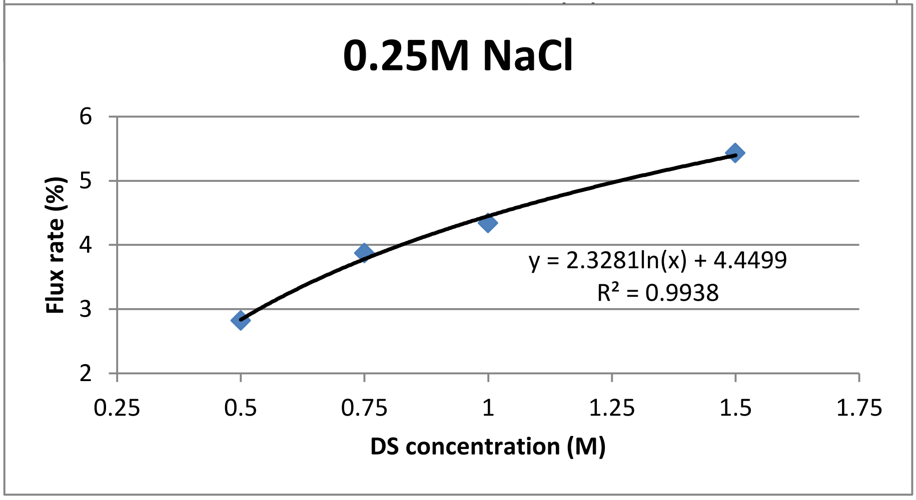
2. NaCl Solution Water Flux

Table D.2 Relation between DS different concentrations and flux for NaCl solutions.

NaCl Conc.	DS Concentration (M)			
(M)	**0.5**	**0.75**	**1**	**1.5**
	Flux Rate (L/m^2.h)			
0.085	3.56	4.77	5.64	**6.63**
0.17	3.21	4.32	4.95	**6.04**
0.25	2.82	3.87	4.34	**5.43**



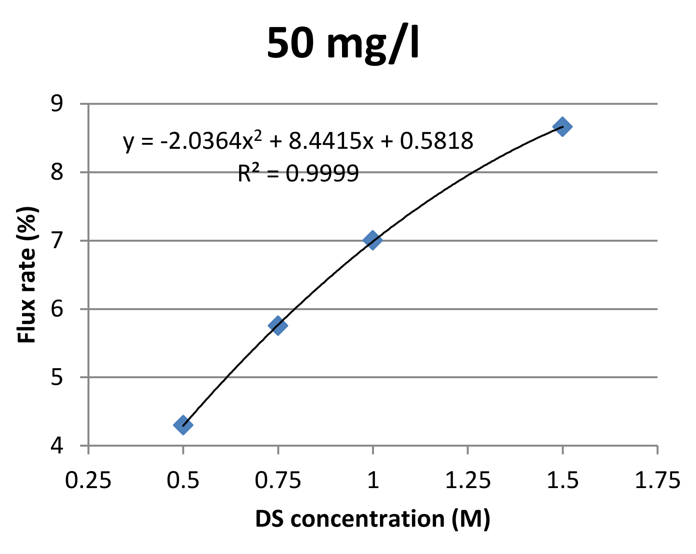


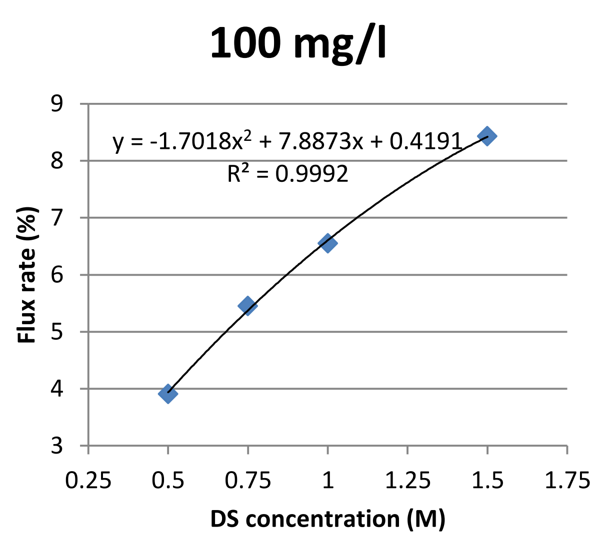


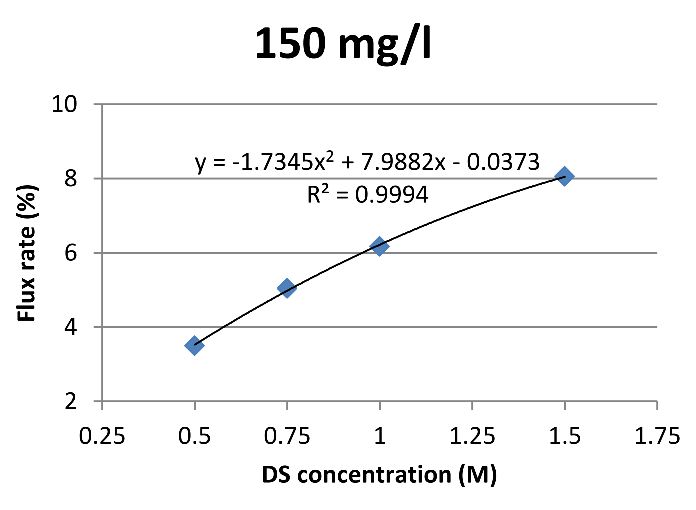
3. NO_3 Solution Water Flux

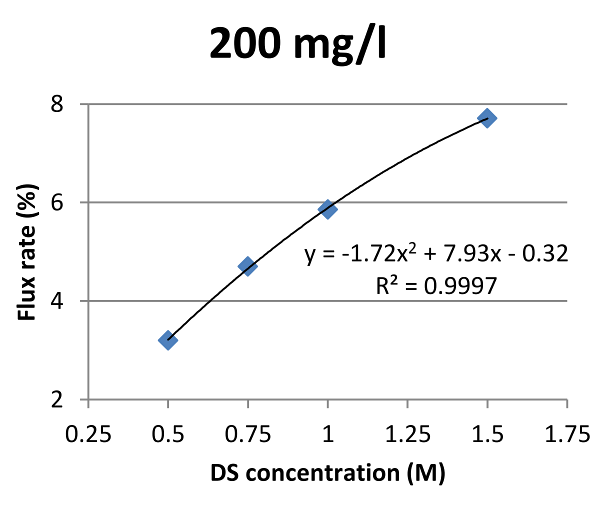
Table D.3 Relation between DS different concentrations and flux for NO_3 solutions.

Nitrate Conc. (mg/L)	**DS Concentration (M)**			
	0.5	**0.75**	**1**	**1.5**
	Flux Rate (L/m2.h)			
50	4.23	5.80	7.15	**8.66**
100	3.85	5.45	6.82	**8.43**
150	3.50	5.04	6.44	**8.05**
200	3.20	4.73	6.00	**7.61**


50 mg/l


100 mg/l

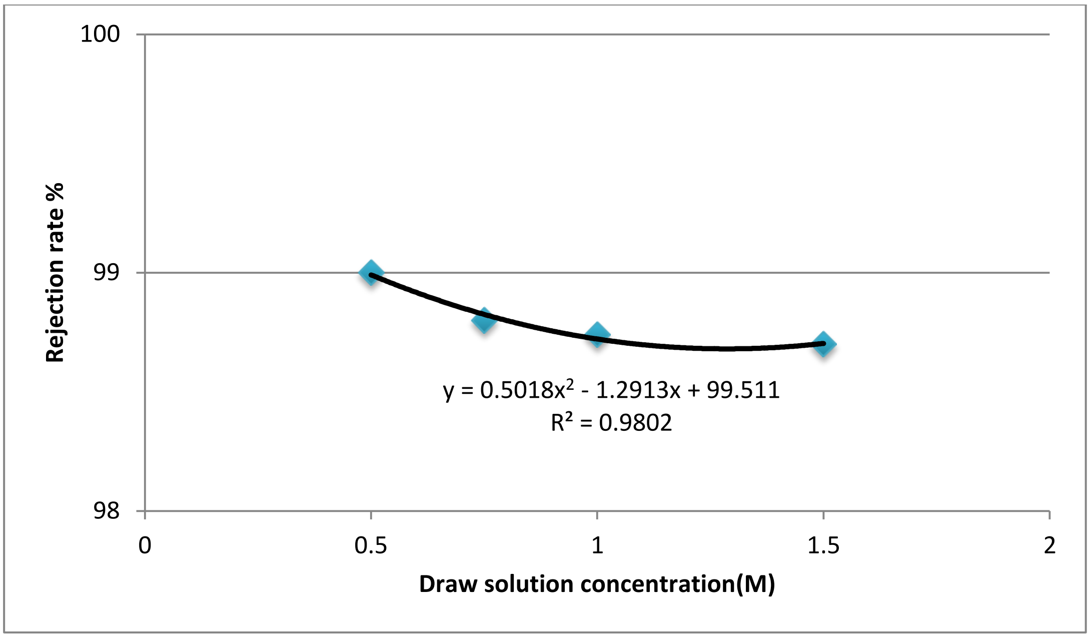

150 mg/l


200 mg/l

4. NaCl Solution rejection

Table D.4 Relation between DS concentration and rejection rate for 0.085M NaCl.

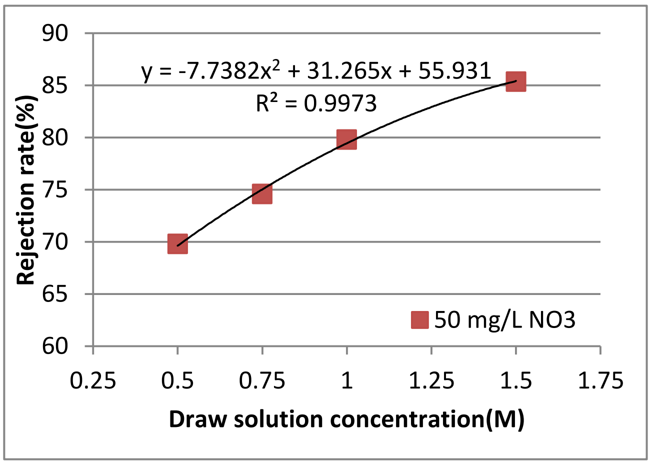
NaCl Conc.	**DS Concentration (M)**			
(M)	**0.5**	**0.75**	**1**	**1.5**
	Rejection Rate (%)			
0.085	99	98.8	98.65	**98.57**

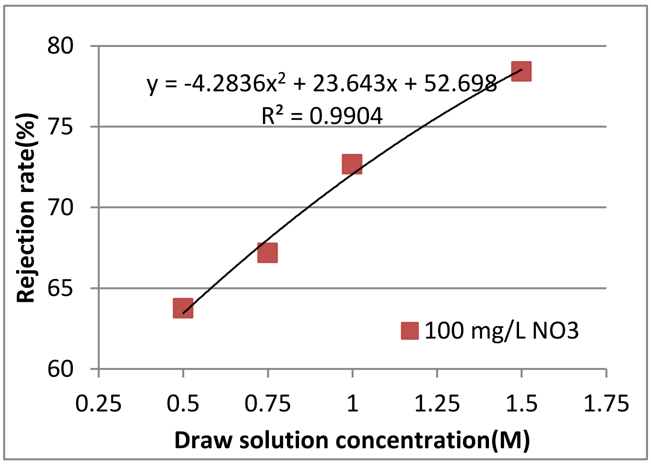


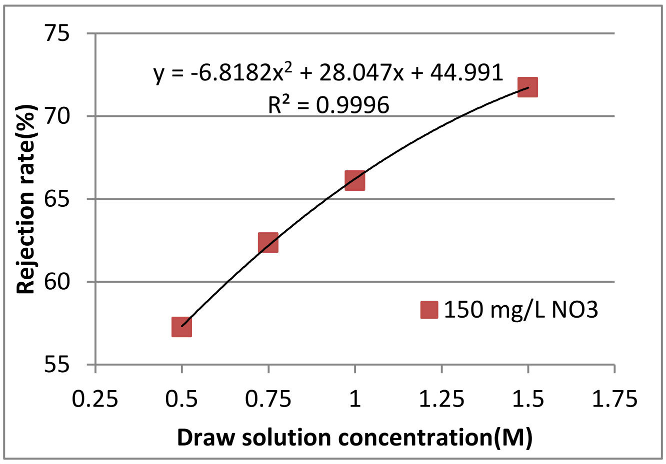
5- NO$_3$ Solution Rejection Rate

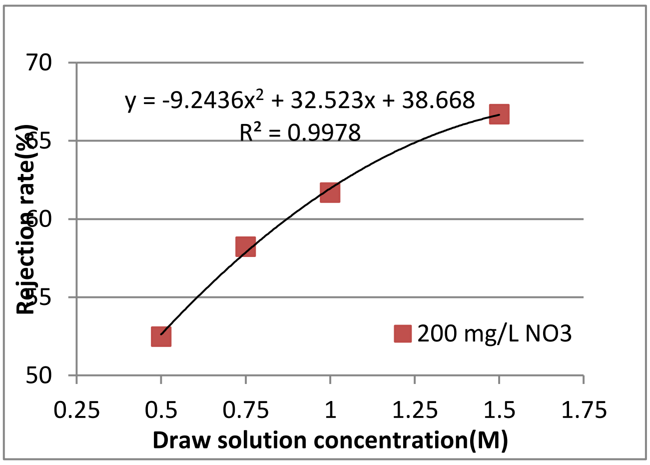
Table D.5 Relation between DS concentrations and rejection rate for NO$_3$ concentrations.

Nitrate Conc. (mg/L)	**DS Concentration (M)**			
	0.5	**0.75**	**1**	**1.5**
	Rejection Rate (%)			
50	69.80	74.57	79.80	**85.36**
100	63.76	67.19	72.68	**78.42**
150	57.55	62.35	66.21	**71.74**
200	52.48	58.23	61.67	**66.7**









6- Performance of membrane for real brackish water in the flux

Table D.6 Flux rate of FO membrane for Radwan 9

Draw solution concentration (M)	$J_v(L/m^2.h)$
0.5	3.35
0.75	4.34
1.00	5.42
1.50	6.63

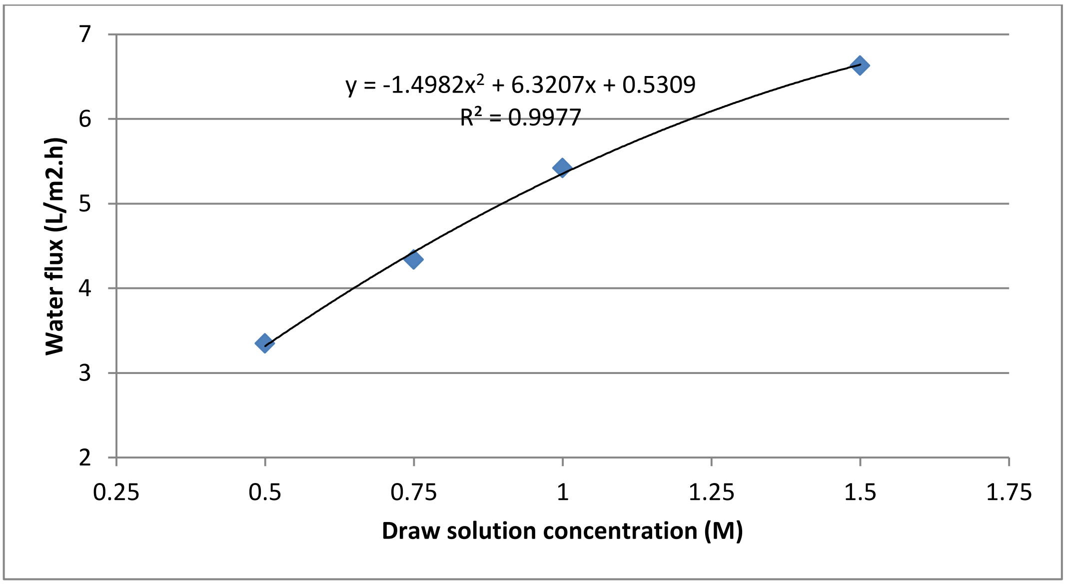


Table D.7 Flux rate of FO membrane for Aljalaa 14

Draw solution concentration (M)	J_v(L/m^2.h)
0.50	3.00
0.75	3.94
1.00	4.95
1.50	6.02

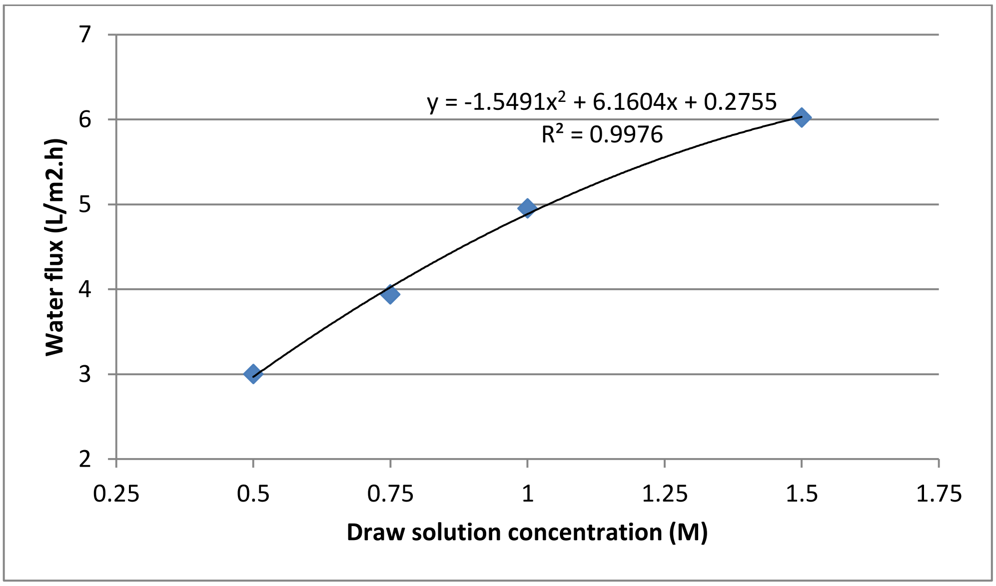


Table D.8 Flux rate of FO membrane for Radwan A3

Draw solution concentration (M)	J_v(L/m^2.h)
0.50	**2.72**
0.75	**3.67**
1.00	**4.52**
1.50	**5.43**

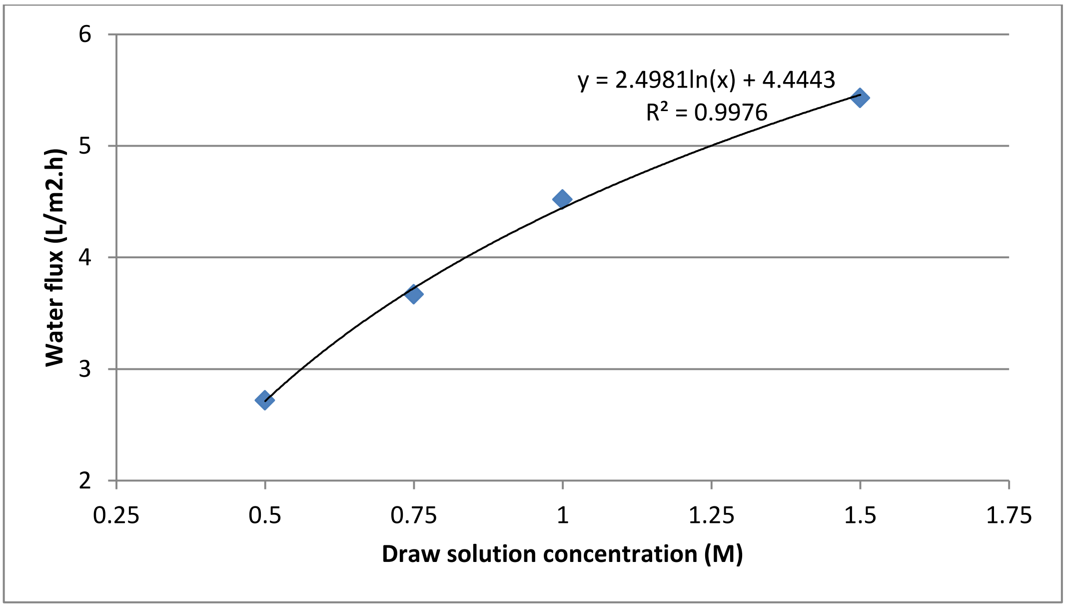
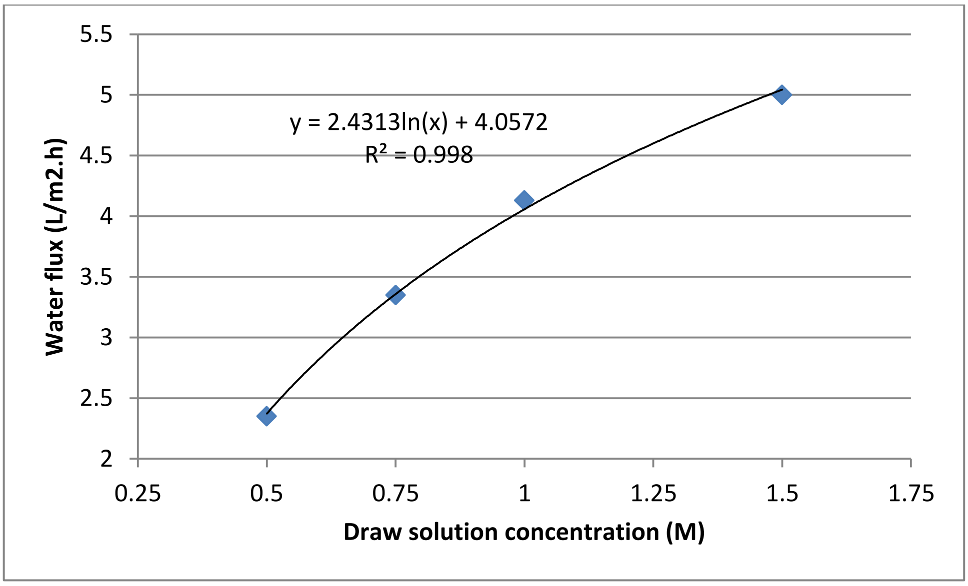


Table D.9 Flux rate of FO membrane for Remal 4 Becdar

Draw solution concentration (M)	J_v(L/m^2.h)
0.50	**2.35**
0.75	**3.35**
1.00	**4.13**
1.50	**5**



7-Rejection of NO_3 in real brackish water

Table D.10 Performance of FO membrane for Radwan 9

Well Name	TDS	NO_3
Radwan 9	**2450**	**81**

draw solution concentration	Nitrate concentration (mg/L)		Rejection rate %
	Before FO	After FO	
0.50	81	31.9	60.6
0.75		28.27	65.1
1.00		24.54	69.7
1.50		19.68	75.7

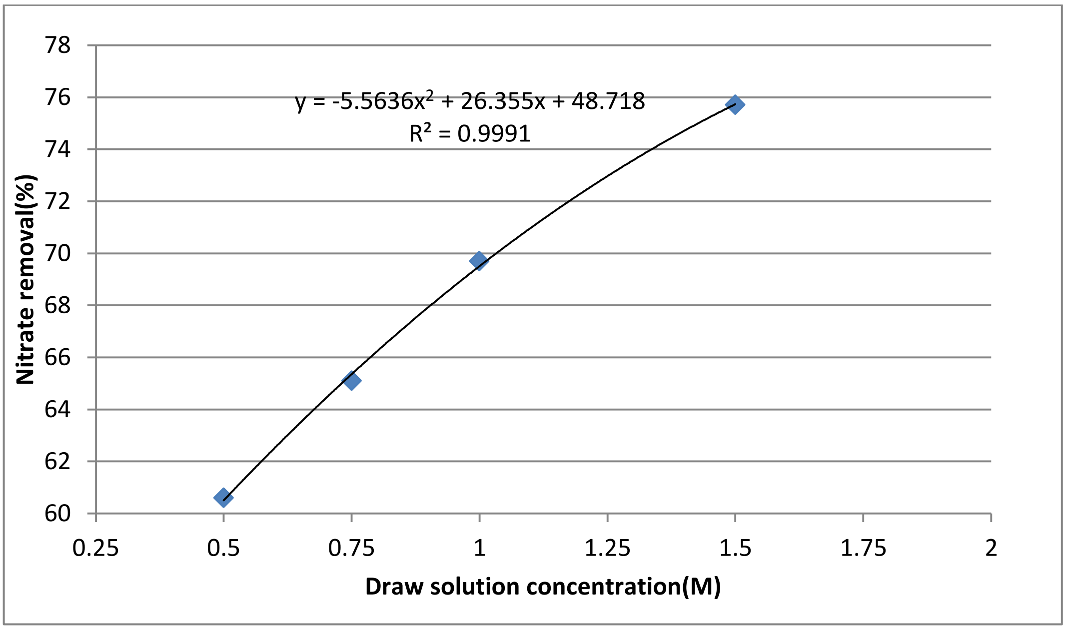


Table D.11 Performance of FO membrane for Aljalaa 14

Well Name	TDS	NO_3
Aljalaa 14	**4768**	**69**

draw solution concentration	Nitrate concentration (mg/L)		Rejection rate %
	Before FO	After FO	
0.50	69	29.05	57.96
0.75		26.81	61.14
1.00		23.68	65.68
1.50		20.41	70.42

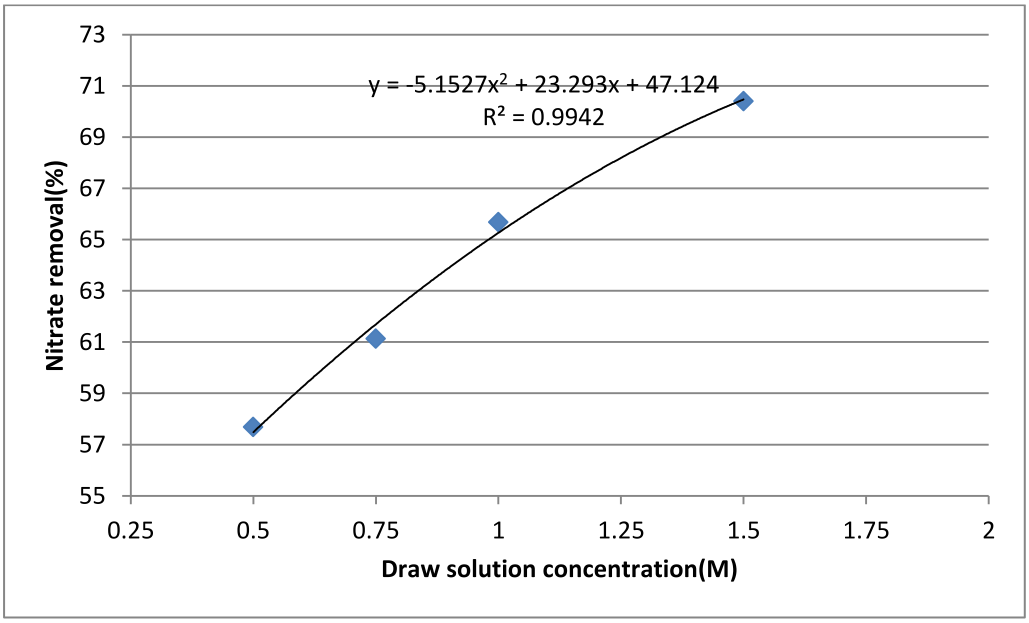


Table D.12 Performance of FO membrane for Radwan A3

Well Name	TDS	NO_3
Radwan A3	**8650**	**193**

Draw solution concentration	Nitrate concentration (mg/L)		Rejection rate %
	Before FO	After FO	
0.50	193	91.77	52.45
0.75		84.05	56.45
1.00		74	61.66
1.5		66.39	65.6

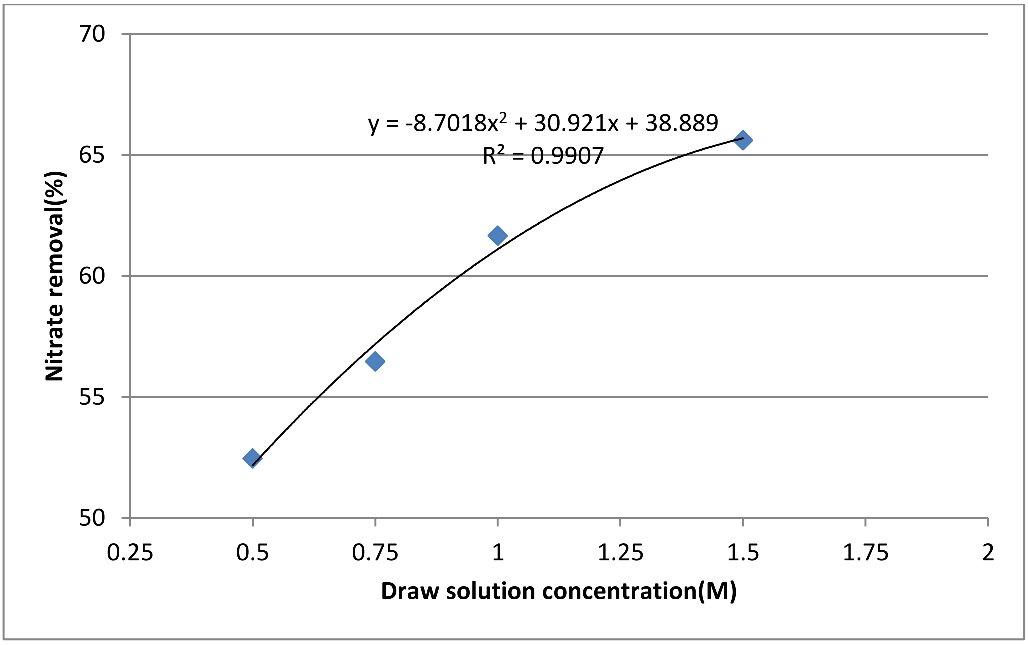
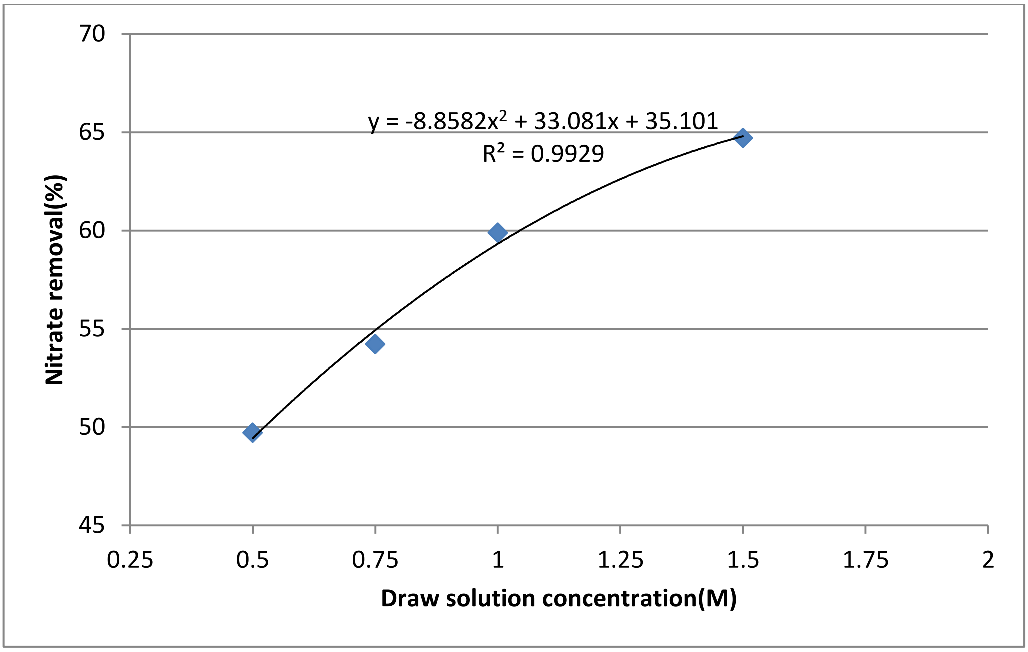


Table D.13 Performance of FO membrane for Remal 4 Pecdar

Well Name	TDS	NO_3
REMAL 4 PECDAR	**15200**	**111**

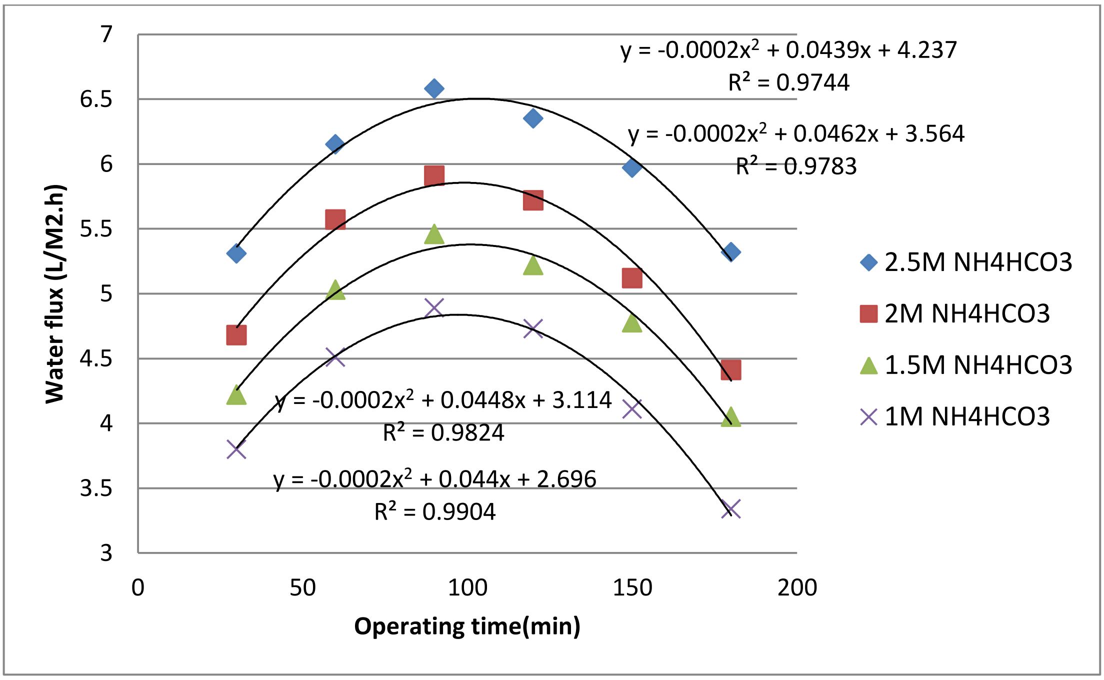
Draw solution concentration	Nitrate concentration (mg/L)		Rejection rate %
	Before FO	After FO	
0.50	111	55.85	49.68
0.75		50.80	54.23
1.00		44.54	59.87
1.50		40.30	63.7



8- Flux rate and rejection rate for synthetic seawater

Table D.14 Performance of FO membrane for synthetic seawater

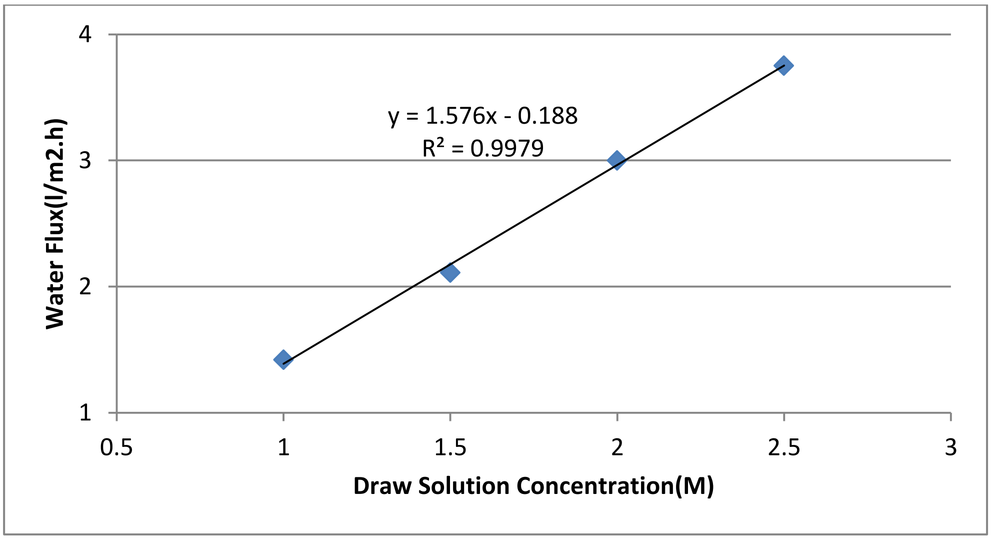
Draw solution concentration (M)	$J_v(L/m^2.h)$
1.00	4.89
1.50	5.46
2.00	5.94
2.50	6.58



9- Flux rate and rejection rate for real seawater

Table D.15 Performance of FO membrane on flux

Draw solution concentration (M)	$J_v(L/m^2.h)$
1.00	2.11
1.50	3.16
2.00	4.03
2.50	4.83



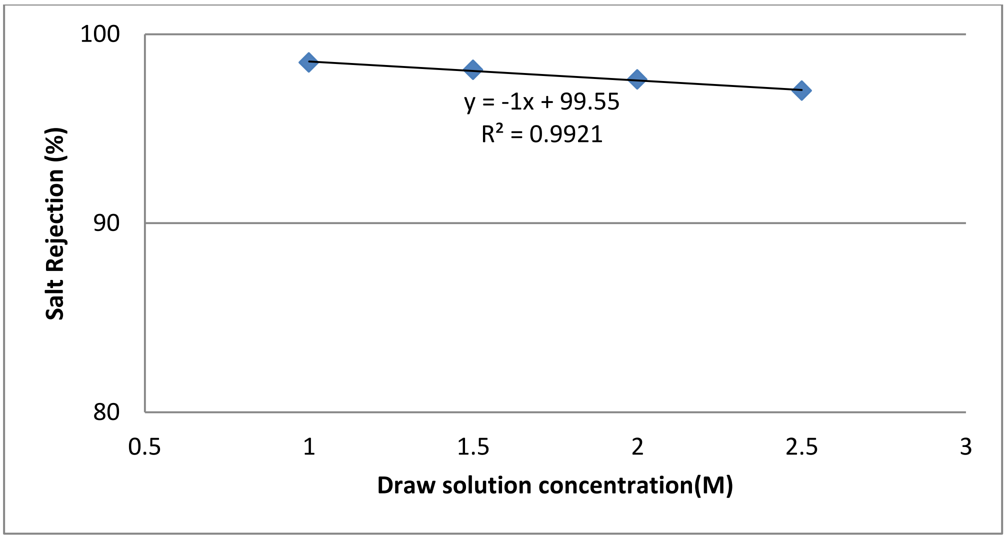


Table D.16 Effect of heating process on removal different initial NH_4HCO_3 concentrations

Time (hr)	Initial NH_4HCO_3 Concentration(M)	Final NH_4HCO_3 Concentration (M)	Time (hr)	Initial NH_4HCO_3 Concentration (M)	Final NH_4HCO_3 Concentration (M)
1	0.75	0.45	1	0.5	0.29
2		0.39	2		0.24
3		0.3	3		0.2
4		0.203	4		0.125
5		0.13	5		0.1
6		0.13	6		0.085
7		0.11	7		0.085

Time (hr)	Initial NH_4HCO_3 Concentration(M)	Final NH_4HCO_3 Concentration (M)	Time (hr)	Initial NH_4HCO_3 Concentration (M)	Final NH_4HCO_3 Concentration (M)
1	0.25	0.138	1	0.1	0.048
2		0.105	2		0.048
3		0.075	3		0.03
4		0.075	4		0.027
5		0.075	5		0.027
6		0.063	6		0.027
7		0.063	7		0.02