



Ain Shams University
Faculty of Science
Chemistry Department

Preparation and Characterization of Composite Reverse Osmosis Membranes and Its Application for Saline Water Desalination

A Thesis submitted for PH.D.

By

Amera Marey Mohammed Hassanien
M.Sc. (2009)

A THESIS SUBMITTED

By

Amera Marey Mohammed Hassanien

M. Sc. (2009)

Under Supervision of

Approved

1. **Dr. Maher Abd El Aziz El Hashash**
Prof. of Organic chemistry
Chemistry dept., faculty of Science, Ain Shams University
2. **Dr. Mohamed Ahmed Mekewi**
Prof. of Polymer chemistry
Chemistry dept., faculty of Science, Ain Shams University
3. **Dr. Dalal Basanty Guirguis**
Assistant Professor of Organic chemistry
Chemistry dept., faculty of Science, Ain Shams University

Head of
Chemistry Department

Prof.Dr. Hesham Ahmed Madian

ACKNOWLEDGEMENT

ACKNOWLEDGEMENT

The author would like to express her deepest gratitude's to **Dr. Maher Abd El Aziz El Hashash**, Prof. of Organic chemistry, chemistry department, faculty of science, Ain Shams University, for suggesting the research point and supervising the thesis and his valuable discussions and kind cooperation.

My appreciation is obliged to **Dr. Mohammed Ahmed Mekewi**, Prof. of polymers, chemistry department, faculty of science, Ain Shams University, for his effective guidance, fruitful discussions and sincere assistance to bring the present work to its deserved level of acceptance.

Many sincere are also due to **Dr. Dalal Besanty Guirguis**, assistant Professor of organic chemistry, for her kind help and support for carrying out this work.

Finally, my gratitude's are sincerely due to my family especially husband whose devotions and sincere understanding was my motive to accomplish this work in its presented form.

The present work

In the present study, thin film PVA/CA+PEG membranes are to be prepared and the PVA layer to be cross-linked by varying maleic acid concentration at different reaction periods. The polymer composite is to be employed for the reverse osmosis process of brackish, saline and sea water purification. The water flux and salt rejection selectivity of the RO membranes are to be monitored. The structural characterization of the polymer composite membranes, degree of crosslinking, crystallinity, surface roughness and hydrophobicity of the thin CA layers are to be emphasized using FT-IR, SEM, X-ray diffraction and the thermal stability viability through TGA performance.

Two factors must be balanced for a reverse osmosis membrane to work properly, namely, water permeability and salt rejection. Both water flux and salt rejection are also dependent on membrane properties, solution chemistry, and operating conditions. Finally, the antimicrobial activities of the synthesized membranes are to be assessed.

Thesis frame-work

The thesis is presented in a sequential structure in order to fulfill the requirements of the objectives and scope of the study. The thesis is presented in the following chapters:

Chapter 1: Introduction

Chapter 2: Experimental and methodology.

Chapter 3: Results and Discussion.

A -Synthesis, characterization and performance of reverse osmosis membranes.

B- Application of synthetic PVA+CA&PEG composite membranes in desalination of saline water.

Summary and Conclusions

References

Arabic Abstract

List of symbols and abbreviations

Abbreviation

Atomic force microscopy	(AFM)
Cellulose acetate	(CA)
Differential scanning microscope	(DSC)
Electric conductivity	(EC)
Escherichia coli	(E.coli)
Fourier transform infrared spectroscopy	(FTIR)
Membrane distillation	(MD)
(MF)Membrane filtration	
Nano filtration	(NF)
Polyacrylic acid	(PAA)
Polyethylene glycol	(PEG)
Polyvinyl alcohol	(PVA)
Reverse osmosis	(RO)
Staphylococcus-aureus	(S-ureus)
Scanning electron microscope	(SEM)
Total dissolved solid	(TDS)
Thin film composite	(TFC)
Thermal gravimetric analysis	(TGA)
Ultra-filtration	(UF)

List of symbols and abbreviations

Total dissolved solids (TDS)

Total dissolved solids

LIST OF CONTENTS

LIST OF CONTENTS

Acknowledgement-----	I
List of Content-----	II
List of Figures-----	VII
List of Tables-----	IX
Abstract-----	XI
List of Symbols and Abbreviations-----	XIII

CHAPTER (I) INTRODUCTION

1	General Outline-----	1
2	Water desalination review and literature -----	3
	2.1 Distillation process -----	3
	2.2 Solar evaporation -----	4
	2.3 Freezing process-----	4
	2.4 Ion exchange process-----	5
	2.5 Electro dialysis process-----	5
	2.6 Membrane Filtration -----	6
	2.7 Reverse osmosis (RO) -----	6
3	Membrane technology-----	8
4	Synthetic polymers and composite separation membranes.-----	11
5	Desalination of saline water using reverse osmosis membranes-----	29
6	Antimicrobial effect on the synthetic membrane and desalinated water quality-----	33

LIST OF CONTENTS

CHAPTER (II) EXPERIMENTAL AND METHODOLOGY

	Advantages of the reverse osmosis process	42
	Materials and Methodology	43
1	Chemicals-----	43
2	Membrane Preparation -----	44
	2.1 Microporous PVA support membrane-----	44
	2.2 Fabrication of composite membranes (dip Coating method)-----	45
	2.3 Swelling measurement of the dip coating Membranes-----	47
3	Membrane characterization and functional features-----	47
	3.1 FT-IR spectroscopic analysis-----	47
	3.2 Microstructure studies-----	48
	3.3 Thermal stability profile (TGA)-----	48
	3.4 Mechanical properties-----	48
	3.5 Reverse Osmosis measurement-----	49
	3.6 Antimicrobial studies-----	51

LIST OF CONTENTS

CHAPTER (III) RESULTS AND DISCUSSIONS PART A

Synthesis, Characterization and Performance of Reverse Osmosis Membranes

	General Outline-----	52
1	Membrane synthesis optimization factors----	53
	1.1 Cellulose acetate bilayering-----	53
	1.2 Polyethylene glycol (PEG) addition effect	54
	1.3 Cross-linking agent concentration effect	56
	1.4 Effect of reaction temperature-----	57
	1.5 Effect of overall reaction time-----	58
2	Effect of membrane thickness on RO	59
	efficiency-----	
3	Effect of chemical treatment on the membrane	60
	Chemistry-----	
4	Effect of solvent evaporation-----	61
5	Effect of feed concentration-----	63
6	Effect of applied pressure-----	64
7	Effect of operation time-----	66
8	Synthetic membranes characterization-----	67
	8.1 Structural characterization studies by	67
	FT-IR Spectroscopy -----	
	Microstructure and topographical features----	70
9	9.1 Scanning electron microscopy studies	71
	(SEM)-----	
	9.2 Atomic force microscopy (AFM)-----	74
10	Synthetic membranes thermal stability studies	75
11	Mechanical properties-----	77

LIST OF CONTENTS

CHAPTER (3) RESULTS AND DISCUSSIONS PART B

Applications of synthetic PVA/CA reverse osmosis membranes in the desalination process of natural saline water

1	PVA/CA RO membranes and effect of PEG addition viability-----	83
2	Calibration of RO properties of PVA/CA composite membranes-----	85
3	Application of PAC ₂₅ RO membrane in the desalination of water-----	86
	3.1 Desalination of highly saline water (sea water)-----	86
	3.2 Desalination of brackish water-----	87
	3.3 Desalination of sea water (extremely saline water)-----	88
4	Electrolyte permeation mechanism through the synthetic reverse osmosis membrane-----	93
5	Antimicrobial activity and RO synthetic membrane-----	98
	5.1 Microorganisms profiles in sea water-----	98
	5.2 Which microorganisms in water cause diseases? -----	100
	5.3 Development of antimicrobial membranes via the surface of RO composite membrane	104
	5.4 Evaluation of PEG modified PVA/CA RO membrane antimicrobial activity-----	104
	5.5 Antimicrobial protection-----	107

LIST OF CONTENTS

Summary and Conclusions	109-110
References-----	111-118
Arabic Summary-----	1-2

LIST OF FIGURES

No	List of Figures Description	Page
1	Schematic cross-linking mechanism of PVA	44
2	The principle of operation of. membrane processing	46
3	Schematic representation of membrane distillation with a composite membrane	46
4	Reverse osmosis system, model Lab.20	50
5	Feed circulating pump& R.O Module	50
6	Effect of membrane thickness on the performance of pure composite PAC ₂₅ + PEG membrane	55
7	Effect of reaction temperature on swelling, conversion and water insoluble part (%) of PAC ₂₅ + PEG	58
8	Effect of reaction time on swelling, of PAC ₂₅ + PEG	59
9	Effect of applied pressure on salt rejection and water flux of: :(M ₁ is PVA), (M ₂ is PAC ₂₅) and (M ₃ is PAC ₂₅ + PEG) composite membrane	65
10	Effect of operation time on reverse osmosis performance of Pac ₂₅ and PAC ₂₅ +PEG) composite membrane	67

LIST OF FIGURES

11	(a) FT-IR spectroscopic features of pure polyvinyl alcohol (PVA)	68
	(b) FT-IR spectroscopic features of crosslinked polyvinyl alcohol PVA _I	68
	(c) FT-IR spectroscopic features of PAC ₂₅	69
	(d) FT-IR spectroscopic features of PAC ₂₅ + PEG	70
12	(A): SEM of PVA at different malice acid concentration	72
	(B): SEM of (a) pure cellulose acetate, (b) PVA-CA membrane and (c) PVA-CA&PEG composite membranes	74
13	AFM images showing the 2D and 3D surfaces of (a) CA, (b) PAC ₂₅ and (c) PAC ₂₅ +PEG membranes	75
14	Thermo-gravimetric diagram showing the effect of PEG grafting on thermal stability of polyvinyl alcohol and cellulose acetate membranes. A = PAC ₂₅ and B = PAC ₂₅ +PEG	77
15	Electrolyte transport through reverse osmosis (RO) (A) may occur through two path ways (B) Ion- pair mechanism and (C) Coupled transport of ions Mechanism	97
16	Images of Gram-ve and Gram +ve bacteria on the PEG modified PAC ₂₅ RO membrane	107

LIST OF TABLES

List of Tables

No.	Description	Page
1	Effect of CA addition on the PVA membrane reverse osmosis parameters.	54
2	Effect of PEG addition on PAC ₂₅ membrane on reverse osmosis parameters.	55
3	Effect of crosslinking agent concentration on the membrane swelling characterization.	57
4	Effect of membrane thickness on reverse osmosis parameters.	60
5	Effect of chemical treatment or quaternization on the swelling of PAC ₂₅ composite membrane	61
6	Effect of evaporation temperature on RO parameters	61
7	Effect of evaporation time on RO parameters	62
8	Effect of feed concentration on reverse osmosis Parameters.	64
9	The mechanical properties for some synthetic composite reverse osmosis membranes.	79
10	The selected reverse osmosis membranes used as desalination in saline water.	83
11	Reverse osmosis functional parameters for the selected membranes	84