

شبكة المعلومات الجامعية التوثيق الإلكتروني والميكروفيلو

بسم الله الرحمن الرحيم





MONA MAGHRABY



شبكة المعلومات الجامعية التوثيق الإلكتروني والميكروفيلو



شبكة المعلومات الجامعية التوثيق الالكتروني والميكروفيلم



MONA MAGHRABY



شبكة المعلومات الجامعية التوثيق الإلكترونى والميكروفيلم

جامعة عين شمس التوثيق الإلكتروني والميكروفيلم قسم

نقسم بالله العظيم أن المادة التي تم توثيقها وتسجيلها علي هذه الأقراص المدمجة قد أعدت دون أية تغيرات



يجب أن

تحفظ هذه الأقراص المدمجة بعيدا عن الغبار



MONA MAGHRABY



Radiation Modification of Reverse Osmosis Membranes for Desalination of Saline Water

Thesis Submitted for the requirements of philosophy Degree (Ph. D.)
In Chemistry

Hany Marzouk Gayed Marzouk

(M.Sc. in Chemistry 2015)

To

Chemistry Department, Faculty of Science, Ain Shams University

National Center for Radiation Research and Technology, Atomic Energy Authority

2020



Radiation Modification of Reverse Osmosis Membranes for Desalination of Saline Water

Thesis Submitted for the requirements of philosophy Degree (Ph. D.) In Chemistry

By Hany Marzouk Gayed Marzouk

(M.Sc. in Chemistry 2015)

To

Chemistry Department- Faculty of Science Ain-Shams University

Thesis advisors

Prof. Dr. Mohamed Sabry A. Abdel-Mottaleb Prof. Dr. Nabila Ahmad Maziad

Prof. Emeritus of Inorganic chemistry, Department of Chemistry, Faculty of Science, Ain Shams University

Prof. of Radiation Chemistry, National Center for Radiation Research and Technology, Atomic Energy Authority

Prof. Dr. Abdel-Hameed Mostafa El-Aassar

Prof. of water desalination, Egyptian Desalination Research Center of Excellence, Desert Research Center

Ass. Prof. Dr. Faten Ismail Abou El Fadl

Ass. Prof of Radiation Chemistry, National Center for Radiation Research and Technology, Atomic Energy Authority



APPROVAL SHEET

Title of Ph.D. Thesis:

Radiation Modification of Reverse Osmosis Membranes for Desalination of Saline Water

Name of the candidate: Hany Marzouk Gayed Marzouk

This thesis has been approved by:

Radiation Research and Technology, Atomic Energy

Authority

Prof. Dr. Mohamed Sabry A. Abd El-Mottaleb Prof. Emeritus of Inorganic chemistry, Department of Chemistry, Faculty of Science, Ain Shams University Prof. Dr. Nabila Ahmad Maziad Prof. of Radiation Chemistry, National Center for Radiation Research and Technology, Atomic Energy Authority Prof. Dr. Abdel-Hameed Mostafa El-Aassar Prof. of water desalination, Egyptian Desalination Research Center of Excellence, Desert Research Center Ass. Prof. Dr. Faten Ismail Abou El Fadl Ass. Prof of Radiation Chemistry, National Center for

Head of chemistry department Faculty of Science - Ain-Shams University **Prof. Dr. Ayman Ayoub Abdel-Shafi**

Acknowledgement

It's a great pleasure to acknowledge my deepest thanks and gratitude to **Prof. Dr. Mohamed Sabry A. Abdel-Mottaleb,** Professor of Inorganic Chemistry, faculty of Science Ain-Shams University for sponsoring this thesis, his continuous interest and support.

I would like to express my deepest thanks and sincere appreciation to **Prof. Dr. Nabila A. Maziad,** Professor of Radiation Chemistry, National Center for Radiation Research and Technology, Atomic Energy Authority, Atomic Energy Authority for suggesting the problem, her supervision, encouragement, creative and comprehensive advice until this work came to existence.

Deep appreciation and sincere thanks are also due to **Prof. Abdel-Hameed**Mostafa El-Aassar, Prof. of water desalination, Egyptian Desalination Research

Center of Excellence, Desert Research Center for his supervision, encouragement and
quidance through this thesis.

I would like to express my sincere gratitude to **Ass.Prof. Faten Ismail Abou El Fadl**, Assistant prof. of organic Chemistry, National Center for Radiation

Research and Technology, Atomic Energy Authority, for her encouragement and support through this work.

Special gratitude is expressed to EDRC team who helped me and facilitated conditions to achieve this work.

Thanks are also due to all the staff members of the Polymer Chemistry Department and National Center for Radiation Research and Technology for their cooperation.

LIST of CONTENTS				
ABSTRACT		I		
AIM of WORK				
LIST of FIGU	RES	IV		
LIST of TABLES		IX		
LIST of SCHEMES		X		
LIST of ABBR	REVIATIONS	XI		
	Chapter 1. Introduction			
1.1	General outline.	1		
1.2	Problem definition	1		
1.3	Water desalination	2		
1.3.1	Challenges of water desalination	3		
1.3.2	Different desalination techniques	5		
1.3.2.1	Thermal distillation technique	5		
1.3.2.2	Membrane desalination	6		
1.3.2.2.1	Reverse osmosis (RO)	7		
1.3.2.2.2	Electrodialysis (ED)	8		
1.4	Reverse osmosis membrane technology	9		
1.4.1	Reverse osmosis membrane materials	10		
1.4.1.1	Cellulose acetate (CA)	10		
1.4.1.2	Polyamide thin film composite membranes	11		
1.4.2	Membrane fouling	12		

1.4.3	Membrane modification	15
1.4.3.1	Coating	16
1.4.3.2	Plasma treatment	17
1.4.3.3	Grafting	18
1.4.3.4	High energy particles	19
1.4.3.5	Nanoparticles Impact on Membrane Performance	22
	Chapter 2. Literature review	
2.1	General outline	26
2.2	Water desalination	26
2.3	Reverse osmosis membrane desalination	27
2.4	Surface modification of RO membrane	29
2.5	Fouling properties	35
2.6	Radiation modification	42
	Chapter 3. Materials and Methods	
3.1	General outline.	45
3.2	Materials	45
3.3	Experimental techniques	46
3.3.1	Radiation preparation of modified solution	46
3.3.2	Preparation of membranes for coating	47
3.3.3	Characterizations	48

3.3.3.1	Transmission electron microscopy (TEM)	48
3.3.3.2	The x-ray diffraction (XRD)	48
3.3.3.3	FTIR spectroscopic analysis	48
3.3.3.4	Scanning electron microscopy (SEM)	48
3.3.3.5	Atomic Force microscopy (AFM)	49
3.3.3.6	Thermal Gravimetric Analysis (TGA)	49
3.3.3.7	Gamma radiation source	49
3.3.3.8	Conductivity measurements	50
3.3.3.9	Contact angle measurements	50
3.3.4	Reverse osmosis performance of modified membranes	50
3.3.5	Fouling resistance	53
	Chapter 4. Results and discussion	
4.1	General outline	55
4.2	Pre-Irradiation of chitosan before coating PA membrane	55
4.2.1	Preparation and characterizations of CS/TiO ₂ nanodispersion	57
4.2.1.1	Transmission electron microscopy of CS/TiO_2 nanodispersion	57
4.2.1.2	The XRD of CS/TiO ₂ nanodispersion	58
4.2.2	Preparation and characterizations of CS/Ag nanodispersion	59
4.2.2.1	Transmission electron microscopy of CS/Ag	61

	nanodispersion	
4.2.2.2	The XRD of CS/Ag nanodispersion	63
4.2.3	Modification of PA membranes with chitosan, CS/TiO ₂ , and CS/Ag nanodispersions.	64
4.3	Characterizations of PA neat and modified membranes	67
4.3.1	FTIR analysis	67
4.3.2	Morphological study	73
4.3.3	X-Ray diffraction	75
4.3.4	Thermal properties	78
4.4	Performance evaluation of neat and modified membranes	80
4.4.1	4.4.1 Effect of irradiated chitosan on performance of PA membrane	81
4.4.1.1	4.4.1.1 Effect of chitosan concentration	81
4.4.1.2	Effect of radiation doses	84
4.4.2	Effect of irradiated CS/TiO ₂ and CS/Ag nanodispersions on performance of PA membrane	86
4.4.2.1	Effect of CS/TiO ₂ nanodispersion concentrations	87
4.4.2.2	Effect of CS/Ag nanodispersion concentration	89
4.4.2.3	Effect of irradiation dose	92
4.4.2.4	Effect of applied pressure	96
4.4.3	Hydrophilicity of PA, PA/CS/TiO ₂ PA/CS/Ag modified membranes	101

4.5	Fouling resistance of neat and modified membranes	104
4.5.1	Bio-fouling resistance	105
4.5.2	Mineral scaling propensity	111
	Summary and conclusion	113
	References	119
	Arabic summary	١

ABSTRACT

This research explored surface modification using different irradiated mixtures, at various compositions, of chitosan/Ag (CS/Ag) and Chitosan/TiO₂ (CS/TiO₂) nanodispersions to improve the membrane characteristics and fouling resistance of polyamide membranes as well.

The irradiated CS/Ag and CS/TiO₂ nanodispersions at various concentrations were used for coating, PA membrane to improve its The performance. radiation prepared CS/Ag and CS/TiO₂ nanodispersions were characterized to monitor the shape and particle size of TiO₂ and Ag by transmission electron microscopy (TEM) and X-Ray diffraction (XRD). The surface morphology, membrane chemical composition and surface hydrophilicity were evaluated by scanning electron microscope (SEM) and atomic force microscopy (AFM), FT-IR spectroscopy (FTIR) and contact angle measurements respectively. FT-IR spectroscopy of the modified membranes proved the incorporation of CS, TiO₂ and Ag nanoparticles on the polyamide membrane. The performance of both neat and modified membranes for water desalination was also, evaluated.

Studying the results obtained from various modifications of PA membrane through the coating with different concentrations of irradiated chitosan, chitosan/TiO₂ and chitosan/Ag nanodispersions. The results of contact angle measurements showed that the permeability of the PA membrane was enhanced at low concentrations of the coating mixtures. Also, the water flux and salt

rejection were comparable with that reported in the literature. The biofouling resistance of PA membrane after modification with both CS/Ag and CS/TiO₂ nanodispersion against two types of bacteria gram positive and gram negative models; Staphylococcus aureus and Escherichia coli were examined. The PA/CS/TiO₂ modified membranes significantly reduced the number of viable cells by 90% and 69.5% for E. coli and S. aureus respectively, which is higher than that of the PA membrane which reduced it by 33% and 47.8% for both bacteria, respectively. Whereas the results in case of PA/CS/Ag modified membranes, showed reduction in the number of viable cells by 83% and 97% for E. coli and S. aureus respectively, which also still higher than that of the commercial polyamide membrane.

Aim of work

As the efforts to enhance the performance of neat PA reverse osmosis membrane are still growing many decades ago, it is still interesting and attracting for many researches to do their best in this field. So the aim of this work is mainly, based on; radiation and chemical modification of PA membrane by different examples of nano materials namely CS/TiO₂ and CS/Ag nanodispersions, to reach the optimum values for water flux and salt rejection. Also, it concerns with studying the PA, PA/CS/Ag and PA/CS/TiO₂ membranes by various techniques. This will be carried out to prove the interaction of CS/Ag and CS/TiO₂ nanodispersions with the surface of the PA membrane as FTIR, SEM, AFM, XRD, TGA, and contact angle measurements. In addition, we are going to evaluate the performance of neat and modified membranes. Furthermore, we are concerned with investigating the biofouling resistance of modified membranes.