

**IMPROVING ANTIFOULING AND ANTIMICROBIAL
CAPACITY OF REVERSE OSMOSIS DESALINATION
MEMBRANES BY THE SOL-GEL COUPLING OF SILANES**

BY

CHIDERA CHURCHILL NNADIEKWE

A Thesis Presented to the
DEANSHIP OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

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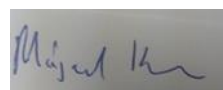
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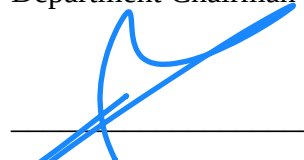
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2020

DEDICATION

To my beloved father and mother (Late) |

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I am completely thankful to Almighty God who granted me this prestigious opportunity to be alive in good health and sound mind to accomplish this great feat. If not for Him (God almighty), it would have ended in a gross failure...I am forever grateful.

I would also dedicate the proceeding few lines to recognize and acknowledge my family: My father, who went out of his comforts to pay every dime needed for my up-bring and academic pursuit; my mother, who brought me into this world and laid a formidable foundation of love, peace, hard work and righteousness in me. She never stopped praying for my breakthroughs and successes, although she is gone, she will forever be remembered! My siblings, for the warm support and decent encouragement they lavished on me...I am grateful!

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TABLE OF CONTENTS

ACKNOWLEDGMENTS	V
TABLE OF CONTENTS.....	VII
LIST OF TABLES.....	IX
LIST OF FIGURES.....	X
LIST OF ABBREVIATIONS.....	XII
ABSTRACT	XIV
ملخص الرسالة	XVI
CHAPTER 1 INTRODUCTION.....	1
1.1 Global water shortage	1
1.2 Desalination of Seawater.....	3
1.3 The technology of Reverse Osmosis.....	6
1.4 Research Objectives.....	9
1.5 Thesis outline.....	10
CHAPTER 2 LITERATURE REVIEW	12
2.1 The fouling of reverse osmosis membranes.....	12
2.1.1 Membrane biofouling.....	13
2.1.2 Critical Biofouling Effects.....	14
2.2 Controlling Fouling of RO Membranes.....	16
2.2.1 Types of RO Membrane Surface Modification.....	16
2.2.2 Physical treatment.....	17
2.2.3 Chemical Treatment.....	18
2.2.4 Sol-Gel Coupling of Silanes for RO Membrane Antifouling.....	19

CHAPTER 3 RESEARCH MATERIALS AND METHODOLOGY	21
3.1 Materials	21
3.2 Silane Film deposition on the RO membrane.....	22
3.3 Quaternization.....	22
3.4 Membrane Characterization.....	25
3.5 Adhesion of Bacteria and antibacterial Strength.....	26
3.5.1 Bacterial suspension preparation.....	26
3.5.2 Antibacterial performance of the modified membranes.....	27
3.5.3 Bacterial adhesion test.....	28
3.6 Membrane Filtration Testing.....	28
CHAPTER 4 RESULTS AND DISCUSSIONS.....	30
4.1 Surface Chemistry.....	30
4.2 Surface Morphology.....	32
4.3 Surface Wettability.....	35
4.4 Surface Elemental Analysis.....	38
4.5 Bacterial adhesion.....	40
4.6 Bacterial Killing.....	44
4.7 Filtration Testing.....	50
CHAPTER 5 CONCLUSION.....	54
REFERENCES.....	55
VITAE	67

LIST OF TABLES

Table 1. The bacteriostasis rate for the gram-negative <i>P. aeruginosa</i> for the 3-APS and 6-AHAS.....	48
Table 2. The water permeation flux (L/m ² hr.) obtained by the pristine and the modified membrane as well as the corresponding salt rejection degree.....	52

LIST OF FIGURES

Figure 1.	Trends of consumption of water within the last 20 th century; (A) Regional and (B) global	2
Figure 2.	The diagrammatic illustration of the techniques of desalination.....	4
Figure 3.	Major process classifications of desalination.....	4
Figure 4.	Desalination Technology Market (IDA in Koschikowski.....	5
Figure 5.	The feed water desalination industries make use of across the globe in percentage, and the world's desalination plant strength for various technology.....	6
Figure 6.	Illustration of water movement in natural and reverse osmosis processes.....	8
Figure 7.	The sequential steps of biofouling formation.....	13
Figure 8.	Diagrammatic illustration of an increase in hydraulic resistance taking place during the development of biofilm on the surface of the membrane.....	15
Figure 9.	The modification of the surface of thin-film composite polyamide reverse osmosis (RO) membrane via chemical reactions between amine groups and the epoxy.....	19
Figure 10.	The general mechanism of the sol-gel reaction process for the modification of the membrane surface with trialkoxyalkylsilane compounds.....	20
Figure 11.	The molecular structure of the two silanes depicting the similarities and contrasts between them.....	21
Figure 12.	Schematic sketch and chemical reactions depicting the deposition of silane molecules and the subsequent quaternization of the N atoms on the surface of the RO membranes.....	24
Figure 13.	The laboratory filtration setup for cross-flow membrane filtration.....	29
Figure 14.	Fourier Transform Infrared spectra of the pristine membrane, 3-APS-C, 3-APS-CQ, 6-AHAS-C, and 6-AHAS-CQ.....	31
Figure 15.	The enlarged view of the FTIR spectra shown in fig. 4.1 within 600cm ⁻¹ to 1500cm ⁻¹ wavenumber.....	32
Figure 16.	FESEM images of the membrane before and after modification with silane.....	33

Figure 17.	FESEM images of membranes coated with 3-APS (a,c) and 6-AHAS (b,d) and quaternized at very high magnifications.....	35
Figure 18.	Images of water droplets and the corresponding CA values (a) 3-APS coating only, (b) 3-APS after quaternization, (c) 6-AHAS coating only, (d) 6-AHAS after quaternization.....	37
Figure 19.	High-resolution XPS scans for the membrane coated with the silane films.....	39
Figure 20.	FESEM images of the membranes after exposure to a static culture of <i>P. aeruginosa</i> , the top row is for the original membrane, the middle for the membrane after coating with the 6-AHAS, and the bottom row after quaternization of the coating.....	42
Figure 21.	FESEM images of membrane coated with 3-APS and before quaternization after exposure to the bacterial strain of <i>P. aeruginosa</i>	44
Figure 22.	FESEM images of the control (Fig. 4.9 (a))and the modified membranes surface; 3-APS-C (Fig. 4.9 (b)), 3-APS-CQ (Fig. 4.9 (c)), 6-AHAS-C (Fig. 4.9 (d)), and 6-AHAS-CQ (Fig. 4.9 (d)), after exposure to gram-negative <i>P. aeruginosa</i>	45
Figure 23.	The colonies of <i>P. aeruginosa</i> grown on agar plates from suspensions exposed to the surfaces of the membranes for 6 hours at 37°C.....	47
Figure 24.	Bacteriostatic rates of <i>P. aeruginosa</i> for the membranes modified with silanes: 3-APS and 6-AHAS before and after quaternization.....	47
Figure 25.	Schematic sketch of the outer cell wall structures for gram-positive and gram-negative bacteria.....	49
Figure 26.	The permeation behavior of the membrane samples before and after the deposition of film and after quaternization.....	53

LIST OF ABBREVIATIONS

UN	:	United Nations
WWDR	:	World Water Development Report
MED	:	Multiple Effect Distillation
VC	:	Vapor Compression
MSF	:	Multistage Flash Distillation
RO	:	Reverse Osmosis
ED	:	Electrodialysis Process
UF	:	Ultrafiltration
PEI	:	Polyethyleneimine
SPEEK	:	Sulfonated poly ether ether ketone
3-APS	:	3-Aminopropyltriethoxysilane
6-AHAS	:	6-Aminohexylaminotriethoxysilane
FBP	:	Feed-brine-pressure
TFC	:	Thin-Film Composite
MeTES	:	Methyltriethoxysilane
OctES	:	Octyltriethoxysilane
EtI	:	Ethyl iodide

EtOH	:	Ethanol
DI	:	Deionized
FESEM	:	Field Emission Scanning Electron Microscope
EDX	:	Energy Dispersive X-ray
FTIR	:	Fourier Transform Infrared
XPS	:	X-ray Photoelectron Spectroscopy
NB	:	Nutrient Broth
CFU	:	Colony-forming units
Rpm	:	Revolution per minute
TDS	:	Total Dissolve Solid

|

ABSTRACT

Full Name : Chidera Churchill Nnadiyekwe

Thesis Title : Improving Antifouling and Antimicrobial Capacity of Reverse Osmosis Desalination Membranes by The Sol-Gel Coupling of Silanes

Major Field : Chemistry

Date of Degree : April 2020

We report herein this research, the deposition of two different but important silanes, 3-APS and 6-AHAS on commercially procured RO membranes and the subsequent quaternization of their nitrogen, N, atoms. The modified and the original membranes were then characterized for their relevant surface characteristics using advanced techniques. FESEM images showed that the ‘peak and valley’ structure of the polyamide layer remains intact after film deposition; however, quaternization reduced the height difference between the peaks and valleys. The membranes coated with 3-APS and 6-AHAS became hydrophilic after deposition and even more hydrophilic after quaternization. The improved quaternization made the samples significantly susceptible to seawater foulants. Spectroscopic analyses with FTIR and XPS confirms the presence of the silanes and the quaternary nitrogen atoms on the surface of the membranes. Bacterial adhesion and studies with *P. aeruginosa* showed excellently reduced cell attachment on the membrane surfaces coated with the silanes. The bacteriostatic rates for the modified membranes with 3-APS and 6-AHAS showed an excellent killing rate of over 80% both with coated-only and coated with quaternization for the bacteria. Furthermore, salt rejection and water permeation flux

also significantly improved after the modification of the membrane with the silanes, thereby making the study a successful one.

ملخص الرسالة

الاسم الكامل: شيدرا تشرشل ناديكوي

عنوان الرسالة: تحسين القدرة المضادة للانسداد ومضادات الميكروبات لأغشية تحلية التناضح العكسي بواسطة دمج مركبات السيلان

التخصص: الكيمياء

تاريخ الدرجة العلمية: ابريل 2020

تهدف هذه الرسالة العلمية الى تحسين قدرة أغشية تحلية التناضح العكسي بواسطة دمج مركبات السيلان. في هذه الرسالة تم اثنين من مركبات السيلان الهامة مع اغشية تحلية التناضح العكسي. مركبات السيلان التي تم دمجها هي مركب 3-أمينو بروبيل ثلاثي ايثوكسي سيلان ومركب 6-أمينوهيكسيل 3-أمينوبروبيل ثلاثي ميثوكسي سيلان. تم دمج هذه المركبات على أغشية تحلية التناضح العكسي التجارية متبوعا بالنيتروجين الرباعية. ثم تم توصيف الأغشية المعدلة التي تم تحضيرها والأصلية لخصائصها السطحية ذات الصلة باستخدام أجهزة مختلفة. أظهرت صور الفحص المجهرى الالكتروني للانبعاثات الميدانية أن بنية طبقة البولي أميد لا تزال سليمة بعد عملية دمج وترسيب الفيلم على الاغشية. الا انه لوحظ ان عملية النترجة الرباعية قللت من الفروق بين القمم والمنخفضات على سطح الأغشية المطلية بمركبات السيلان الجاذبة او المحبة للماء بعد الترسيب وحتى أكثر جاذبية للماء بعد التثييط. تؤكد التحليلات الطيفية باستخدام جهاز طيف الأشعة تحت الحمراء وجهاز الأشعة السينية الضوئية الطيفي على وجود مركبات السيلان وذرات النيتروجين الرباعية على سطح الأغشية. أظهر دراسات الالتصاق البكتيري والدراسات على بكتيريا سلبية الغرام هوائية انخفاضا ممتازا في الخلايا على أسطح الغشاء المغلفة بالسيلان. أظهرت معدلات الجراثيم للأغشية المعدلة مع مركبات السيلان ان معدل انخفاض البكتريا ممتاز ويزيد عن 80 ٪. علاوة على ذلك، تحسن رفض الملح وتدفق نفاذ الماء بشكل ملحوظ بعد تعديل الغشاء مع مركبات السيلان، مما جعل الدراسة ناجحة.

CHAPTER 1

INTRODUCTION

1.1 Global water shortage

The report of the United Nations (UN) on world water development (WWDR) [1] of the 2018 edition, has provided a piece of updated information on the direction of the availability of clean water and future expectation. The ability of a given population of humans to preserve the sustainable opportunity to enough volume of water (water security) is presently risky for numerous persons and unfortunately, the condition will deteriorate even more in decades to come [2]. In today's world of about 7.7 billion people, scarcity of clean water is already a critical event. By the year 2050 when the world's population would attain about 10.2 billion, a 22% to 34% increase, the demand for a clean water system will skyrocket. This pull on the system of clean water will be more pronounced in Asia and Africa continents where the population growth is on the rapid increase. Presently, over 3.5 billion people, or 47%, stay in an area with a high scarcity of water at least a full month yearly [1]. In the view of some reports [3], the population of people experiencing high water scarcity is about 4.0 billion or 52% of the world's population.

The population of the globe has nearly quadrupled over the last 100 years and has reached about 6.5 billion in the 2000s [4]. The patterns of water consumption within the last 20th century, weren't the same globally as shown in **Figure 1(a)**. The consumption per capita

appears to have rather been static in a lot of regions, namely, South America and South Africa but reduced in Northern Africa, South Asia, and the Middle East since the 1950s. However, in Australia-Pacific, the consumption per capita increased rapidly by over 6-folds more than in the 2000s when compared to that of the 1900s. Furthermore, in the Eastern and Western Europes, and Asian Central (until the 1990s), the increase was recorded but less rapidly [5].

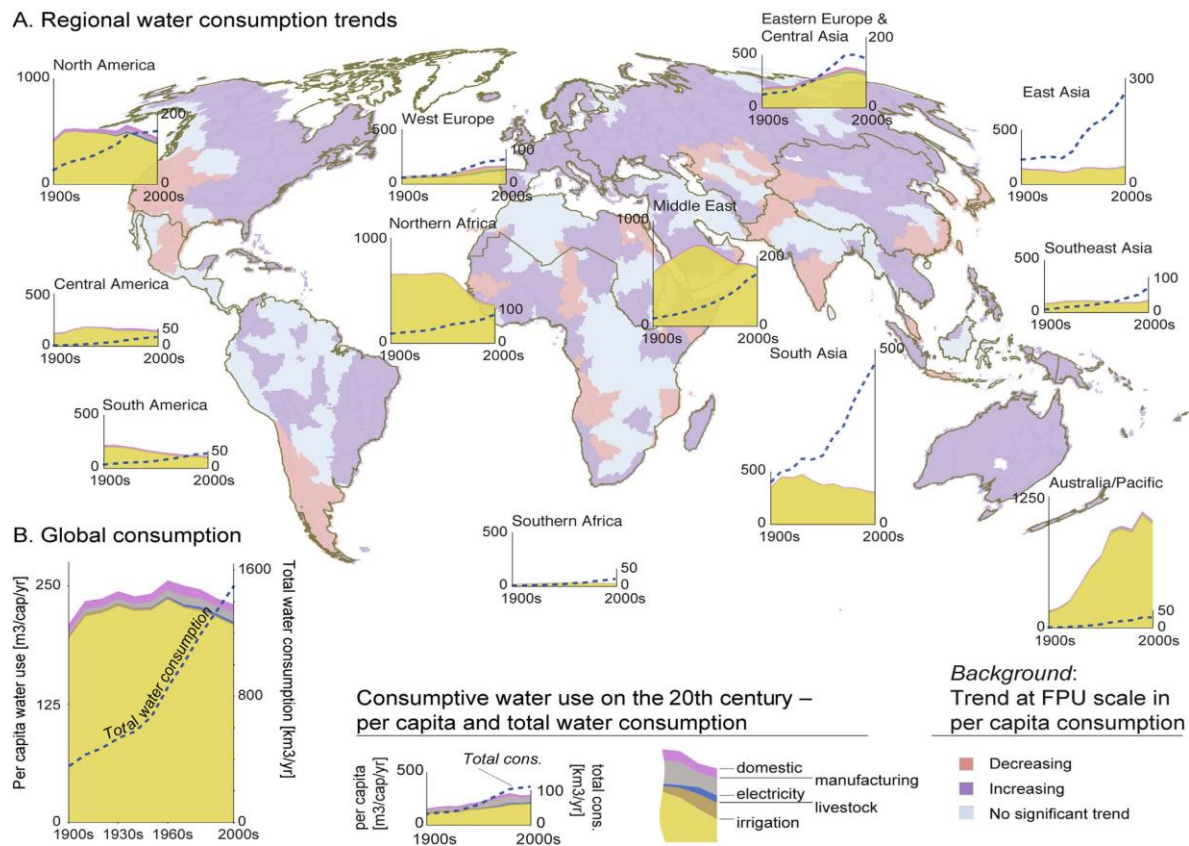


Figure 1. Trends of consumption of water within the last 20th century; (A)Regional and (B) global. Water consumption per capita trends are represented by the filled area while the total water consumption trends are represented by dashed lines. The consumption per capita of water is classified into different sectors that use water [5].

Presently, global demand for water for various applications or uses is about $4600\text{km}^3/\text{year}$ and will increase by 20% to 30% by the year 2050, up to $6000\text{km}^3/\text{year}$ [6]. For agricultural demand for water, it will increase by 60% by 2025 [7]. The majority of the world's population outburst will take place in Africa (over 1.3 billion population or over 108% of the present-day statistics), and the Asian (over 0.75 billion or 18% of the present-day statistics) [8].

1.2 Desalination of Seawater

The process of removing excessive saline and dissolved minerals from water in order to transform it to be potable and healthy for use by humans is called desalination. An instrument used for desalination separates freshwater (containing a negligible quantity of dissolved salt) and brine (dissolved salt) from the saline water as depicted in **Figure 2**. Different desalination techniques have so far been established within the last few years and based on their result breakthroughs, the different desalination techniques can also be grouped into a membrane and thermal-based desalination processes. The thermal process comprises vapor compression (VC), multiple-effect distillation (MED), and Multistage Flash Distillation (MSF). The membrane-based technique comprises of subdivisions: Reverse Osmosis (RO) and Electrodialysis process (ED). **Figure 3** depicts the major classifications of the process of desalination, while **Figure 4** shows the global desalination capacity contribution of each of the processes shown in **Figure 3**. With the technology of desalination in place, an alternative source of water to meet up with the scarcity of fresh water in the industries, irrigation systems, and domestic use, has been managed and curbed.

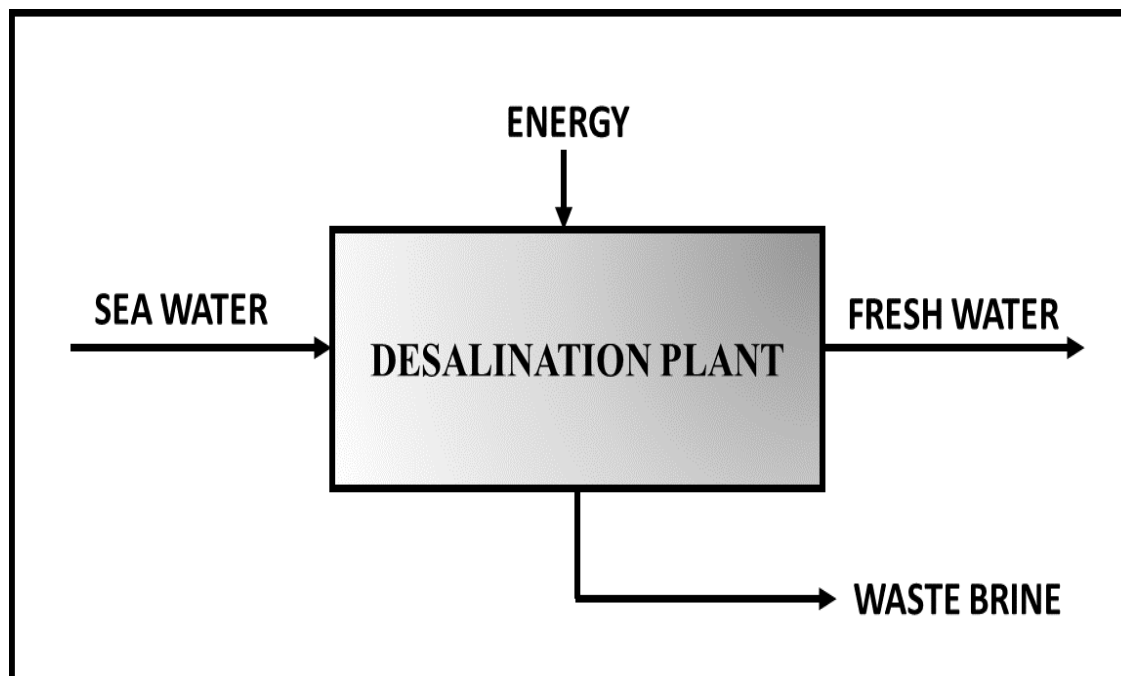


Figure 2. The diagrammatic illustration of the techniques of desalination

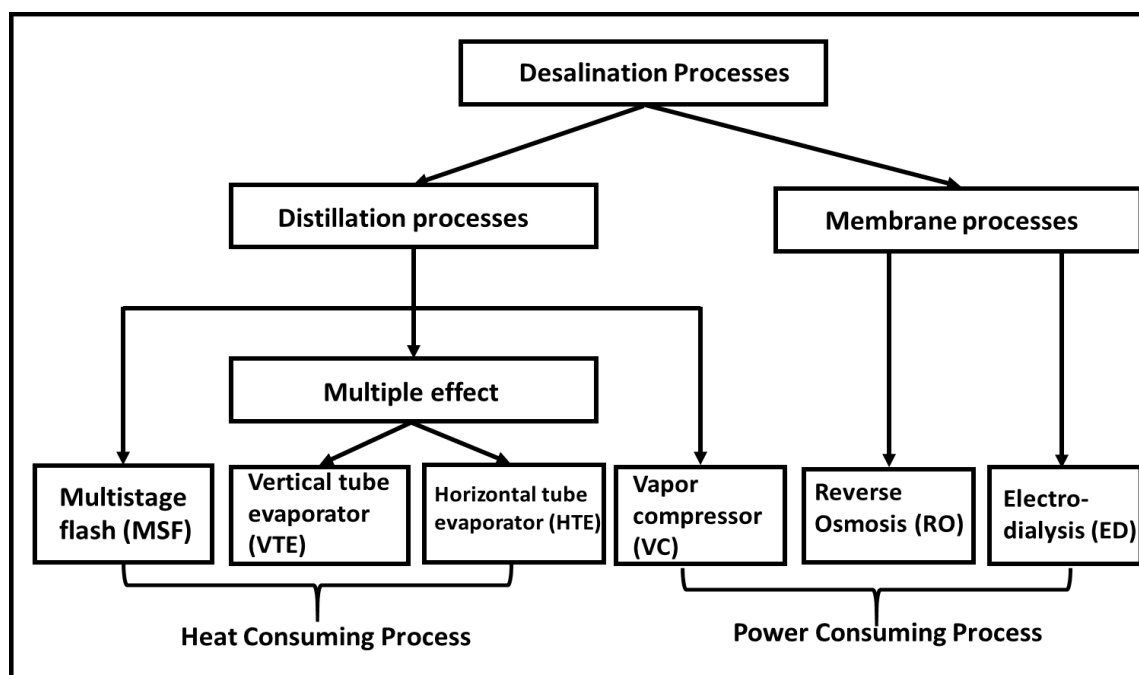


Figure 3. Major process classifications of desalination. (<http://www.wioa.org.au/>)

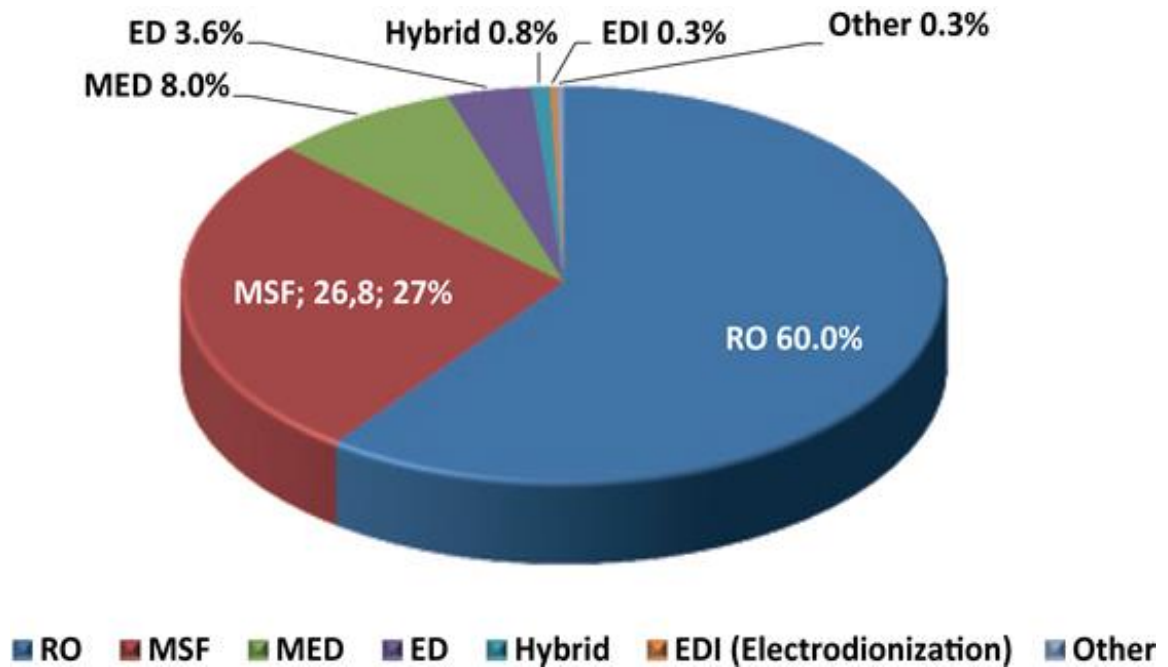


Figure 4. Desalination Technology Market (IDA in Koschikowski, 2011)

The technology of membrane has offered a wide range of applications commercially, starting from purification of drinking water to separation of gaseous compositions, with an expected market growth of over \$10 billion by 2010 [9]. Due to minimal cost and ease of operation, the membrane-based desalination technology is rapidly overtaking thermal desalination. Membranes offer tremendous advantages such as minimal capital cost, easy maintenance, and smaller footprint, over other known desalination technologies [10]. As depicted in **Figure 5**, over fifty percent (50%) of the plants for desalination scattered all over the globe make use of the RO technology due to their level of simplicity, the efficiency of energy and considerably minimal cost of operation [11].

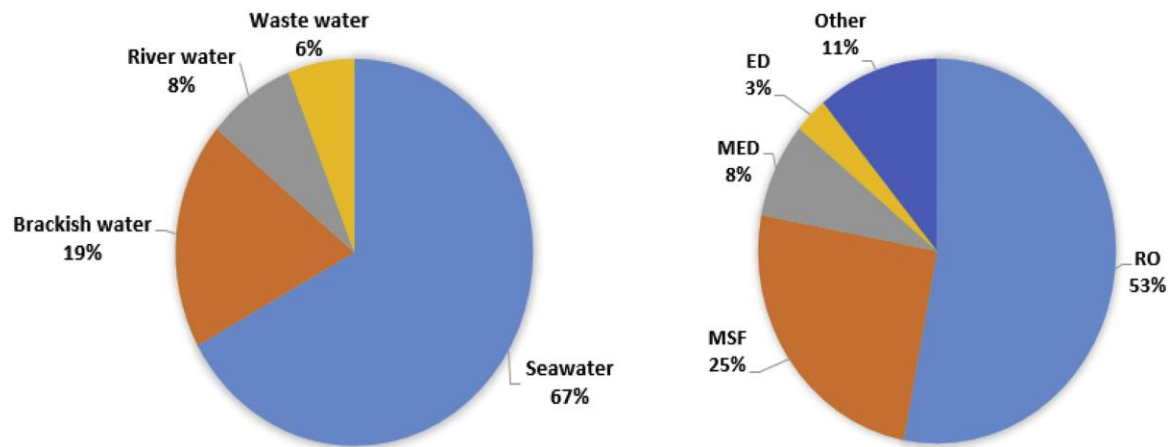


Figure 5. The feed water desalination industries make use of across the globe in percentage [12], and the world's desalination plant strength for various technology [12].

The type of membrane used for the processes of treatment of water relies on the size of the species they are engineered to reject or filter. Microfiltration membranes are known for their largest sizes of pore and in turn filter off large particles and microorganisms, while ultrafiltration membranes are known for their smaller pore sizes than microfiltration membranes [13]. They can filter off or reject soluble macromolecules such as proteins and bacteria. Reverse osmosis membranes are known for their effective nonporous nature and are capable of rejecting particles and species of low molar masses such as saline ions [14]. Nanofiltration membranes are called loose RO membranes sometimes because of their porosity which are in the order of tens of Angstroms. Consequently, their strength of rejection falls between those RO and UF membranes [11].

1.3 The technology of Reverse Osmosis

Reverse osmosis, RO, is defined as a process of water purification that involves the use of semi-permeable thin membrane with pores small enough to allow water passage and at the same time reject larger molecules such as dissolved salts or ions and bacteria. In recent times, RO technology has widely been recognized and used as the best desalination approach and water treatment technology globally [15]. It is utilized industrially to generate pure water fit enough for purposes of drinking, agricultural activities, and industrial processes by simply getting rid of dissolved salts, ions, and minerals from the feedwater [15]. The operational parameters and the nature of the feedwater confirm the efficiency of the process of reverse osmosis (RO). In the technology of reverse osmosis for desalination, external pressure exceeding the natural osmotic pressure is supplied to the feedwater stream.

In a natural osmosis process, the solvent flows from the region of the low concentration of the solute to the region of high concentration of the solute through a semi-permeable membrane. The solvent movement is maintained until a point of equilibrium of the solute concentration is reached on both sides of the semi-permeable membrane which generates osmotic pressure.

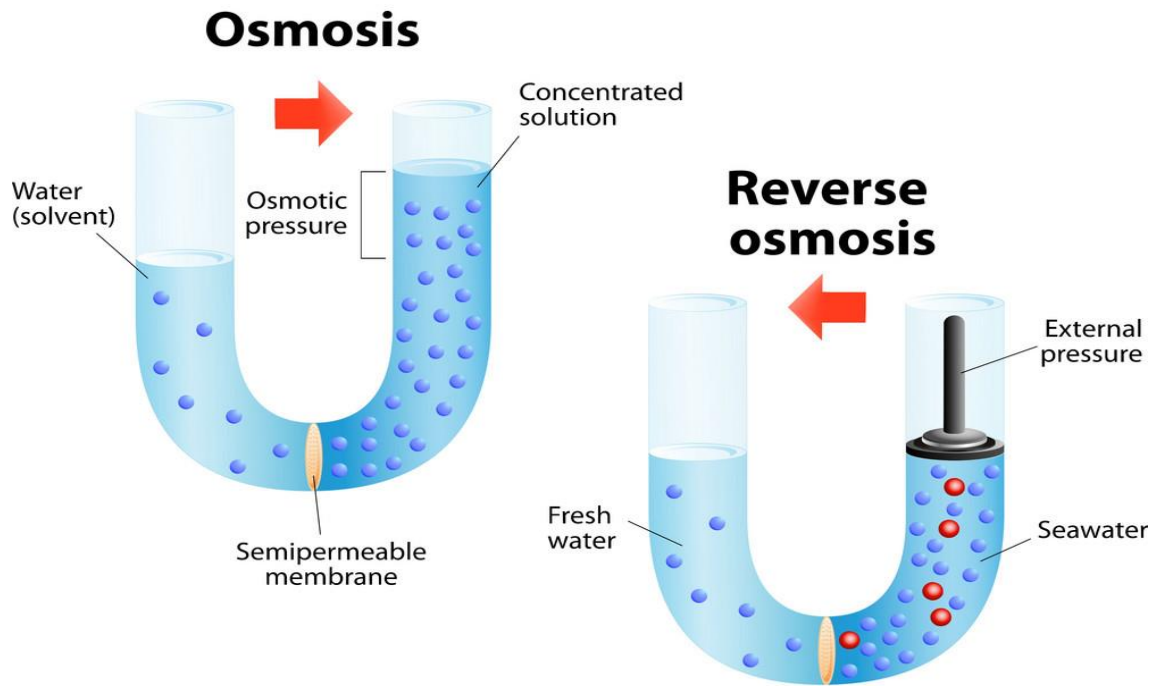


Figure 6 Illustration of water movement in natural and reverse osmosis processes (<https://www.kenyaengineer.co.ke/use-of-reverse-osmosis-membrane-technology-in-the-desalination-of-sea-water/>).

With the purpose of reversing the direction of flow of solvents, the pressure is applied on the RO membrane and as soon as the externally applied pressure (Δp) exceeds the natural osmotic pressure ($\Delta p > \Delta \pi$), feedwater starts to permeate through the semi-permeable membrane. Consequently, dissolved salts or ions, minerals, and bacteria are left behind while the water that passed through the membrane comes out purified (**Figure 6**). Water permeation flux and salt rejection are the two underlining factors that affect the general performance of the RO membranes [16].

$$J = (\Delta p - \Delta \pi)A \quad (1)$$

J represents the water permeation flux, Δp represents the transmembrane pressure (TMP) difference, $\Delta\pi$ represents the osmotic pressure difference between the feedwater and the permeate water, and A is the coefficient of water permeability which explains the membrane [11].

In the past many years, there have been remarkable advances recorded in favor of the RO membranes preparation from different precursors. Owing to this positive progress, the marketability of reverse osmosis-based desalination technology has steadily risen high. The RO-based tech improvement has encouraged reasonably, the reduction in the consumption of energy and cost for clean water generation [17]. The reverse osmosis (RO) desalination plant houses four (4) major processes; feedwater pre-treatment, pressurization/high-pressure pumps, membrane separation and post-treatment of permeates [17-20]. The major challenges that surround the application of the reverse osmosis (RO) membrane in the purification of seawater which must be taken care of through fabrication and modification techniques include scaling, chlorination, fouling of membrane, boron removal, brine disposal, a tradeoff between permeability and salt rejection [15].

1.4 Research Objectives

The principal objective of this research thesis is to improve the antifouling and antimicrobial capacity of RO desalination membranes by the sol-gel coupling of silanes.

The specific objectives are:

- Modify the surface of the RO polyamide desalination membrane by nano-coating it with 3-Aminopropyltriethoxysilane (3-APS) and 6-Aminohexylaminotriethoxysilane (6-AHAS).
- Quaternizing the already modified RO polyamide desalination membrane surface for more effectivity.
- Compare the operational efficiency of the “coated-only” and “coated-and-quaternized” RO polyamide desalination membranes.
- Demonstrate the effectiveness of the combined approach in combating membrane biofouling.
- Simulate the efficiency of this approach in the long-term filtration test.

1.5 Thesis outline

The core outline of this thesis includes:

❖ Chapter 1: Introduction

Chapter one discussed the extent of clean water scarcity globally, major techniques of water desalination, classifications of water desalination methods and their respective contributions towards water desalting and increase in global membrane market trends.

❖ Chapter 2: Literature Review

This chapter reviewed RO membranes and the different types of RO membranes biofouling. It also exposed the severe effects of biofouling and the possible approaches towards mitigating or controlling the biofouling of RO membranes. The sol-gel coupling of silanes for improved performance of RO membranes is also detailed herein.

❖ **Chapter 3: Research Materials and Methodology**

This covered the basic approach of achieving the underlining objectives of this research and the vital materials used. It also detailed the preparational procedures of the sol-gel solutions and meticulous modification of the RO membranes. It further explained the method of quaternization of the already modified RO membrane. Bacteria testing and filtration methods are also detailed herein.

❖ **Chapter 4: Results and Discussions**

This chapter covered the methods of characterizations used and the discussion of the results obtained for possible comparison between modified RO membrane samples and the pristine RO membrane samples. Also, antifouling, antibacterial, and filtration results are elucidated herein.

❖ **Chapter 6: Conclusions and Recommendations**

In this chapter, a decisive conclusion was reached based on the research findings which is in line with the targeted objectives. More so, recommendations where necessary were rendered to further extend the research scope beyond the limit expressed herein the thesis. |

CHAPTER 2

LITERATURE REVIEW

2.1 The fouling of reverse osmosis membranes

The fouling of the RO membranes is the process of deposition of undesired materials on the surface and/or within the membranes' pores and in turn, hinders the smooth process of desalination[15]. Membrane fouling has significantly affected the quality of permeation, water flux, rejection of salt, and the general performance of the membrane. Fouling of membrane has also increased the cost of operation of membrane desalination plants and reduced the lifespan of membranes [15]. Therefore, devising an articulative method of controlling and/or preventing fouling of RO membranes, is highly recommended as an approach towards adding life to the economy of the technology of seawater RO desalination. The fouling of membranes can be reversible and at the same time, irreversible. Irreversible form of membrane fouling has introduced a long-term reduction of flux and has rendered the recovery of the membrane via cleaning, futile. Fouling of the RO membrane is categorized into inorganic fouling, colloidal or particulate fouling, organic fouling, and microbiological fouling or biofouling [21]. Inorganic fouling, organic fouling, and colloidal fouling can be minimized to a larger extent by using pretreatment process; however, pretreatment alone will not suffice to reduce biofouling [14] because the deposited microbial cells on the RO desalination membrane surface is capable of growing, replicating, and changing locations (**Figure 7**).

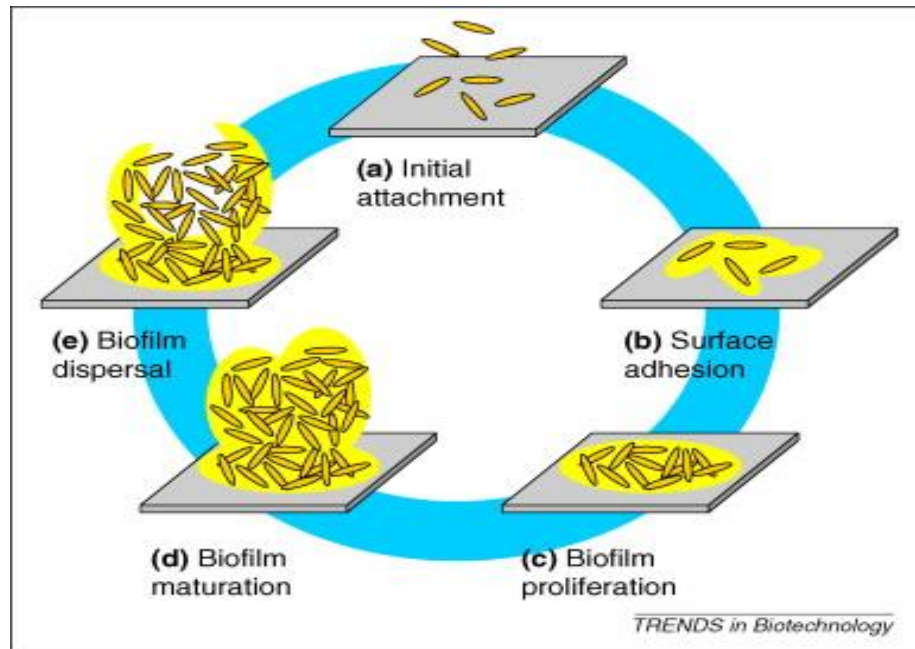


Figure 7. The sequential steps of biofouling formation [22].

2.1.1 Membrane biofouling

Generally, biofouling of membrane is considered to be the adhesion and accumulation of unwanted biological polymers or microorganisms such as animals, microorganisms, algae, and plants on the membrane, which can develop as a “biofilm” on the membrane surface [23]. Biofilm, on the other hand, is the building up of surface-associated cells of microbes [23]. The process of biofilm formation on the surface of an RO membrane is permanent, in other words, it is not removed by rinsing gently. Virtually all water systems are contaminated with a microorganism which can colonize virtually any water system [24]. According to **Figure 7**, biofouling of membrane surface follows the following sequence (a) initial foulants attachment on the surface of the membrane, (b) surface adhesion, (c) proliferation of biofilm, (d) biofilm maturation, and (e) dispersion of biofilm. The

sequential stages contribute to the formation of biofilms on the surface of the reverse osmosis (RO) membranes.

Factors such as surface roughness, surface charge, and hydrophilicity, have a recognizable impact on the ease with which foulants attack desalination membranes. The surface roughness of the membrane is directly proportional to the susceptibility of the foulants on the membrane surface [14]. This implies that the rougher the membrane surface, the more susceptible to fouling the surface becomes and vice versa because smooth surfaces do not allow the growth and replication of foulants. Generally, membranes having a high degree of wettability, low negative charge, and smoother surface, displayed superior resistance to fouling [13].

2.1.2 Critical Biofouling Effects

When the matrix of biofilm coats an RO membrane, the matrix behaves as a secondary membrane, thereby affecting or preventing the process of separation. Also, the irregular and viscoelastic surface of the biofilm encourages fluid frictional resistance and leads to a feed–brine–pressure (FBP) drop as shown in **Figure 8**. The major effects of the biofouling on the RO membrane operations are as follows:

- ❖ Biofouling in reverse osmosis module element.
- ❖ Frequent cleaning of the RO membrane surface which decreases the life span of the RO membrane.
- ❖ Declination in the water permeation flux of the RO membrane due to the reduction in the pressure across the surfaces of the reverse osmosis (RO) membrane.
- ❖ Increase in the operating pressure, which results in increased cost of operation.

- ❖ A decrease in salt rejection.

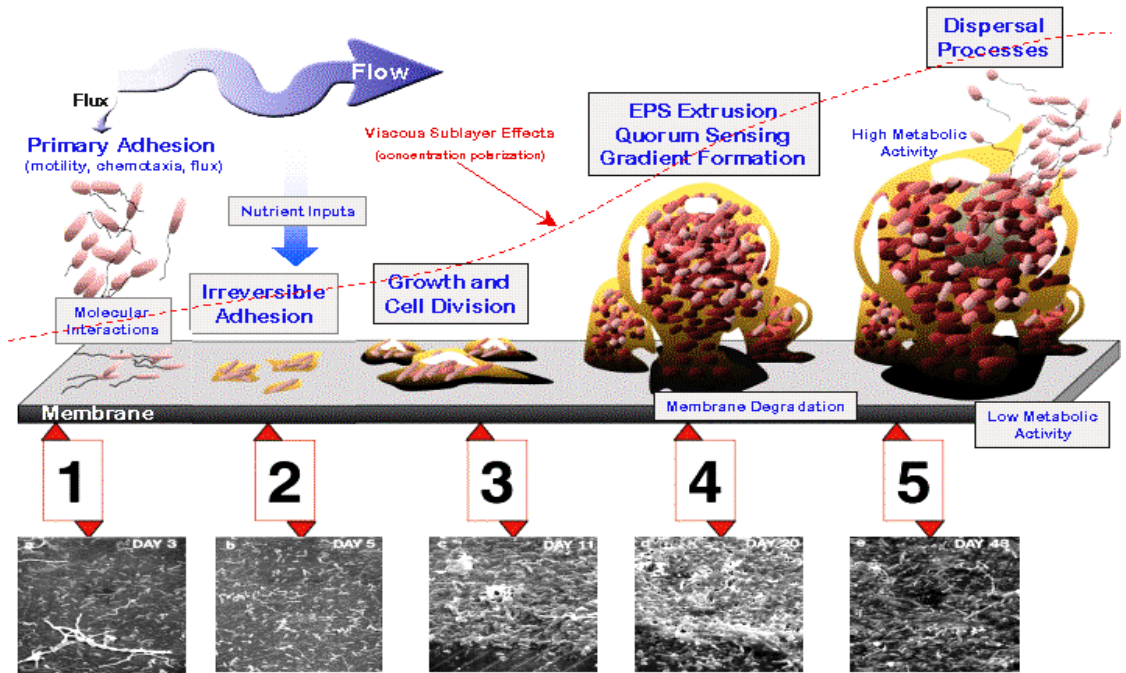


Figure 8. Diagrammatic illustration of an increase in hydraulic resistance taking place during the development of biofilm on the surface of the membrane. The SEM images of the biofilm stage are shown at the bottom part of the figure.

The biofilm formation on the surface of reverse osmosis (RO) desalination membranes behaves like a second layer and results in a reasonable reduction in transmembrane pressure [25]. This causes a reduction in flux permeation over a while. With higher operating pressure, optimum flux permeation can be maintained. Furthermore, the physical damage inflicted on the surface of the membrane due to the operations of the biofilm, increases undesirably, the passage of salt, i.e., reduction in salt rejection. However, to reduce the negative impact of biofouling, constant cleaning with chemicals could be used but this

shortens the membrane lifespan. All these negative effects put together incurs significant jump in the cost of operation of the desalination process [26].

2.2 Controlling Fouling of RO Membranes

Through techniques such as chemical cleaning [27], feed water pretreatment [28], or surface modification of the RO membrane surfaces [29-34], biofouling of the RO membrane can be tackled. Mitigation of biofouling through feed water pretreatment and chemical cleaning is expensive and time-consuming as well. However, the development of anti-fouling coatings through surface modification is a viable method that has attracted active investigations by researchers. This method seeks to relay the three (3) important parameters to the reverse osmosis (RO) membrane surfaces. They include enhancement of hydrophilicity, reduction of the roughness of the surface and production of neutral or near-neutral surfaces. The antifouling coatings have been successfully applied to coatings for ship 16 hulls [35], biomedical implants [36], marine equipment [36], biomedical devices and sensors [37], packaging of food and industrial equipment. However, the technology of RO membrane surface modification has not been adequately explored.

2.2.1 Types of RO Membrane Surface Modification

The important stage in the development of biofilm on the surface of an RO membrane is the attachment of bacteria, the configuration of micro-colony, and the maturation of the biofilm [34]. The basic aim or intention of any surface modification approach of desalination technology is to hamper or discourage any one of these stages. Bacterial attachment on the surface of an RO membrane has proven to be reasonably tackled by making the surface smoother, charged and more hydrophilic. Modification of already

existing RO membranes is as well regarded as an effective approach to developing antifouling membranes. Membrane surface modification technique cuts across physical and chemical treatments as detailed in the proceeding section.

2.2.2 Physical treatment

Physical adsorption and polymer surface structuring is one simple method of modifying the surface of an RO membrane. Industrially, the surface adsorption of RO membranes are modified by making use of any of the following:

- Surfactants of polyethylene oxide (T-X series and P series) [38].
- Electrostatic self-assembly of PEI on the membrane surface [39]. The polyelectrolytes, in this case, are charged.
- Film adsorption of negatively charged sulfonated poly (ether ether ketone) (SPEEK) onto the surface of a positively charged NF membrane [40].
- Coupling of silanes.

Coating of the membrane surface is another form of physical treatment that utilizes the application of a protective layer to remove or reduce the adhesion and adsorption of foulants onto the surface of the RO membrane. The coating of the membrane surface has been employed to change the surface behaviors of conventional reverse osmosis membranes. In this case, hydrophilic polymers with OH, ethylene oxide and -COOH groups are deposited on membrane surfaces in order to enhance the membrane's antifouling properties. It is worth pointing out here that the penetration of the coating materials into the ridge-valley structures of the polyamide reverse osmosis (RO) membrane, may result in increased resistance to permeation [41]. Consequently, this will cause a decline in the

water flux after the membrane has been modified. Therefore, a successful RO membrane coating should be of a thin film and have a high permeability of water in order to keep a high flux of water.

2.2.3 Chemical Treatment

When it comes to the chemical treatment of the RO membrane surfaces, chemical reactions are used to alter the chemistry of the RO membrane surface. The chemical reactions take place between the surface of the membrane and the chemical species present in the modifying agent(s) or precursor(s). Different kinds of chemical treatment are but not limited to:

- Hydrophilization treatment [42] of thin-film composite (TFC) reverse osmosis (RO) membranes,
- Radical grafting of the polyamide membrane surface,
- Chemical coupling of relatively active groups presents on the reverse osmosis (RO) membranes [43, 44] as depicted in **Figure 9**.

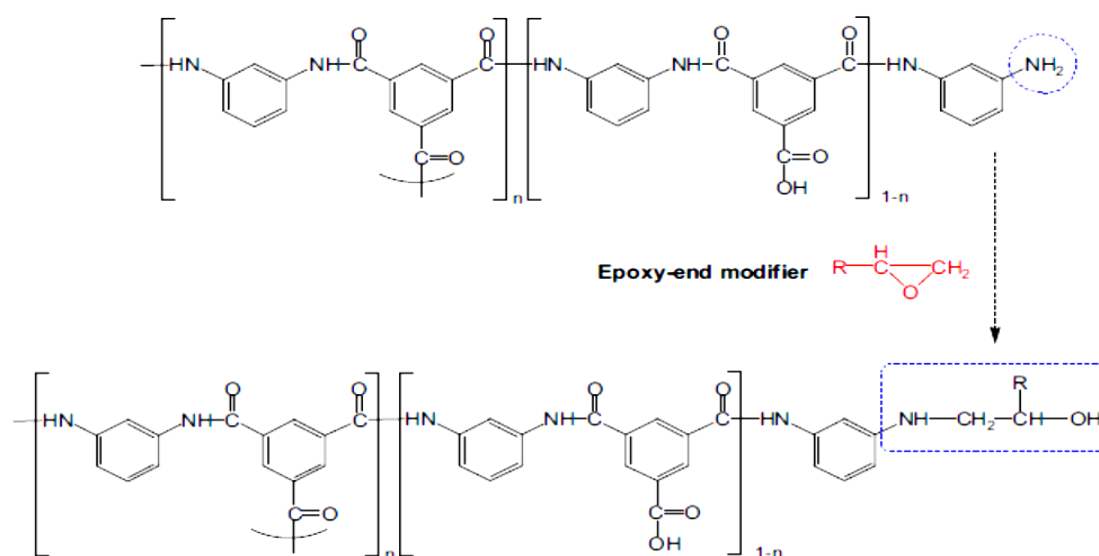


Figure 9. Illustrates the modification of the surface of thin-film composite polyamide reverse osmosis (RO) membrane via chemical reactions between amine groups and the epoxy.

2.2.4 Sol-Gel Coupling of Silanes for RO Membrane Antifouling

The chemistry of sol-gel coupling relied on the polymerization of starting materials from inorganic materials such as metallic alkoxides [45]. The reaction of sol-gel is partitioned into two different stages: hydrolytic reaction and the condensational reaction of metal alkoxide which leads to the formation of the inorganic network [46]. Recently, the reaction of sol-gel was used in preparing the organic-inorganic hybrid materials [46]. The properties of composite material do not depend only on the properties of each component, but also depend on the phase morphology of the composite and interfacial properties. Thus, the

controls of the morphology and phase separation are crucial in the preparation of composites of organic-inorganic [45]. Different types of polymers such as poly(methylmethacrylate) [47], poly(vinyl acetate) [45], poly(vinylpyrrolidone) [48], poly(dimethylsiloxane) [49], polyimides [50], and epoxy [51], were incorporated successfully into inorganic networks by the sol-gel reaction process and these hybrid materials can show outstanding optical transparency [45].

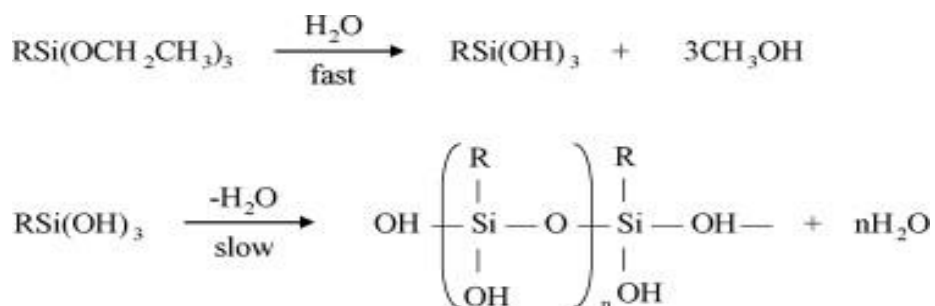


Figure 10. The general mechanism of the sol-gel reaction process for the modification of the membrane surface with trialkoxyalkylsilane compounds [53].

Shin and his co-researchers [52] reported a method that improved the salt rejection capacity of an RO polyamide membrane by modifying the membrane with a TFC reverse osmosis membrane via the sol-gel reaction. By treating the thin-film composite reverse osmosis membranes with methyltriethoxysilane (MeTES) or octyltriethoxysilane (OctTES), the salt rejection capacity of the membrane significantly increased [53]. The most important step is the sol-gel methods of silane coupling reagents on the surface of the polyamide membrane. The general reaction mechanism of the sol-gel method with trialkoxyalkylsilane molecules to generate polysiloxane is depicted in **Figure 10**.

CHAPTER 3

RESEARCH MATERIALS AND METHODOLOGY

3.1 Materials

All the commercial Reverse Osmosis (RO) membranes used in this research were ordered from Sterlietch Corporation, Kent, Washington WA 98032. The reagents and chemicals used in this research include N-(6-aminohexyl)-aminomethyltriethoxysilane (6-AHAS), 3-(aminopropyl)triethoxysilane (3-APS), ethylene glycol (EG), ethyl iodide (EtI), which were procured from Sigma Aldrich. Then, absolute ethanol (EtOH), potassium persulfate ($K_2S_2O_8$), and sodium pyrosulfate ($Na_2S_2O_5$) were gotten from Fluka. Finally, Hydrochloric acid, HCl, was obtained from the Fisher Scientific. All these chemicals and reagents were of pure standards. They were made use of during the research without further treatment and/or purification. All solutions prepared during this research were prepared using deionized (DI) water.

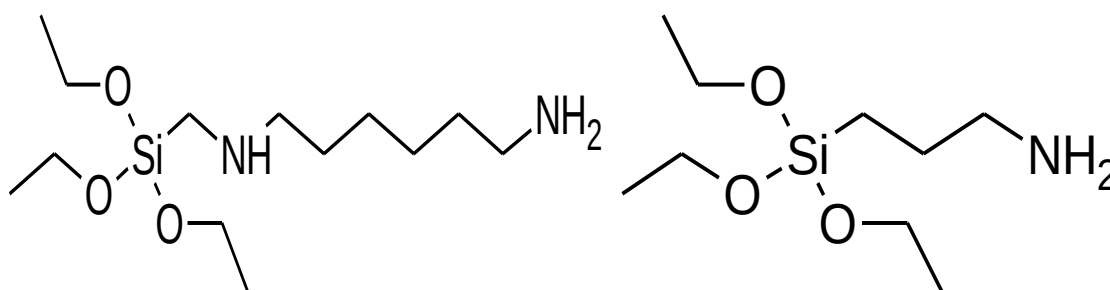


Figure 11. The molecular structure of the two silanes depicting the similarities and contrasts between them (a) N-(6-aminohexyl)-aminomethyltriethoxysilane with two

quaternizable Nitrogen atoms (b) 3-(aminopropyl)triethoxysilane with only one Nitrogen atom for quaternization.

3.2 Silane Film deposition on the RO membrane

The deposition of the films on the membrane was exactly as reported by Akili *et al.* [20], with minor changes. The commercial RO membrane sheets were cut into the sizes of 5cm by 5cm, cleaned with deionized water, and then submerged into 5% weight/volume of glycol for 30 minutes. The drying of the membranes took place at about 70°C in a vacuum oven. Further immersion of the membranes in 0.1M $K_2S_2O_8$ and $Na_2S_2O_5$ in the ratio of 1:1, lasted for 30 minutes and subsequently, rinsed with deionized (DI) water to remove loosely bonded films. The reason behind this step is to enhance the etching and activation of the functional groups on the surface of the deposited membrane. To prepare the silane coupling solution (sol), *N*-(6-aminohexyl)-aminomethyltriethoxysilane and 3-(aminopropyl)-triethoxysilane were added independently to absolute ethanol (EtOH) in the ratios of 1:1 into a round-bottomed flask. This was accompanied by 16ml of DI water and some drops of concentrated hydrochloric acid. These were kept stirring for 60 minutes at 60°C. These solutions were later introduced into a flask where the already etched membranes were immersed and kept to stay for one hour (1hr), a process called gelation. After that, the membrane samples were brought out, rinsed multiple times with DI water and exposed to a temperature of 70°C in a vacuum oven for about 10 minutes.

3.3 Quaternization

Quaternization (introduction of positive charge on the N atoms) of the silane molecules occurred after the silane molecules had been deposited on the surface of the membrane. It

involved the replacement of the hydrogen atoms of the amine groups of the silane molecule by alkyl groups. This process initiated positive charge(s) on all the Nitrogen atoms of the silane molecules and creates a strong electrostatic pull of attraction and interaction between the quaternized Nitrogen atoms of the molecules and the negatively charged microorganism domicile in the water. As soon as the quaternized silane molecules established contact with the negatively charged microorganisms, the lipophilic chain of the hydrocarbon of the silane molecules destroys the structure of the cell membrane [21]. This interferes with the function of the membrane, which eventually leads to the loss of the constituents of the cytoplasm thereby resulting in the death of the cell [21].

According to Ikeda *et al.* [22], polymers possessing quaternized groups have shown a higher tendency to inhibit bacterial activities against various bacteria much more than their unquaternized counterparts. The membranes modified with silanes were exposed to the aqueous solution of 4% volume by volume (V/V) iodoethane (EtI) and ethanol (C_2H_5OH) for a duration of 1 hr. This allowed the nitrogen (N) atoms of the amino groups present in the silanes to be quaternized. This was accompanied by multiple (3 times) rinsing with DI water and exposure to a temperature of 70°C in a vacuum oven for about 10 minutes. The entire steps of the quaternization are shown in **Figure 12**. About 10-20 nm thickness of the deposited thin film layer was achieved.

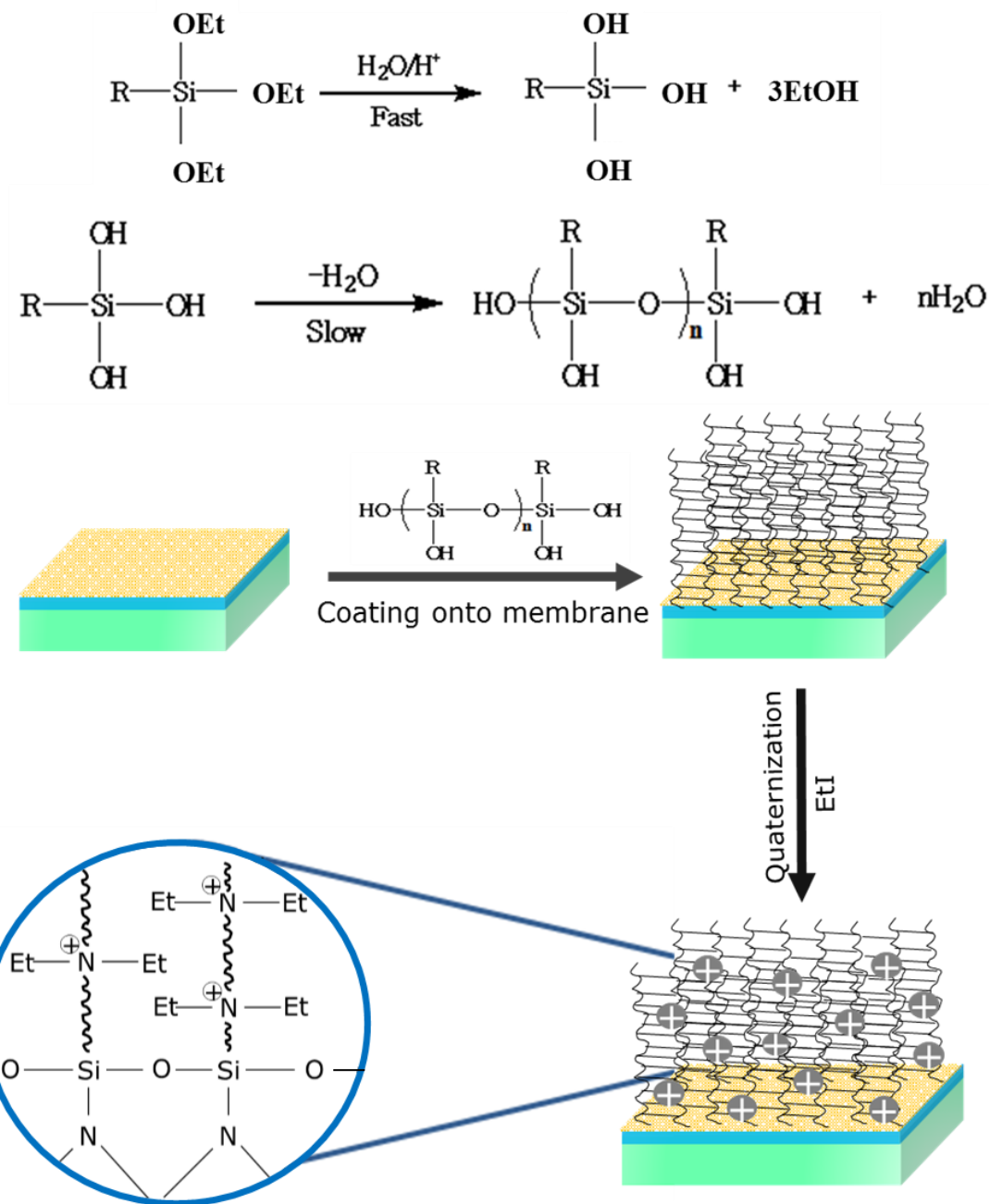


Figure 12. A schematic sketch and chemical reactions depicting the deposition of silane molecules and the subsequent quaternization of the N atoms on the surface of the RO membranes. Hydrolysis & condensation of the silane groups to form silanols (Si-OH) take place first, followed by the siloxane (Si-O-Si) groups. The point of interaction between the surface of the RO membranes and the film of the silanes happened through the Silicon-

Nitrogen (Si-N) sites, where N atoms came from the polyamide surface of the membrane and Si from the siloxane. The quaternization resulted in the replacement of H atoms by alkyl groups, endowing a positively charged particle to the N atom(s).

3.4 Membrane Characterization

Field-emission scanning electron microscope (FESEM, LYRA 3, Dual Beam, Tescan), coupled with energy dispersive X-ray spectrometer (EDX, Oxford Instruments), was used to ascertain the morphologies of the surface of the membrane before and after coupling and quaternization. In order to achieve this, the membrane samples were imparted with a thin film of gold by the use of sputter deposition. This is to make the samples electrically charged (conductive). The entirety of the sample surfaces was scanned, and images of varying magnifications were captured. Comparatively, the varying surface morphologies of the unmodified, modified-only, and modified-and-quaternized, were deduced to study the contribution of the modification on the morphology of the surface.

By using measurements of contact angle with an Attention Theta Optical Tensiometer (Biolin Scientific, Finland), the degree of affinity for water of the membrane surfaces was studied. To secure reliable results, the samples were cut into a small rectangular or square shape and placed on slides (preferably glass), where droplets of water of vol. approximately 20 μ L were cautiously dropped on the membrane samples. With the help of a highly resolved camera from the tensiometer, the image of the samples was captured. An average of 5-6 different measurement locations, were evaluated.

By using a Thermo Nicolet 6700 FTIR spectrometer coupled with Smart Orbit diamond micro-ATR, the chemistry of the surface of the membrane samples was studied. Before

sample analysis, background correction was necessary and was duly taken care of by taking scans of the blank stage. To guarantee reproducibility and accuracy, a total number of 32 scanings were executed for each measurement. Furthermore, to accommodate a reasonable band of wavenumber for each measurement, a wavenumber range of 600 cm^{-1} – 4000 cm^{-1} was covered. The resulting spectra for the membrane samples were studied for the purpose of identifying the representative functional groups on the sample surface and their relative intensities.

Analysis by using X-ray Photoelectron Spectroscopy (XPS) was utilized to verify whether the modified RO membranes contain the coating of the silanes or not. Rectangular-shaped membrane samples of the area 1 cm^2 were prepared from the pristine and the modified membrane surface and placed on the stage of the X-ray Photoelectron Spectroscopy (XPS). The investigations were performed on an Axis Ultra DLD system under ultra-high vacuum conditions (1.6×10^{-12} bar) using a Thermo Scientific ESCALAB 250 Xi x-ray photoelectron spectrometer in the Surface Science Laboratory of the Physics department, King Fahd University of Petroleum and Minerals. The scan survey was done in the binding energy range of 0.000 eV–1000 eV with a resolution of 1 eV. A high-resolution scan for each of N1s, O1s, and Si2p orbitals was deduced under the same conditions with 0.050 eV steps, pass energy 20.00 eV.

3.5 Adhesion of Bacteria and antibacterial Strength

3.5.1 Bacterial suspension preparation

The anti-adhesion & antibacterial of the bare membrane (unmodified membrane), modified only, & modified and quaternized were studied with a pure culture of *Pseudomonas*

aeruginosa. The *P. aeruginosa* culture was developed in a Nutrient Broth, NB, in a shaking incubator (150 rpm) all through the night at a temperature of 37 °C. The bacterial biomass was cleaned with PBS after an incubation period in order to get rid of the media. Then the final suspension of *P. aeruginosa* was diluted with sterile 0.9% sodium chloride to attain a concentration of approximately 10^7 colony-forming units (CFUml⁻¹).

3.5.2 Antibacterial performance of the modified membranes

By standard plate count methods, the antibacterial characteristics of the pristine membrane, modified only and modified and quaternized, were assessed to enumerate the number of the viable colonies of bacteria left in the suspensions. The rates of bacteriostasis were adopted to quantify the bacterial behavior on the surface of both the pristine and the modified membrane surfaces. The samples of the membranes (pristine and modified) having a surface area of 6 cm², were placed in 6 flat-bottom polystyrene plates from Sigma Aldrich, accommodating 5.3×10^3 CFUml⁻¹ for 3-APS and 1×10^4 CFUml⁻¹ for 6-AHAS of *P. aeruginosa* suspension for a total duration of 6 hrs. at a temperature of 37 °C while shaking at 150 rpm. The samples of the membrane were brought out from the suspension of the bacterial and were diluted using 10-fold serial dilution after incubating them. Thereafter, 100 µl of each diluted bacterial suspension was distributed onto agar plates and incubated for a duration of 24 hrs. at a temperature of 37 °C. In the end, the population of the colonies found on the plates of the agar was enumerated by the standard plate count method. The relation below was used to calculate the bacteriostasis rate (BR):

$$BR = \frac{(X-Y)}{X} \times 100\% \quad (2)$$

From the relation, X denotes the population of the bacteria colonies on the pristine sample, while Y denotes the population of the bacteria colonies on modified samples.

3.5.3 Bacterial adhesion test

To perform the adhesion test, 2cm by 3cm (6cm²) of each membrane (pristine and modified) were submerged into the suspension of the *P. aeruginosa* in a 6 flat-bottom polystyrene plates. At 150 rpm and 37 °C for 12 hours, the plates were incubated. After incubation, to remove loosely bound/attached planktonic bacteria, each membrane sample was removed and cleaned with DI water. The membranes were then fixed with a 2.5% solution of glutaraldehyde at a temperature of 4 °C for 6 hrs. The membrane samples were then subjected to a dehydration series of 30%, 50%, 70%, 90% and 100% ethanol (10 minutes each) and then dried at a temperature of 30 °C in a desiccator. Samples were placed on aluminum stubs and gold-coated before imaging. In the end, all the exposed membrane samples were studied under a Scanning Electron Microscope (SEM) at an accelerating voltage of 20 kV [24].

3.6 Membrane Filtration Testing

It is a confirmatory practice to check for the filtration behavior of the membranes after their surfaces have been modified. This is to be sure that the deposition of a thin film on their surfaces does not incur an undesirable barrier to permeation of water. To this end, a laboratory filtration setup as shown in **Figure 13** was applied for cross-flow membrane filtration. The operating pressure was maintained ~ 800 psi with a high-pressure pump (Wanner Engineering, Inc.) and a cross-flow velocity of approx. 8 cm/s. The temperature of the feed was maintained ~ 24°C by using a constant temperature circulating bath (Polystat, Inc.). After performing an initial membrane compaction process for each

membrane sample, the setup operated interruptedly for 5-10 minutes and thereafter, the water permeation flux was recorded. By measuring the Total Dissolved Solid (TDS) of the feed seawater, the %salt rejection was ascertained. The permeated water was collected in a cylindrical ware and measured.



Figure 13. The laboratory filtration setup for cross-flow membrane filtration

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Surface Chemistry

The modified and original membranes were characterized to ascertain the different functional groups and linkage sites present on the surface. This was achieved by using an FTIR spectrometer coupled with a Smart Orbit diamond micro-ATR. The samples were scanned for the complete range of Infrared wavelengths i.e. $300\text{--}4000\text{ cm}^{-1}$ and then the regions of interest focused. The following peaks were visible in almost all the specimens (i) stretching band at about 3200 cm^{-1} owing to the N-H vibration, (ii) stretching band at about 2900 cm^{-1} coming from C-H vibration, (iii) Si-O in-plane vibrational stretch at about 1100 cm^{-1} , & (iv) stretching band of about 1200 cm^{-1} coming from the C-N vibration.

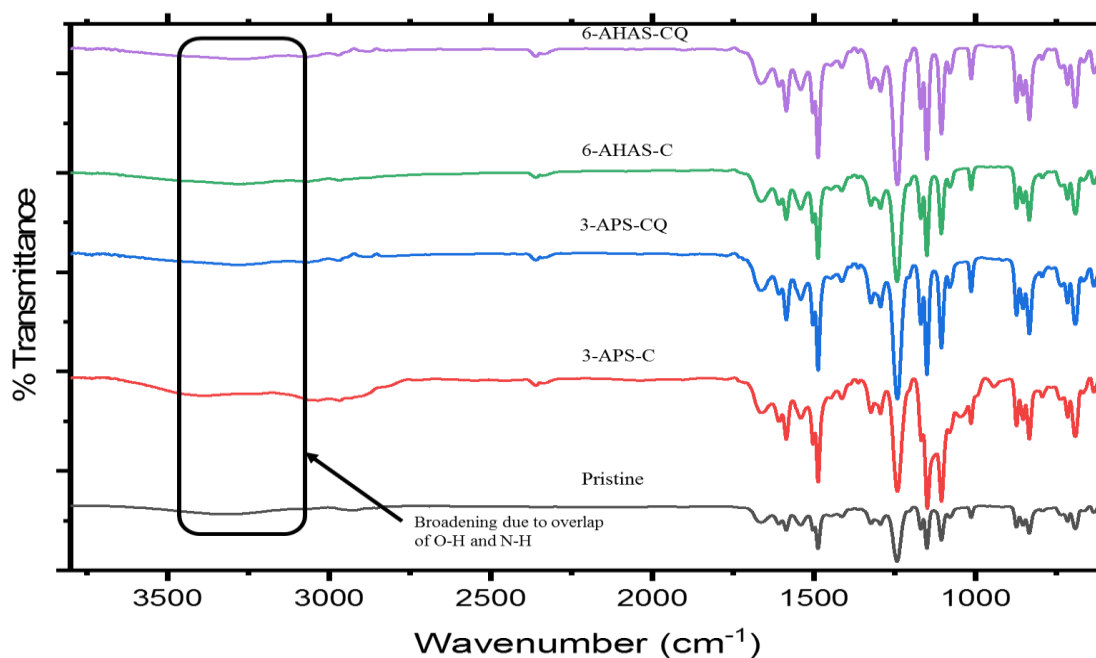


Figure 14. Fourier Transform Infrared spectra of the pristine membrane, 3-APS-C, 3-APS-CQ, 6-AHAS-C, and 6-AHAS-CQ. The obvious spectra observation can be seen around 1150cm^{-1} wavenumber which represents the Si-O and Si-N bands overlap. The weak intensity within this region is due to the deposition of a few layers.

For the pristine membrane, the following notable FTIR spectra peaks were observed (i) a broad peak at about $3300/\text{cm}$, corresponding to hydroxyl (O-H) adsorption from the atmospheric moisture [54], (ii) two small peaks ~ 2850 and 2928 cm^{-1} from the symmetric and asymmetric vibrational stretching of C-H group [55], (iii) a small peak $\sim 1720\text{ cm}^{-1}$ corresponding to vibrational stretching of C=O group, and (iv) 1200 cm^{-1} vibrational stretching coming from C-N group. These groups so identified, are characteristic of the top-most layer of the bare polyamide membrane studied.

There is an obvious similarity between the spectra of the silane-modified membranes and that of the pristine (bare) membrane but with a notable distinction of O-H band broadening due to overlap with N-H bands of the silane molecules as depicted in **Figure 14**. So also, is the broad Si-N stretch band which occurred at about $1100/\text{cm}$ is a result of the overlap with the Si-O band (**Figure 15**). This is an indication of the presence of the molecules of silane on the modified membranes in the forms of N-(6-aminohexyl)-aminomethyltriethoxysilane and 3-(aminopropyl) triethoxysilane as shown in **Figure 15**. The spectra of the coated and quaternized membranes (**Figure 14**) however is closely like those of the coated-only membranes. This reveals that the quaternization process of the coated-only membranes did not alter negatively the already present silane molecules but

rather imparted quaternized nitrogen groups on the membrane surfaces for enhanced antifouling performance.

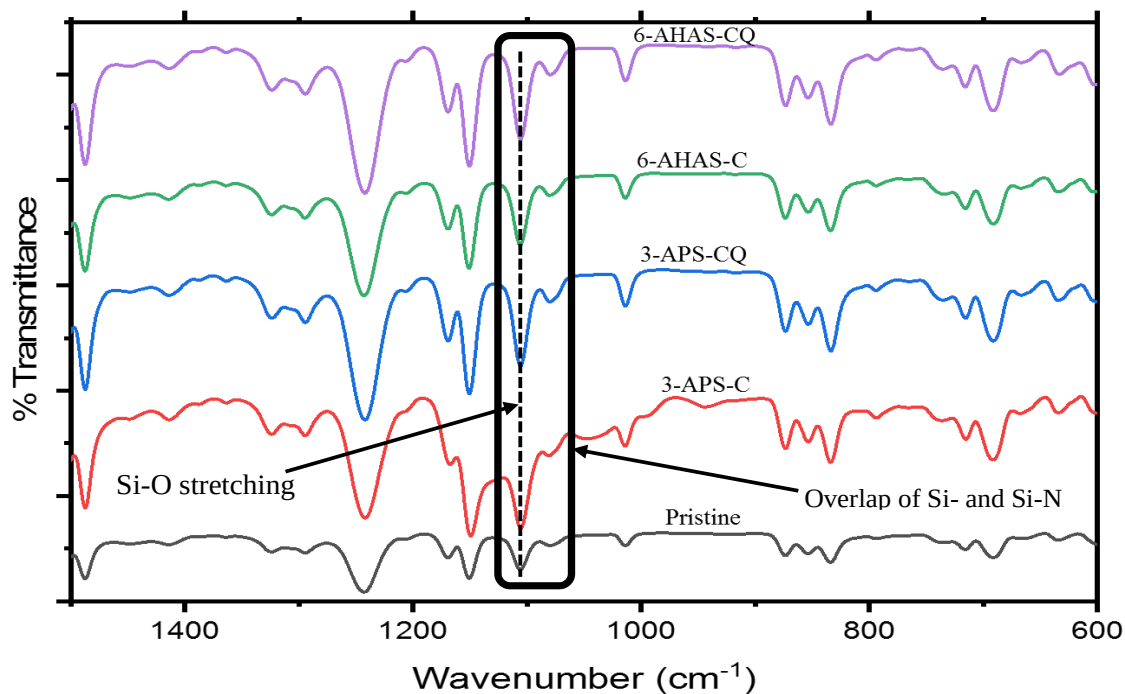


Figure 15. These spectra show the enlarged view of the FTIR spectra shown in **Figure 14** within 600cm^{-1} to 1500cm^{-1} wavenumber. Between 1000cm^{-1} and 1150cm^{-1} , the Si-O broadened stretch can be noted. This is present for both the coated only and coated with quaternization.

4.2 Surface Morphology

Figure 16 shows representative FESEM images of the membranes before and after the modification of the surface. The characteristic ridge-and-valley symmetry linked to

polyamide chains [56] produced by the interfacial polymerization process can be seen clearly in **Figure 16(a)**. Also, the morphology of the surface for these polyamide membranes is leaf-like as was noted in researches [57] for the SW30HR (Dow FilmTec) and TFROAD (GE Osmonics, Inc.) membranes. In contrast, some commercial membranes e.g. UTC-80B (Toray, Inc.) exhibit a nodular morphology. Conditions such as type of monomer, time of reaction, concentration, and temperature of curing determine the specific morphology that will be obtained [58][59].

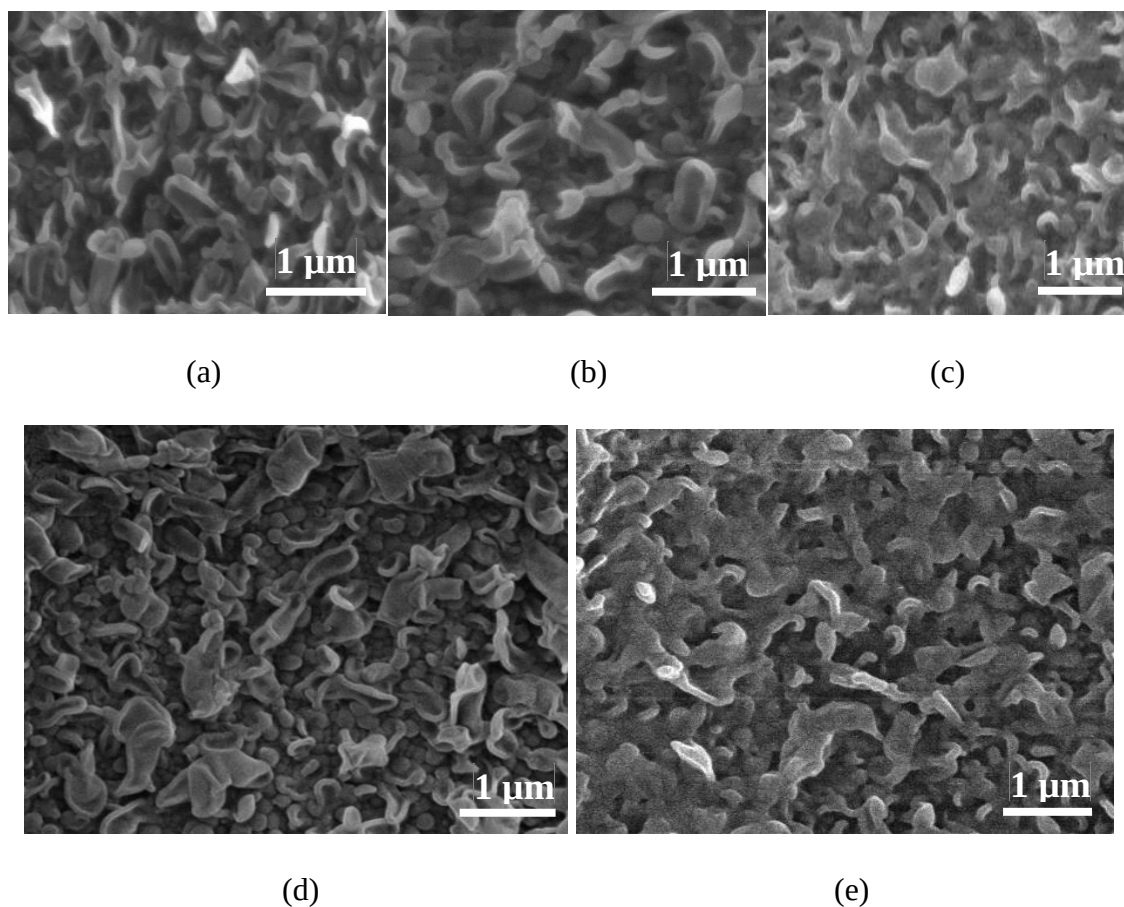
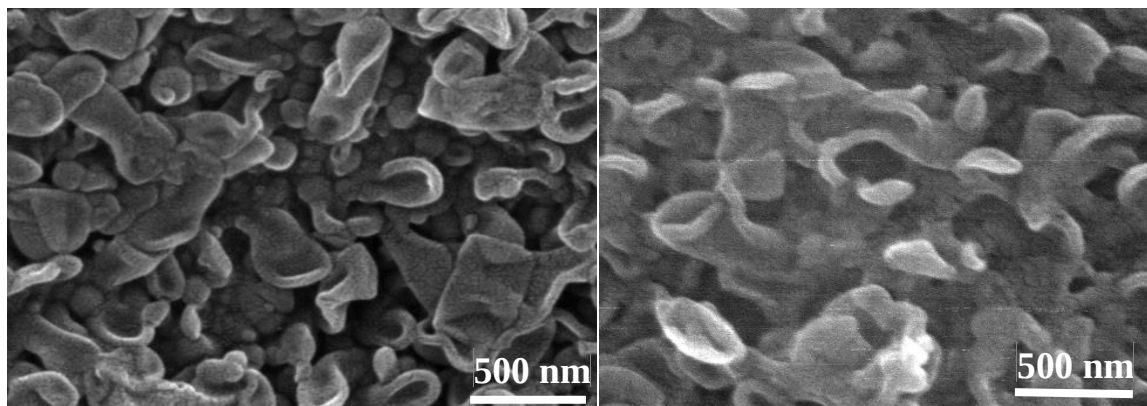


Figure 16. FESEM images of the membrane before and after modification with silane. Pristine membranes (a), membrane coated with 3-APS (b), membranes coated with 6-AHAS (c), membrane coated with 3-APS and quaternized (d), and membrane coated with

6-AHAS and quaternized. Note the leaf-like morphology and the valley and ridge structure linked to the layer of polyamide RO membrane. Also, note filling of valleys for all the modified membranes which is more prominent in the higher magnification image.

The deposition of the molecules of silane onto the surface of the membrane results in the formation of chemical bonds between the Si atoms and the C atoms. For the silane with the longer alkyl chain (6-AHAS), film deposition alone does not cause a significant change in surface morphology. As is evident from the relatively higher magnification images **[Figures 16(e)]**, the difference between the peaks and valleys is similar. This was also observed in the previous study that involved the deposition of N1-(3-trimethoxysilylpropyl) diethylenetriamine [60]. However, the quaternization of the N atoms of this silane resulted in leveling off between the peaks and valleys. This is more prominent in the higher magnification image (**Figure 17**) which shows a less difference of heights between the two opposing surface features. This can be explained by the interactions of the oppositely charged ions (R_4N^+ and negative charges) that causes the neighboring functional groups and moieties to come closer and acquire a coil-like shape.



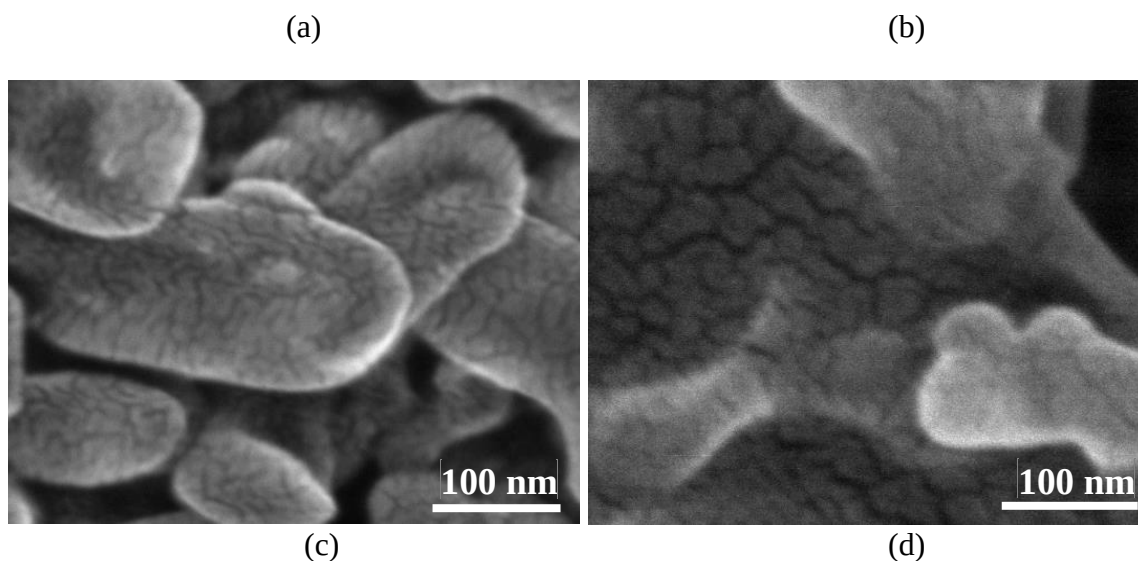


Figure 17. FESEM images of membranes coated with 3-APS (a,c) and 6-AHAS (b,d) and quaternized at very high magnifications. Note the difference in morphology as the valleys get filled up after quaternization.

Higher magnification images (**Figure 17**) make the differences more prominent. Interestingly, this change in morphology is more pronounced for the membrane coated with 6-AHAS as compared to the one modified with 3-APS. This may be attributed to the longer alkyl chain (hexyl) as well as the presence of 2 amino groups in the former that facilitate closer interactions with neighboring molecules (**Figure 11**). The 3-APS is a relatively short molecule with a lone amine group that is unlikely to foster strong interactions with neighboring molecules.

4.3 Surface Wettability

By contact angle measurement of any surface material, its hydrophilicity and/or hydrophobicity will be determined. This contact angle is determined by both the properties of the solid and liquid in contact as well as the interaction and/or repulsion forces that exist

between these interfaces. When a surface exhibits a contact angle of less than 90° ($< 90^\circ$), the surface is classified to be hydrophilic while values greater than 90° ($> 90^\circ$) are classified as hydrophobic. According to research findings, highly hydrophilic membrane surfaces show enhanced resistance to bacterial adhesion which would result in biofouling. In other words, for anti-fouling applications, hydrophilic membrane surfaces are preferred.

Figure 18 shows images of water droplets on the pristine and the modified membrane surfaces and the corresponding contact angle values. The average CA value of the original membrane (80LB from Toray, Inc.) is $\sim 92^\circ$. Deposition of a thin silane film on the membrane surface results in a significant change in surface wetting behavior. The average value reduces to $\sim 63^\circ$ and 52° for the membrane coated with 3-APS and 6-AHAS respectively. This significant reduction is attributed to the intrinsic hydrophilicity of the amine groups present in the silanes. The relatively lower CA value for the surface coated with 6-AHAS can be explained by the presence of more amine groups that increases the likelihood of forming hydrogen bonds with surrounding water molecules [61].

Quaternization of the surface coated with 3-APS further increased the hydrophilicity with an angle of $\sim 50^\circ$. This occurs because one of the H atoms in the amine group is replaced by alkyl groups (C_2H_5) from the EtI precursor and the subsequent formation of quaternary ions (R_4N^+) that are hydrophilic in nature due to the polar bonding [62]. However, the quaternization of the 6-AHAS coated surface results in only a minor change in the CA indicating a lower degree of quaternization. The possible reasons for less quaternization of the 6-AHAS are: (i) the longer alkyl chain to which the terminal amine is attached may offer steric hindrance [63] to the alkyl groups of the quaternizing agent, (ii) presence of

intramolecular hydrogen bonding between the N of the molecule and the H of the neighboring one that makes the former unavailable for quaternization [64].

The above hypothesis is strengthened by comparing the high-resolution XPS spectra of N 1s for the two silanes in the quaternized state. The peak corresponding to R_4N^+ is much smaller for the 6-AHAS as compared to the one for 3-APS.

Considering the different stages of formation of biofilm on the desalination membrane surface, the initial bacterial colonies adhesion is definitely one of them [65]. It leads to the undesired degradation or deterioration of the membrane surface thereby hampering the membrane's performance. However, according to several studies, hydrophobic and non-polar surfaces have high susceptibility towards irreversible attachment of bacteria, while with a hydrophilic surface, there is a reduced tendency of bacterial adhesion [66]. Therefore, with this in view, hydrophilic surfaces, especially desalination membrane surfaces, exhibit an increased effective hydrodynamic cleaning process [67] and enhanced membrane lifetime [68].

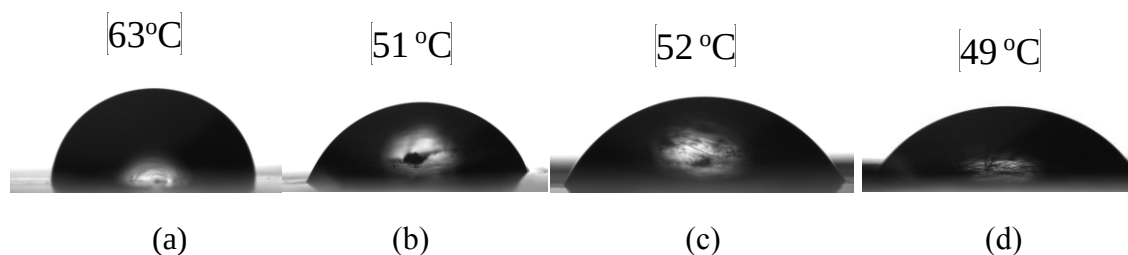


Figure 18. Images of water droplets and the corresponding CA values (a) 3-APS coating only, (b) 3-APS after quaternization, (c) 6-AHAS coating only, (d) 6-AHAS after quaternization. Note the significant reduction in CA after the quaternization of the 3-APS

coated surface. For the 6-AHAS, coating alone gives a decrease in the angle that remains constant even after quaternization.

4.4 Surface Elemental Analysis

X-ray Photoelectron Spectroscopy is a very useful tool for an accurate determination of the elemental composition of any surface. The beauty of this technique is that it scans the top 5 – 10 nm of the surface only and identifies the elements present and their respective ratios. This is of interest to membrane fouling application because the foulants present in natural waters such as bacteria and organic compounds interact with the surface atoms initially. This interaction usually dictates the events to follow.

Figure 19 shows the high-resolution spectra for N 1s and Si 2p orbitals for membrane samples coated with the silanes before and after quaternization. The amide peak (N-H) is clearly the dominant one after film deposition only due to the presence of this functionality in the silane molecule [**Figure 19(a)**]. This also is enough evidence of the presence of a silane layer on the membrane as the XPS of the uncoated membrane shows two distinct amide peaks (N-H, NH₂) virtually stacked on top of each other [69]. However, quaternization reverses the scenario, with the quaternary ammonium (R₄N⁺) peak now dominating and the amide peak significantly reduced in intensity [**Figure 19(b)**]. Similarly, a lone Si 2p peak is seen for the membrane coated with 6-AHAS [**Figure 19(c)**], whereas the quaternized surface has two deconvoluted peaks [**Figure 19(d)**].

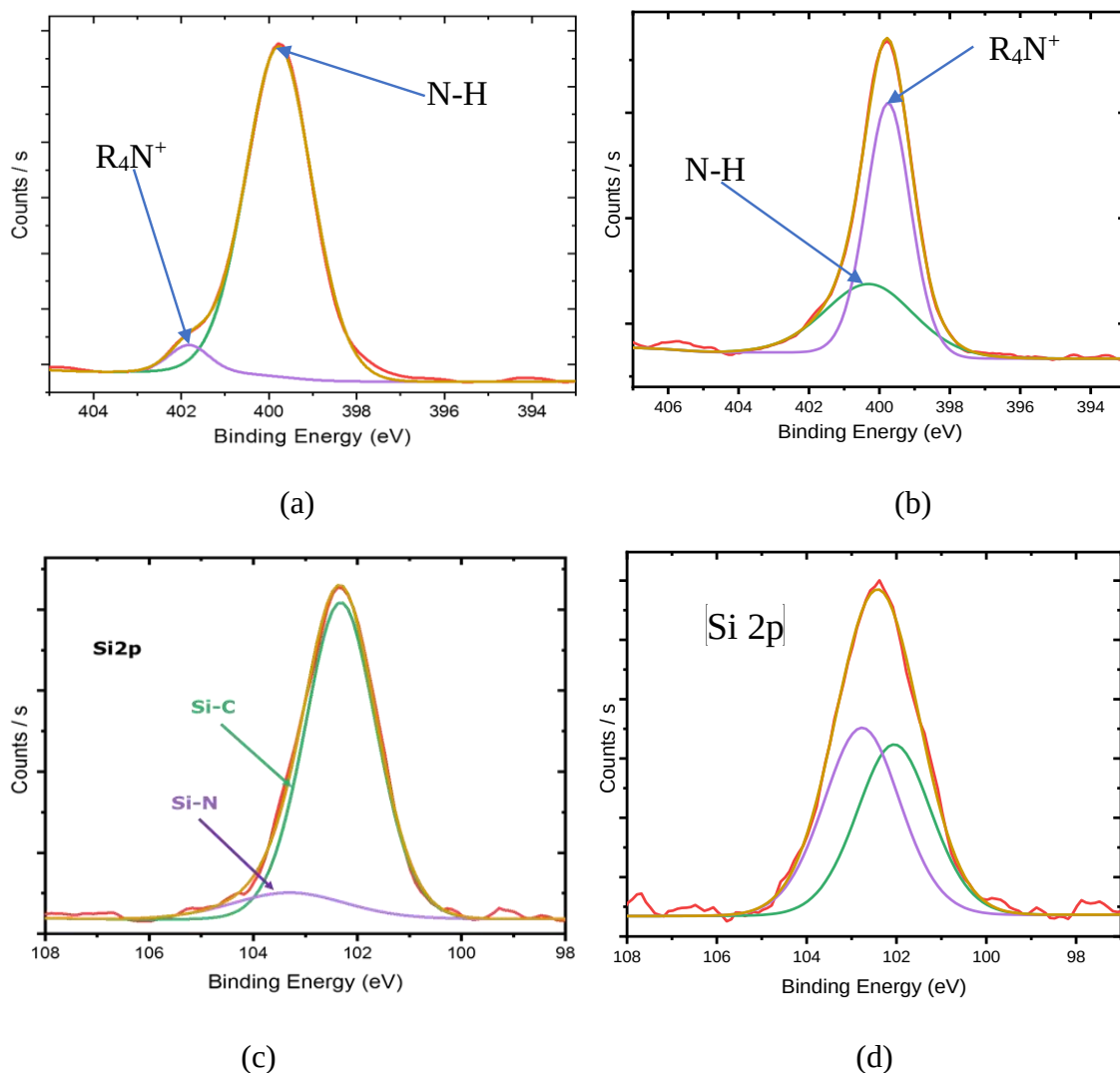


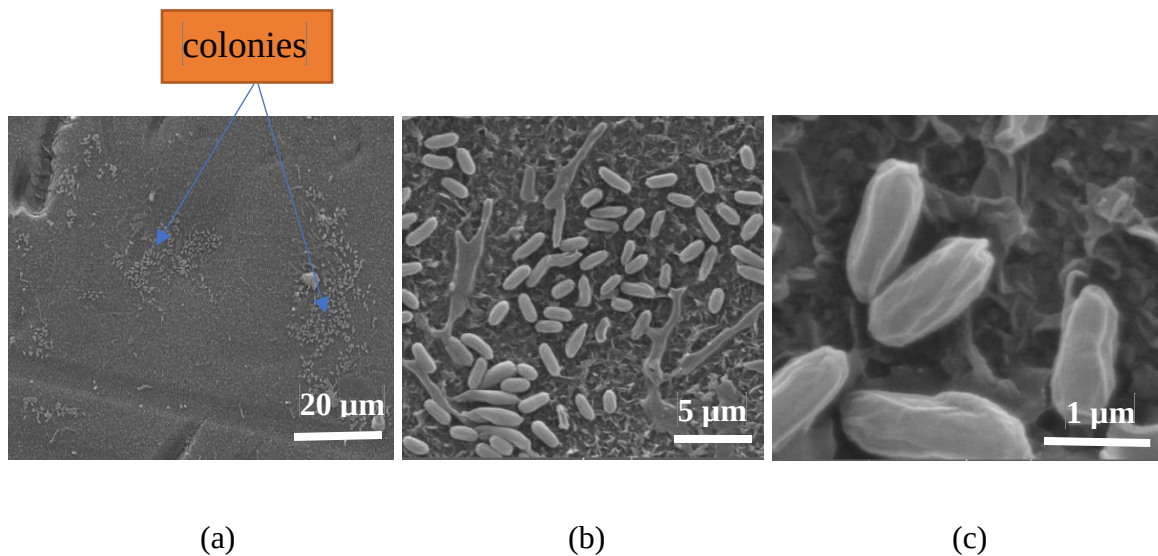
Figure 19. High-resolution XPS scans for the membrane coated with the silane films. N 1s for the APS coated samples (a) before (b) after quaternization, and Si 2p spectra for the AHAS coated samples (c) before (d) after quaternization. Note the difference in the peaks for these two elements before and after quaternization. Before quaternization, the peak corresponding to the amide bond (N-H) dominates, whereas quaternization results in a significant increase in the intensity of the quaternary ammonium (R_4N^+). For Si 2p, a lone peak corresponding to Si-O (~ 103 eV) is visible after the coating, and two distinct convoluted peaks attributed to the former and Si-N can be observed.

4.5 Bacterial adhesion

The attachment of microorganisms to the membrane surface is a critical early-stage event in the overall process of membrane biofouling [70][71]. It is hypothesized that before microbial adhesion, a conditioning film consisting of various organic macromolecules such as proteins, polysaccharides forms on the surface that facilitates or encourages the bacterial attachment [72]. The composition and characteristics of this film depend upon the environment (seawater, brackish water, etc.) to which the substrate is exposed. Loeb and colleagues observed the film formation during the first few minutes and continued growth after a few hours when exposed to seawater [73]. Once the microorganisms attach, they feed on the nutrients present in the surrounding medium to grow, multiply and excrete extracellular polymeric substances (EPS). The EPS is dense and slimy and sticks to the surface to form a matrix that is hard to get rid of. Microorganisms growing within associated biofilms are more resistant against external factors such as biocides, detergent, antibiotic treatments, and host defense responses as compared to planktonic (i.e., free) cells.

An ideal antifouling surface is visualized as one that will discourage or at least significantly delay the adhesion of bacteria. Hydrophilic and polar surfaces are generally thought to be more capable as compared to hydrophobic and non-polar surfaces. However, very few surfaces could deter microorganisms for long periods and bacterial attachment is therefore inevitable. In such situations, a surface with biocidal capability or the ability to kill or deactivate the bacteria upon contact is highly desirable.

Diverse quaternary ammonium (QA) compounds have long been identified to possess outstanding bactericidal properties. These bactericidal properties are credited to be the outcome of two crucial structural features: (1) the positive charge on the N atom in the quaternary ammonium (QA) group establishes an electrostatic attraction and strong interaction with the negatively charged surface of bacterial cells and (2) a lipophilic hydrocarbon chain (usually 12–18 carbon atoms long) can damage the structure of the cell membrane and meddle with the function of the membrane, which eventually results in the loss of the constituents of the cytoplasm thereby leading to the death of the cell [74]. Furthermore, it has been confirmed that polymers possessing quaternary ammonium (QA) groups show higher antibacterial behavior against various types of bacteria than their unquaternized counterpart [75].



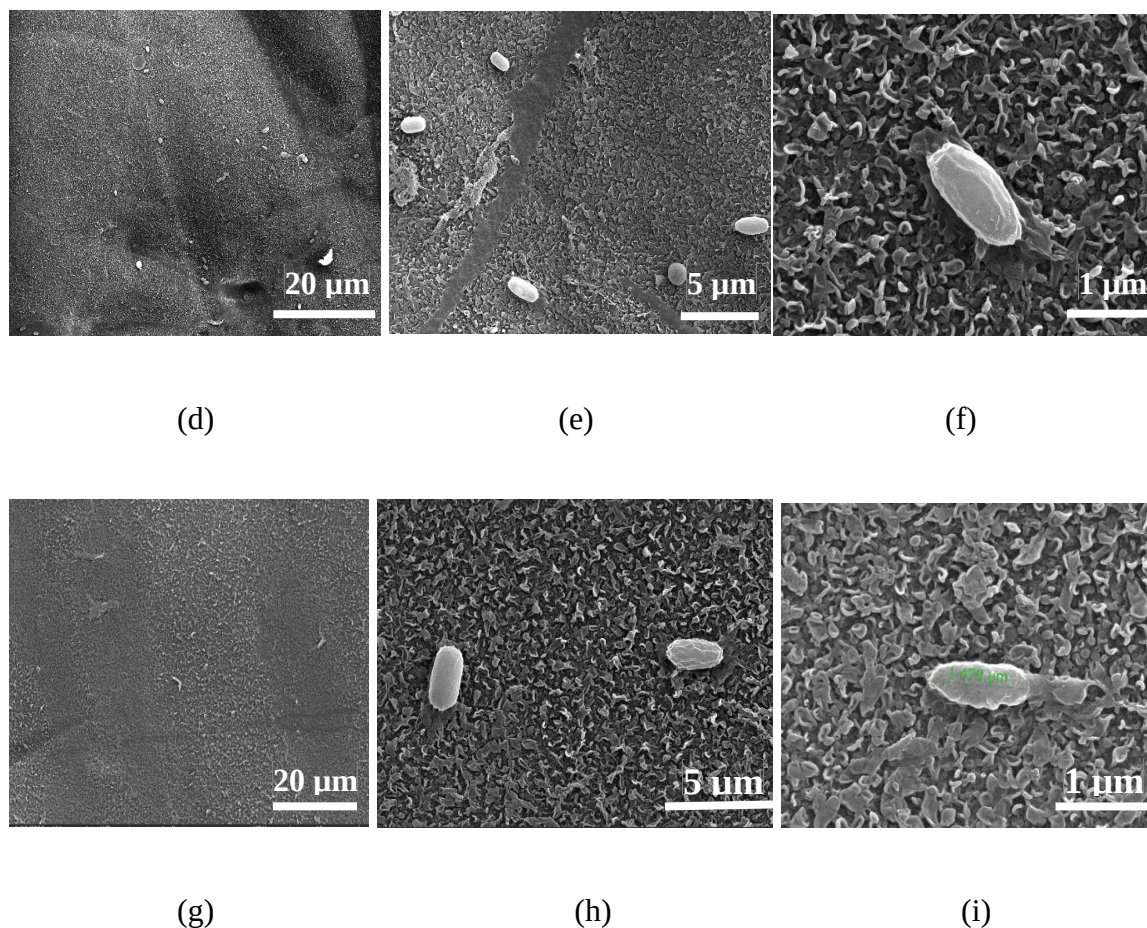


Figure 20. FESEM images of the membranes after exposure to a static culture of *P. aeruginosa*, the top row is for the original membrane, the middle for the membrane after coating with the 6-AHAS, and the bottom row after quaternization of the coating. Note the presence of several colonies and the large no. of cells within the colonies for the uncoated membrane. The presence of the silane coating significantly reduces the number of bacteria and quaternization results in their killing as can be witnessed by the deformed morphology.

Figure 20 shows FESEM images of the membranes after exposure to a concentrated bacterial suspension of gram-negative *P. aeruginosa*. The surface of the original membrane

shows several colonies at different locations and each colony has a sizeable population of microorganisms **[Figure 20(a)]**. Images at higher magnifications reveal the proximity of the bacteria to one another **[Figure 20(b)]** and the presence of EPS **[Figure 20(c)]** that are secreted by the microorganisms during their growth and multiplication. The rapid microbial attachment is explained by the intrinsic surface hydrophobicity ($CA \sim 92^\circ$) of the 80LB membrane from Toray.

In contrast, the membranes with the silane film show fewer bacteria and away from each other **[Figure 20(d) & (g)]**. For the sample coated with 6-AHAS, this is readily explained by the increased hydrophilicity ($CA \sim 52^\circ$) due to the presence of amine groups (N-H, N-H₂). As discussed in detail earlier, hydrophilic and/or polar groups discourage the irreversible attachment of microorganisms due to the formation of a hydrated layer of water. Also, the initial interaction of the bacterial cells with a surface is hydrophobic that don't materialize in the presence of predominantly hydrophilic moieties.

The adhesion trend remains the same after quaternization with a few cells here and there **[Figure 20(g)]**. However, the major difference is in the shape and appearance of the attached microorganisms. Compared to the original membrane surface, the bacteria are deformed **[Figure 20(h) & (i)]** due to attack on the cell wall by quaternary N. The damaged or inactivated bacteria are no longer able to grow, multiply and secrete EPS like their healthy counterparts.

The pattern of cell attachment is similar for the other silane and either species of microorganism. **Figure 21** shows some FESEM images of the membrane coated with 3-APS, the silane with a shorter molecule and the lone amine group at its end. Compared to

the unmodified membrane, the no. of cells is much lower, and they are further apart. The slightly higher attachment and some presence of biofilm on these membranes may be explained by the moderate hydrophobicity (CA $\sim 63^\circ$) of the 3-APS coating as compared to other modified membranes (**Figure 18**).

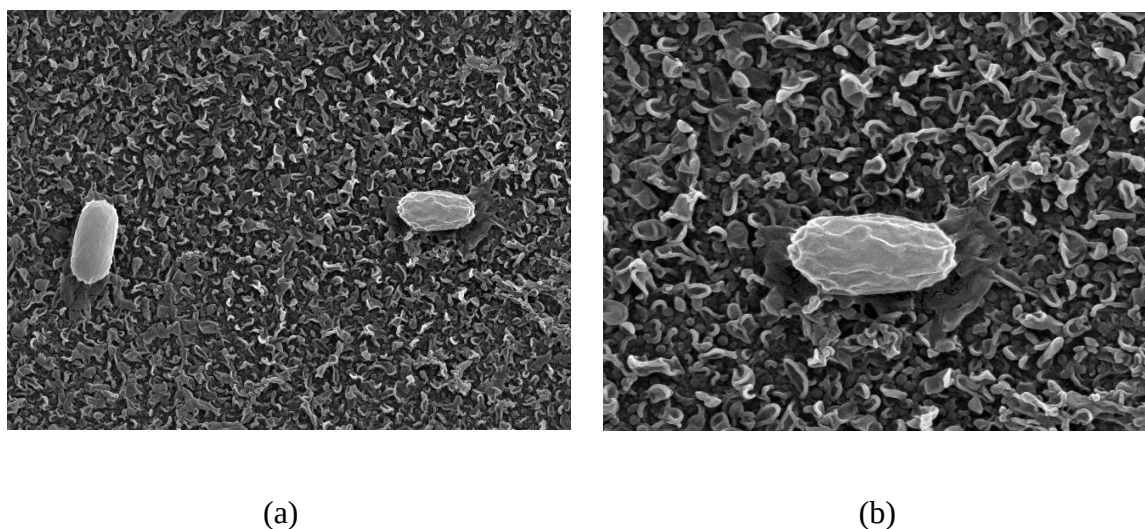


Figure 21. FESEM images of membrane coated with 3-APS and before quaternization after exposure to the bacterial strain of *P. aeruginosa*. Notice trace amounts of biofilm in the vicinity of a few bacteria indicating some microbiological activity.

4.6 Bacterial Killing

In addition to anti-adhesion, another important route or mechanism for biofouling control is the biocidal or bacterial killing capability of a surface. The latter becomes crucial as eventually, microorganisms will attach to the surface no matter how much anti-adhesive the surface is. As discussed above, the quaternized N atoms exhibit excellent antimicrobial activity. The purpose of this section is to compare this activity for the pristine and the modified membranes against *P. aeruginosa* (Gram-negative).

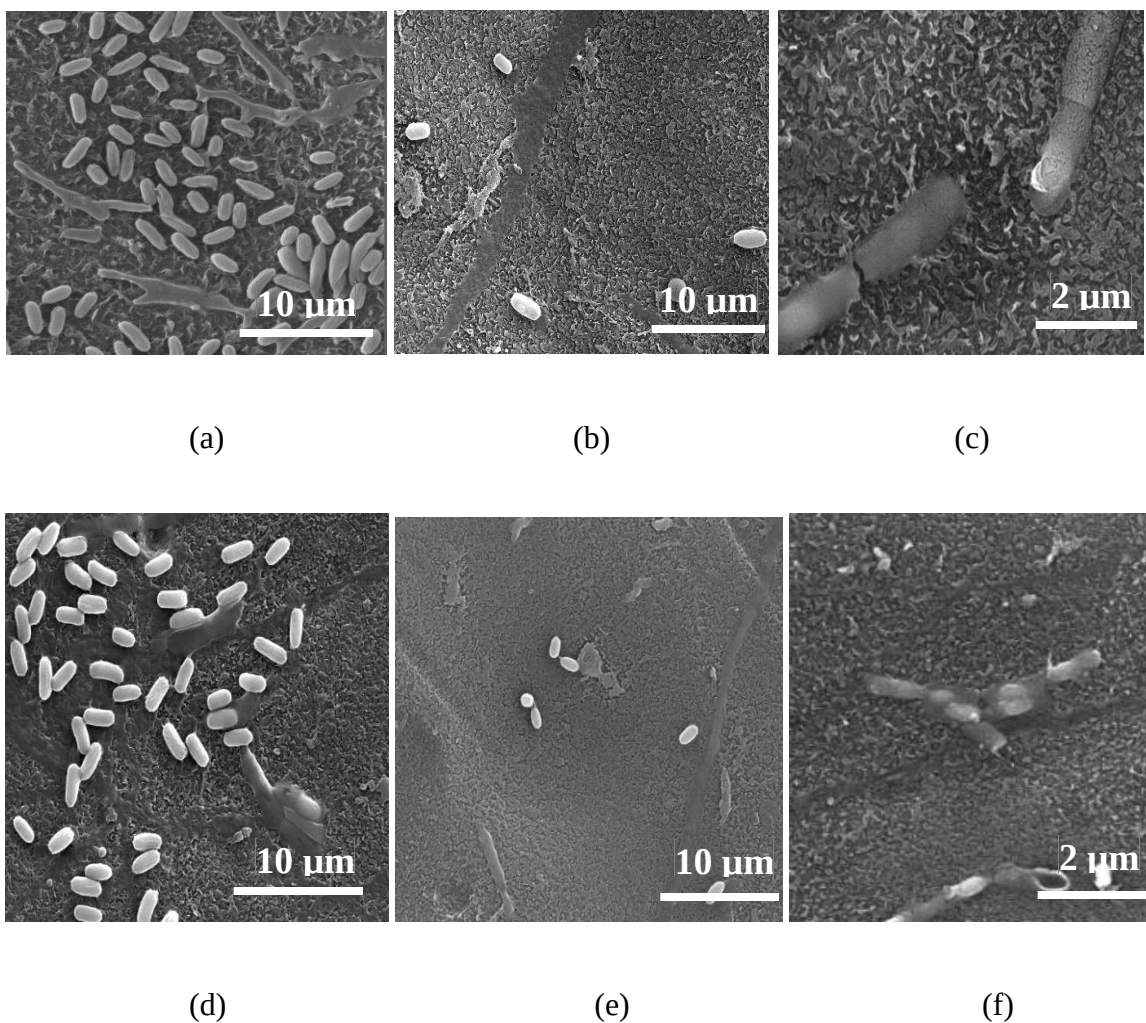


Figure 22. The FESEM images of the control **[Figure 22 (a)]** and the modified membranes surface; 3-APS-C **[Figure 22 (b)]**, 3-APS-CQ **[Figure 22 (c)]**, 6-AHAS-C **[Figure 22 (d)]**, and 6-AHAS-CQ **[Figure 22 (d)]**, after exposure to gram-negative *P. aeruginosa*. In comparison with the virgin membrane that has healthy cells of regular morphology, these appear to have a deformed shape especially along the edges **[Figure 22 (d)]**. Also, cracks are visible and peeling off the outer membrane can be noticed **[Figure 22 (c)]**.

Figure 23 represents the image of the bacteria-killing in the petri dish. It can be seen from the image that there are more bacteria counts in the controls more than there are in both the 3-APS and 6-AHAS membrane-modified silanes. The presence of the quaternary atoms induced as a result of quaternization, incurred more bacterial killings, thereby reducing the bacteria counts.

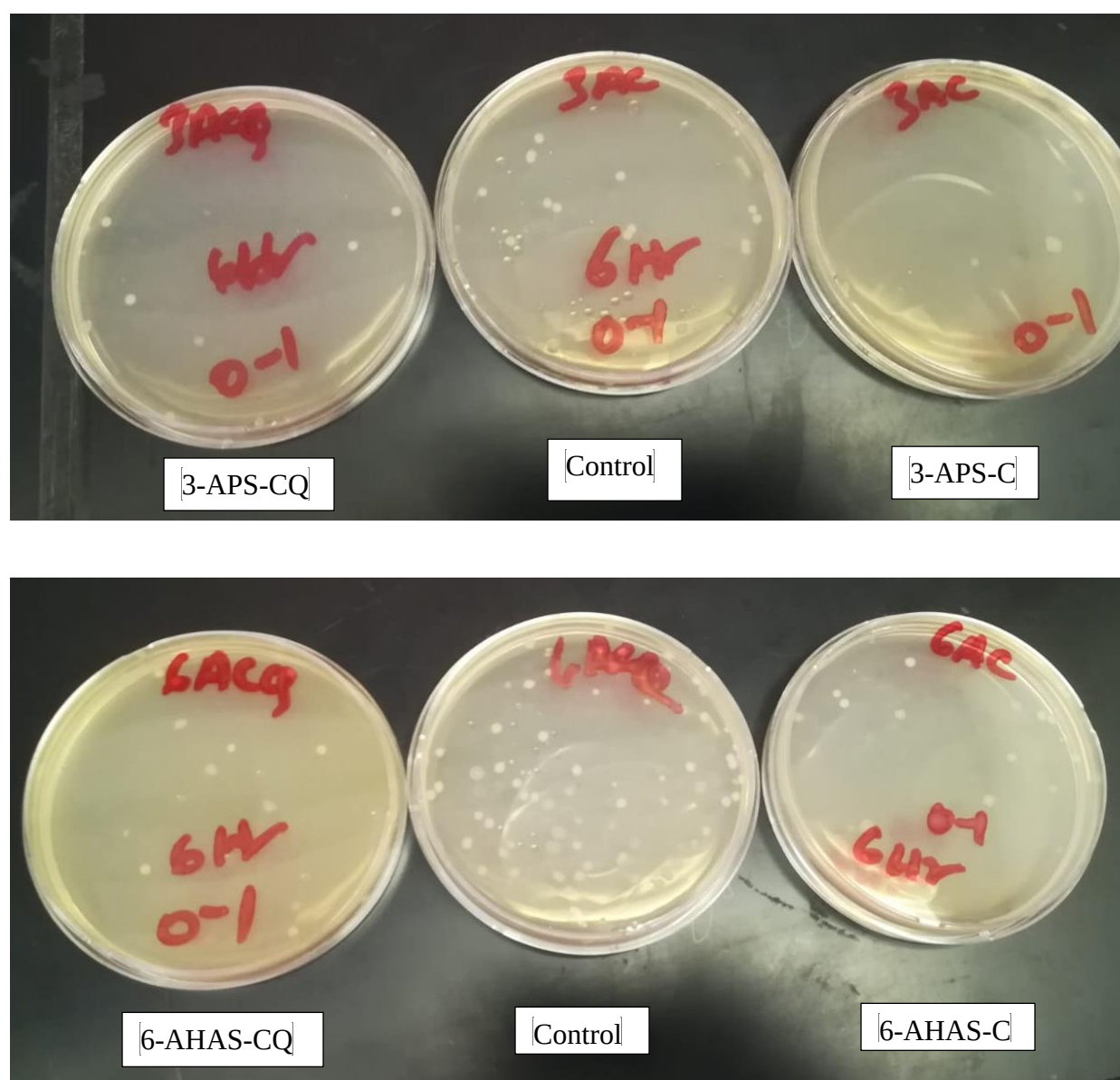


Figure 23. The colonies of *P. aeruginosa* grown on agar plates from suspensions exposed to the surfaces of the membranes for a duration of 6 hours at 37°C. Observe the high number of *P. aeruginosa* colonies for the pristine membrane and fewer colonies for the modified membranes.

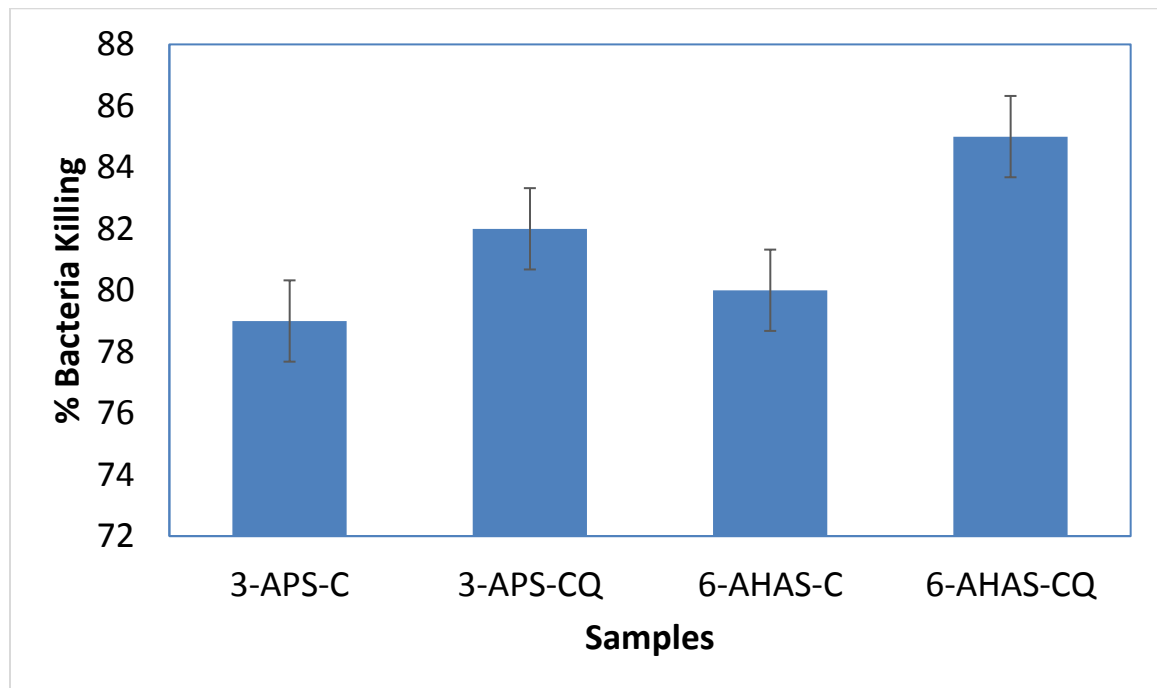


Figure 24. Bacteriostatic rates of *P. aeruginosa* for the membranes modified with silanes; 3-APS and 6-AHAS before and after quaternization. Note the killing rate (~ 79%) for the 3-APS after film deposition that increased (82%) upon quaternization. The membrane coated with 6-AHAS has a killing rate of ~ 80% that increases to 85% after quaternization.

Figure 24 shows the bacteriostasis rates for the modified membranes against a gram-negative bacterium, *P. aeruginosa*. Interestingly, significant biocidal activity is observed

from the coated-only membranes to the coated and quaternized membranes. The 3-APS-coated membrane shows a killing rate of 79%, which increased upon quaternization to ~82%. Even for the membrane coated with 6-AHAS, the killing rate is ~ 80% after the film deposition only. Quaternization of the N atoms results in further improvement to ~ 85% (Table 1).

Table 1. the bacteriostasis rate for the gram-negative *P. aeruginosa* for the 3-APS and 6-AHAS

<i>Pseudomonas aeruginosa</i> /CFU						
Sample	Control	3-APS-C	3-APS-CQ	Control	6-AHAS-C	6-AHAS-CQ
At 6hrs.	5.6x10 ³	1.2x10 ³	1.0x10 ³	1.0x10 ⁴	2.0x10 ³	1.5x10 ³
% Killing	-	79	82	-	80	85

The difference between the two silanes can be attributed to the difference in molecular structure between the two. The 6-AHAS has more amine groups in its molecular structure as compared to the 3-APS hence, it exhibits a more effective biocidal capability. This is possible due to the more amine groups present in 6-AHAS and the availability of N atoms for quaternization. Considering the structure of the outer cell wall of *P. aeruginosa* (gram-negative); while the outer cell wall of a gram-positive bacteria e.g. *B. subtilis*, consist of an inner membrane and a thick layer of peptidoglycan, the gram-negative counterparts, *P. aeruginosa*, have an outer membrane and layers of lipopolysaccharides and periplasm as well (Figure 25). It is the outer membrane that acts as permeability barriers and imparts an intrinsic resistance to biocidal compounds [79].

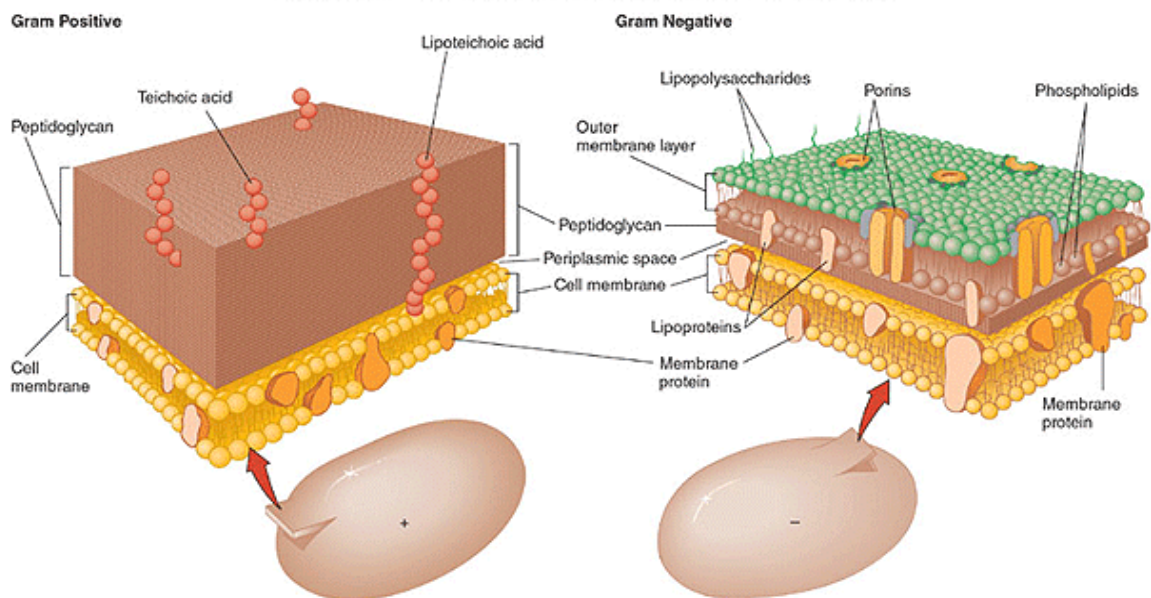


Figure 25. Schematic sketch of the outer cell wall structures for gram-positive and gram-negative bacteria. Note the thick peptidoglycan layer for the positive cell that is also the outermost, and the multi-layered structure for the negative bacterium (www.science.gov).

With regards to the underlying mechanism of antibacterial action, the findings of many recent investigations carried out with different experimental methods, e.g. fluorescence, microscopy techniques (TEM, AFM, etc.), support the hypothesis that quaternized groups kill microorganisms by damaging the OM/CW and cytoplasmic membrane, followed by cell lysis that has been observed in solution [80] and on surfaces [81]. In the case of negatively charged bacteria e.g. *Pseudomonas aeruginosa*, the biocidal polycations are attracted to the microorganisms due to electrostatic interactions and inactivate bacteria by disrupting cellular membrane upon contact. After adsorption onto the bacterial cell, the cations diffuse through the cell wall and disrupt the cytoplasmic membrane to release potassium and other constituents that cause cell death [82].

4.7 Filtration Testing

The basic application of RO membranes is to remove salts from water and produce clean water fit for consumption by human and domestic, agricultural and industrial uses. In that sense, the output parameters that ascertain the desalination efficiency and effectiveness of an RO membrane are salt rejection and permeate water flux. It is a general desire to enhance the two parameters, however, due to the varying mechanism, the two parameters proceed oppositely. The permeate water flux increases with a decrease in the thickness of the layer of the polyamide or an increase in the pore size. These variations both of which encourage the passage of salt across the membrane. Similarly, an increase in the thickness of the polyamide will resist the passage of more salts however, it will make it difficult for water to permeate through the membrane.

The passage of pure water through an RO membrane can be described by the solution-diffusion model and quantitatively expressed by the following equation [76]:

$$J = L_p(\Delta P - \Delta \pi) \quad (2)$$

where J is defined as the volume of water permeating across a unit cross-sectional area of the membrane in unit time, L_p is membrane permeance, ΔP is the applied pressure and $\Delta \pi$ is the osmotic pressure due to the saline content of the feedwater. Where L_{pT} represents the permeability of the coated membrane and is given by:

$$L_{pT} = \frac{1}{\left[\frac{1}{L_p} + \frac{l_c}{P_w} \right]} \quad (1)$$

Here, P_w is the coating's permeability to water, and l_c is the coating thickness when hydrated.

The deposition of a thin film or coating on a membrane surface means the addition of an extra barrier layer that usually results in a flux decline, according to equation (2). The hydraulic resistance of the membrane is directly proportional to the total thickness of the layers combined. If the modification strategy of surface results in a notable decline in flux e.g. more than 30%, it becomes worthless from a practical viewpoint. So, therefore, it is very important to study the effect of the presence of a coating on the permeation characteristics of the membrane.

The filtration experiments were performed with a custom-built laboratory setup as shown in section 3.6 above. Saline water with a NaCl concentration of $\sim 2,000$ ppm was drawn from a feed tank of capacity 30 L and pressurized employing a hydra cell pump (Wanner Engineering, Inc.). The feedwater was flown across the flat-sheet membrane housed in a Teflon permeation cell (Sterlitech, Inc.) with an active area of ~ 16 cm². The concentrate was recycled back to the feed tank whereas the water permeate was collected in a cylindrical ware and measured as per requirement.

Figure 26 shows the permeation behavior of the membrane samples before and after the deposition of film and after quaternization. The pristine membrane recorded an average flux of ~ 31.42 L/m²h at an applied pressure of 800 psi and a feed temperature of $\sim 24^\circ\text{C}$. This result is not unexpected because the UTC-80LB membranes from Toray are specifically made for the desalination of seawater with the membranes having a mean

porosity of fewer than 1×10^{-9} m and a polyamide layer thickness of ~ 250 nm[77].

Surprisingly, after the deposition of the silane

molecules, the flux increased and even more noticeable after the modified surface have been quaternized.

Table 2. The water permeation flux ($\text{L}/\text{m}^2\text{hr.}$) obtained by the pristine and the modified membrane as well as the corresponding salt rejection degree.

	Pristine	3-APS-C	3-APS-CQ	6-AHAS-C	6-AHAS-CQ
WPF ($\text{L}/\text{m}^2\text{hr.}$)	31.42	40.00	53.14	51.43	55.71
Salt Rejection	82.99	88.73	90.96	92.80	95.54

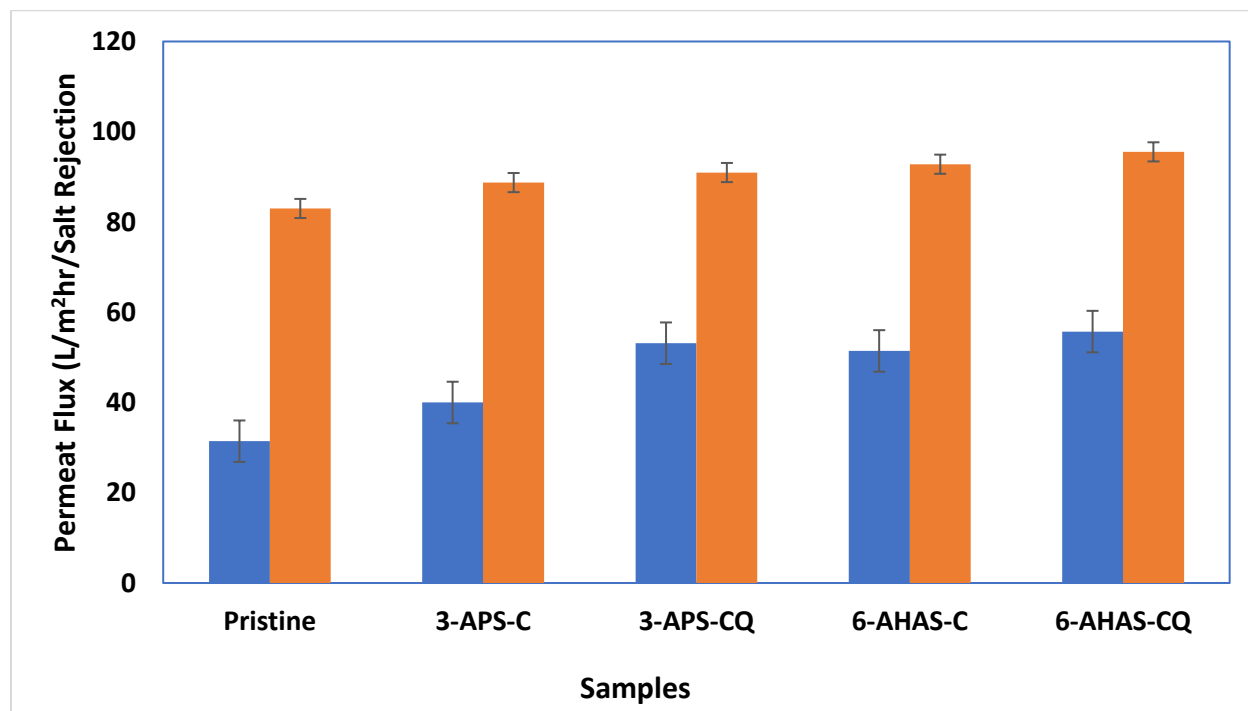


Figure 26. The permeation behavior of the membrane samples before and after the deposition of film and after quaternization. The pink bars represent %salt rejection. Observe the improvement in the %salt rejection and water permeation flux of the membranes after quaternization which can be attributed to the increased hydrophilicity of the membrane.

The water permeation flux increased significantly after the modification of the membrane but is more notable for the quaternized samples (**Table 2**). The reason for this behavior is because of the induced surface hydrophilicity from the silanes present on the membrane surface as noted in the results of the CA measurements (**Figure 18**). The presence of the hydrophobic functional groups in the commercially acquired pristine membrane is the reason for the high contact angle value $\sim 92^\circ$ for the pristine RO membrane [78]. The introduction of the silane molecules displaces these hydrophobic functional groups with more hydrophilic ones such as R_4N^+ , thereby rendering the modified membrane surfaces water-loving and hence reduction in the CA values (**Figure 18**). The effect is more obvious for the quaternized membrane samples as the primary amino nitrogen (NH_2) disappears completely and the ratio of quaternary and pyrrolic N increases.

CHAPTER 5

CONCLUSION

Thin films of silanes with varying Nitrogen content, 3-Amino Propyltriethoxy Silane and 6-Amino Hexyl 3-Aminopropyltrimethoxy Silane, were dip-coated onto commercial RO membranes and the N atoms of the film quaternized. The presence of the coatings and their quaternization were confirmed by spectroscopic techniques, namely, FTIR and XPS. Contact angle measurements showed that with quaternization of the N atom(s) of the silanes, the hydrophilicity of the samples increased. The 6-AHAS coated and quaternized gave the hydrophilicity values ($\sim 49^\circ$).

The coated membranes showed varying antimicrobial properties against the gram-negative strain (*P. aeruginosa*). The killing rate for the membrane modified with 6-AHAS showed the highest response of $\sim 85\%$ after the quaternization of the N atoms. On the other hand, the 3-APS sample showed the least killing rate of $\sim 79\%$ without quaternization of the N atoms. Finally, membranes modified with 6-AHAS showed the best water permeation flux and %salt rejection, with the 6-AHAS-CQ having the best results.

References

- [1] United Nations World Water Assessment Programme, *The United Nations World Water Development Report 2018*, (United Nations Educational, Scientific and Cultural Organization, New York, United States), www.unwater.org/publications/world-water-development-report-2018/. (2018)
- [2] Burek, P. et al. *Water Futures and Solution: Fast Track Initiative (Final Report)*. *IIASA Working Paper* (International Institute for Applied Systems Analysis (IIASA), Laxenburg, Austria, 2016
- [3] M. M. Mekonnen and A. Y. Hoekstra, “Four billion people facing severe water scarcity,” *Sci. Adv.*, vol. 2, no. 2, p. e1500323, Feb. 2016.
- [4] United Nations World Population Prospects: The 2012 Revision, Methodology of the United Nations Population Estimates and Projections. United Nations, Department of Economic and Social Affairs, Population Division. ESA/P/WP.235 (2014)
- [5] M. Kummu *et al.*, “The world’s road to water scarcity: shortage and stress in the 20th century and pathways towards sustainability,” *Sci. Rep.*, vol. 6, p. 38495, Dec. 2016.
- [6] P. Burek, et al., *Water Futures and Solution: Fast Track Initiative (Final Report)*. *IIASA Working Paper* (International Institute for Applied Systems Analysis (IIASA), Laxenburg, Austria, 2016).

- [7] N. Alexandratos, & J. Bruinsma, *World Agriculture Towards 2030/2050: The 2012 Revision. ESA Working paper No. 12-03. Rome, Food and Agriculture Organization of the United Nations (FAO) www.fao.org/docrep/016/ap106e/ap106e.pdf. (2012)*

- [8] United Nations Department of Economic and Social Affairs (UNDESA), *World Population Prospects: Key Findings and Advance Tables – The 2017 Revision. Working Paper No. ESA/P/WP/248* (UNDESA, Population Division, New York, 2017). United Nations Department of Economic and Social Affairs (UNDESA), *World Population Prospects: Key Findings and Advance Tables – The 2017 Revision. Working Paper No. ESA/P/WP/248* (UNDESA, Population Division, New York, 2017). www.esa.un.org/unpd/wpp/Publications/Files/WPP2017_KeyFindings.pdf

- [9] A.G. Fane and G.L. Leslie, Membrane technology – the key to water reuse, Proceedings, IWA Conference on Water Environment-Membrane Technology, 875–883, Seoul, Korea (2004).

- [10] R.W. Baker, *Membrane Technology and Applications*, 2nd ed., John Wiley & Sons, Chichester, New York, 2004.

- [11] M. Asadollahi, D. Bastani, S.A. Musavi, Enhancement of surface properties and performance of reverse osmosis membranes after surface modification: *a review Desalination.*, 420 (2017), pp. 330-383.

- [12] Renewable Energy Opportunities in Water Desalination | IntechOpen, (2019).
(/books/desalination-trends-and-technologies/renewable-energy-opportunities-in-water-desalination accessed July 5, 2018).
- [13] C. Hobbs, J. Taylor, S. Hong, Effect of surface roughness on fouling of RO and NF membranes during filtration of a high organic surficial groundwater, *J Water Supply Res Technol-Aqua*, 55 (2006), pp. 559-570.
- [14] M.F.A. Goosen, S.S. Sablani, H. Al-Hinai, S. Al-Obeidani, R. Al-Belushi, D. Jackson, Fouling of reverse osmosis and ultrafiltration membranes: a critical review *Sep Sci Technol*, 39 (2005), pp. 2261-2297.
- [15] R. H. Hailemariam, Y. C. Woo, M. M. Damtie, B. C. Kim, K.-D. Park, and J.-S. Choi, "Reverse osmosis membrane fabrication and modification technologies and future trends: A review," *Adv. Colloid Interface Sci.*, p. 102100, 2019.
- [16] K.L. McMordie-Stoughton, X. Duan, E.M. Wendel, Reverse osmosis Optimization (2013).
- [17] S.S. Shenvi, A.M. Isloor, A.F. Ismail, "A review on RO membrane technology: developments and challenges", *Desalination.*, 368 (2015), pp. 10-26.
- [18] A.J. Karabelas, C.P. Koutsou, M. Kostoglou, D.C. Sioutopoulos, "Analysis of specific energy consumption in reverse osmosis desalination processes", *Desalination.*, 431 (2018), pp. 15-21.

- [19] A.H. Johir, C. Khorshed, S. Vigneswaran, H.K. Shon, "In-line flocculation–filtration as pre-treatment to reverse osmosis desalination", *Desalination.*, 247 (2009), pp. 85-93.
- [20] A.D. Khawaji, I.K. Kutubkhanah, J.-M. Wie, "Advances in seawater desalination technologies", *Desalination.*, 221 (2008), pp. 47-69.
- [21] J.S. Vrouwenvelder, S.M. Bakker, M. Cauchard, R. Le Grand, M. Apacandié, M. Idrissi, *et al.*, "The membrane fouling simulator: a suitable tool for prediction and characterization of membrane fouling", *Water Sci Technol J Int Assoc Water Pollut Res*, vol. 55, pp. 197-205, 2007.
- [22] B. Rosche, X. Z. Li, B. Hauer, A. Schmid, and K. Buehler, "Microbial biofilms: a concept for industrial catalysis?," *Trends in Biotechnology*, vol. 27, no. 11. pp. 636–643, 2009.
- [23] Y. Wu *et al.*, "Recent advances in mitigating membrane biofouling using carbon-based materials," *J. Hazard. Mater.*, vol. 382, Jan. 2020.
- [24] J. Baker and L. Dudley, "Biofouling in membrane system- a review", *Desalination*, vol. 14, pp. 382-391, 1998.
- [25] A. Matin, Z. Khan, S. Zaidi, and M. Boyce, "Biofouling in reverse osmosis membranes for seawater desalination: phenomena and prevention," *Desalination*, vol. 281, pp. 1-16, 2011.
- [26] H. Flemming, "Biofouling in water treatment," in *Biofouling and Biocorrosion in Industrial Water Systems*, ed: Springer, pp. 47-80, 1991.

- [27] T. Griebbe and H.-C. Flemming, "Biocide-free antifouling strategy to protect RO membranes from biofouling," *Desalination*, vol. 118, pp. 153-IN9, 1998.
- [28] J.-J. Qin, B. Liberman, and K. A. Kekre, "Direct osmosis for reverse osmosis fouling control: principles, applications, and recent developments," *The Open Chemical Engineering Journal*, vol. 3, pp. 8-16, 2009.
- [29] N. H. Lin, M.-m. Kim, G. T. Lewis, and Y. Cohen, "Polymer surface nanostructuring of reverse osmosis membranes for fouling resistance and improved flux performance," *Journal of Materials Chemistry*, vol. 20, pp. 4642-4652, 2010.
- [30] X. Wei, Z. Wang, Z. Zhang, J. Wang, and S. Wang, "Surface modification of commercial aromatic polyamide reverse osmosis membranes by graft polymerization of 3-allyl-5, 5-dimethylhydantoin," *Journal of Membrane Science*, vol. 351, pp. 222-233, 2010.
- [31] S. L. Li, P. Wu, J. Wang, J. Wang, and Y. Hu, "Fabrication of high-performance polyamide reverse osmosis membrane from monomer 4-morpholino-m-phenylenediamine and tailoring with zwitterions," *Desalination*, vol. 473, Jan. 2020.
- [32] A. Salama, M. Zoubeik, A. Henni, K. T. W. Ng, and H. Ibrahim, "On the design of sustainable antifouling system for the crossflow filtration of oily water systems: A multi continuum and CFD investigation of the periodic feed pressure technique," *Sci. Total Environ.*, vol. 698, Jan. 2020.

- [33] P. S. Goh, T. W. Wong, J. W. Lim, A. F. Ismail, and N. Hilal, "Innovative and sustainable membrane technology for wastewater treatment and desalination application," in *Innovation Strategies in Environmental Science*, Elsevier, 2020, pp. 291–319.
- [34] C. Liu *et al.*, "Constructing zwitterionic polymer brush layer to enhance gravity-driven membrane performance by governing biofilm formation," *Water Res.*, vol. 168, Jan. 2020.
- [35] L. D. Chambers, K. R. Stokes, F. C. Walsh, and R. J. Wood, "Modern approaches to marine antifouling coatings," *Surface and Coatings Technology*, vol. 201, pp. 3642-3652, 2006.
- [36] C. Werner, M. F. Maitz, and C. Sperling, "Current strategies towards hemocompatible coatings," *Journal of materials chemistry*, vol. 17, pp. 3376-3384, 2007.
- [37] N. Wisniewski and M. Reichert, "Methods for reducing biosensor membrane biofouling," *Colloids and Surfaces B: Biointerfaces*, vol. 18, pp. 197-219, 2000.
- [38] M. Chapman Wilbert, J. Pellegrino, and A. Zydney, "Bench-scale testing of surfactant-modified reverse osmosis/nanofiltration membranes," *Desalination*, vol. 115, pp. 15-32, 1998.
- [39] Y. Zhou, S. Yu, C. Gao, and X. Feng, "Surface modification of thin film composite polyamide membranes by electrostatic self-deposition of polycations

- for improved fouling resistance," *Separation and Purification Technology*, vol. 66, pp. 287-294, 2009.
- [40] C. Ba and J. Economy, "Preparation and characterization of a neutrally charged antifouling nanofiltration membrane by coating a layer of sulfonated poly (ether ether ketone) on a positively charged nanofiltration membrane," *Journal of Membrane Science*, vol. 362, pp. 192-201, 2010.
- [41] C. Y. Tang, Y.-N. Kwon, and J. O. Leckie, "Probing the nano-and micro-scales of reverse osmosis membranes—a comprehensive characterization of physiochemical properties of uncoated and coated membranes by XPS, TEM, ATR-FTIR, and streaming potential measurements," *Journal of Membrane Science*, vol. 287, pp. 146-156, 2007.
- [42] A. Kulkarni, D. Mukherjee, and W. N. Gill, "Flux enhancement by hydrophilization of thin-film composite reverse osmosis membranes," *Journal of membrane science*, vol. 114, pp. 39-50, 1996.
- [43] W. E. Mickols, "Composite membrane with polyalkylene oxide modified polyamide surface," ed: Google Patents, 2001.
- [44] S. P. Hong, J.-y. Koo, J. H. Lee, and K. Y. Ryu, "Selective membrane having a high fouling resistance," ed: Google Patents, 2009.
- [45] J. Jang and H. Park, "In the situ sol-gel process of polystyrene/silica hybrid materials: Effect of silane-coupling agents," *J. Appl. Polym. Sci.*, vol. 85, no. 10, pp. 2074–2083, Sep. 2002.

- [46] L. L. Hench and J. K. West, "The sol-gel process," *Chem. Rev.*, vol. 90, no. 1, pp. 33–72, May 2002.
- [47] Z. Pu, J. E. Mark, J. M. Jethmalani, and W. T. Ford, "Effects of Dispersion and Aggregation of Silica in the Reinforcement of Poly(methyl acrylate) Elastomers," *Chem. Mater.*, vol. 9, no. 11, pp. 2442–2447, Nov. 1997.
- [48] M. Toki, T. Y. Chow, T. Ohnaka, H. Samura, and T. Saegusa, "Structure of poly(vinylpyrrolidone)-silica hybrid," *Polym. Bull.*, vol. 29, no. 6, pp. 653–660, 1992.
- [49] C. C. Sun and J. E. Mark, "Comparisons among the reinforcing effects provided by various silica-based fillers in a siloxane elastomer," *Polymer (Guildf)*, vol. 30, no. 1, pp. 104–106, 1989.
- [50] A. Kioul and L. Mascia, "Compatibility of polyimide-silicate ceramers induced by alkoxysilane silane coupling agents," *J. Non. Cryst. Solids*, vol. 175, no. 2–3, pp. 169–186, Oct. 1994.
- [51] L. Mascia and T. Tang, "curing and morphology of epoxy resin-silica hybrids," *J. Mater. Chem.*, vol. 8, 2417-2421, 1998.
- [52] D.H. Shin, N.W. Kim, Y.T. Lee, "Surface modification of reverse osmosis membrane skin layer by silane compound", *Membr. J.*, vol. 16, p. 106, 2006.
- [53] N. Kim, D. H. Shin, and Y. T. Lee, "Effect of silane coupling agents on the performance of RO membranes," *J. Memb. Sci.*, vol. 300, no. 1–2, pp. 224–231, Aug. 2007.

- [54] A.K. Ghosh, B.-H. Jeong, X. Huang, E.M.V. Hoek, Impacts of reaction and curing conditions on polyamide composite reverse osmosis membrane properties, *J. Membr.Sci.* 311 (2008) 34–45.
- [55] M. M. Rahman, S. Al-Sulaimi, A. M. Farooque, Characterization of new and fouled SWRO membranes by ATR/FTIR spectroscopy, *Applied Water Science* (2018) 8:183.
- [56] B. Khorshidi, T. Thundat, B. A. Fleck, M. Sadrzadeh, A Novel Approach Toward Fabrication of High-Performance Thin-Film Composite Polyamide Membranes, *Sci. Rep.* 6, 22069.
- [57] A. Matin, H.Z. Shafi, Z. Khan, M. Khaled, R. Yang, K. Gleason, F. Rehman, Surface modification of seawater desalination reverse osmosis membranes: Characterization studies & performance evaluation, *Desalination* 343 (2014) 128–139.
- [58] A.K. Ghosh, B.-H. Jeong, X. Huang, E.M.V. Hoek, Impacts of reaction and curing conditions on polyamide composite reverse osmosis membrane properties, *J. Membr.Sci.* 311 (2008) 34–45.
- [59] Y. Jin, Z. Su, Effects of polymerization conditions on hydrophilic groups in aromatic polyamide thin films, *J. Membr. Sci.* 330 (2009) 175–179.
- [60] I. Abdulazeez, A. Matin, M. Khan, M.M. Khaled, M.A. Ansari, S. Akhtar, S. Rehman, Facile preparation of antiadhesive and biocidal reverse osmosis membranes using a single coating for efficient water purification, *J. Membr. Sci.* 591 (2019) 117299.

- [61] A. Nakajima, T. Miyamoto, M. Sakai, T. Isobe, and S. Matsushita, *App. Surf. Sci.* **2014**, 292, 990-996
- [62] W. Jaeger, J. Bohrisch, A. Laschewsky, Synthetic polymers with quaternary nitrogen atoms—Synthesis and structure of the most used type of cationic polyelectrolytes, *Progress in Polymer Science* 35 (2010) 511–577
- [63] Y. Zhao, W.S. W. Ho, Steric hindrance effect on amine demonstrated in solid polymer membranes for CO₂ transport, *Journal of Membrane Science* 415–416 (2012) 132–138
- [64] S. Hammerum, C. B. Nielsen, Intramolecular Hydrogen Bonding and Hydrogen Atom Abstraction in Gas-Phase Aliphatic Amine Radical Cations, *J. Phys. Chem. A* 2005, 109, 12046-12053
- [65] O. Habimana, A.J.C. Semião, E. Casey, The role of cell-surface interactions in bacterial initial adhesion and consequent biofilm formation on nanofiltration/reverse osmosis membranes, *J. Membr. Sci.* 454 (2014) 82–96
- [66] Y. Yuan, M. P. Hays, P. R. Hardwidge, J. Kim, Surface characteristics influencing bacterial adhesion to polymeric substrates, *RSC Adv.*, 2017, 7, 14254-14261
- [67] A. Al-Amoudi, R. W. Lovitt, Fouling strategies and the cleaning system of NF membranes and factors affecting cleaning efficiency, *J. Membr. Sci.* 303 (2007) 4–28
- [68] J. M. Arnal, B. G.-Fayos, M. Sancho (2011). Membrane Cleaning, Expanding Issues in Desalination, Prof. Robert Y. Ning (Ed.), ISBN: 978-953-307-624-9.

- [69] W. Falath, A. Sabir, K.I. Jacob, Novel reverse osmosis membranes composed of modified PVA/Gum Arabic conjugates: biofouling mitigation and chlorine resistance enhancement. *Carbohydr. Polym.* 155 (2017) 28–39.
- [70] A. Matin, Z. Khan, S.M.J. Zaidi, M.C. Boyce, Biofouling in reverse osmosis membranes for seawater desalination: Phenomena and prevention, *Desalination* 281 (2011) 1–16.
- [71] M. Katsikogianni, Y.F. Missirlis, *Europ. Cells Mater.* 8 (2004) 37.
- [72] G. S. Lorite, C. M. Rodrigues, A. A. de Souza, C. Kranz, B. Mizaikoff, M. A. Cotta, The role of conditioning film formation and surface chemical changes on *Xylella fastidiosa* adhesion and biofilm evolution, *J. Coll. Interf. Sci.* 359 (2011) 289–295.
- [73] G.I. Loeb, R.A. Neihof, *Adv. Chem.* 145 (1975) 319–335.
- [74] T. Ikeda, H. Yamaguchi, S. Tazuke, Phase separation in phospholipid bilayers induced by biologically active polycations, *Biochim. Biophys. Acta* 1026 (1990) 105–112.
- [75] T. Ikeda, S. Tazuke, Biologically active polycations: antimicrobial activities of poly[trialkyl(vinylbenzyl)ammonium chloride]-type polycations, *Makromol. Chem., Rapid Commun.* 4 (7) (1983) 459–461.
- [76] D. R. Paul, Reformulation of the solution-diffusion theory of reverse osmosis, *J. Membr. Sci.*, 241 (2004) 371-386.
- [77] K. Y. Yin, Removal of heavy metal using membrane technology, Project Report Faculty of Engineering and Science Universiti Tunku Abdul Rahman May 2015.

- [78] Mah, S.-K. et al., 2014. The study of reverse osmosis on glycerin solution filtration: Dead-end and crossflow filtrations, transport mechanism, rejection, and permeability investigations. *Desalination*, 352, pp.66–81.
- [79] A. H. Delcour, Outer Membrane Permeability and Antibiotic Resistance, *Biochim Biophys Acta*. 1794 (2009) 808–816
- [80] A.B. Rawlinson, S. M. Ryan, G. Mantovani, J. A. Syrett, D. M. Haddleton, D. J. Brayden DJ Antibacterial effects of poly(2-(dimethylamino ethyl)methacrylate) against selected Gram-positive and Gram-negative bacteria. *Biomacromolecules* 11 (2010) 443–453
- [81] D. Park, J. Wang, A. M. Klibanov, One-step, painting-like coating procedures to make surfaces highly and permanently bactericidal. *Biotechnol Prog* 22 (2006) 584–589
- [82] S. Lenoir, C. Pagnouille, C. Detrembleur, M. Galleni, R. Jerome, *e-Polym*. 2005, 074. |

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Journal Publications

- "Simultaneous enhancement of antifouling and antimicrobial properties of reverse osmosis membranes using a single-pot surface modification technique" **(Submitted)**.
- "Adsorption of methyl blue, methyl orange and methyl red dyes on nitrogen-enriched carbon sheet: a DFT insight" **(Submitted)**.
- "Alkali Metal-Doped Graphitic Carbon Nitride for Efficient Adsorption of Methyl Blue: A DFT Perspective" **(Under Review)**.

- “Spectroscopic studies and DFT evaluation of first-generation Twin and Janus benzamide-based dendrimers” (**Under Review**).