

STUDY ON POLYESTER COMPOSITE NANOFILTRATION (NF)  
MEMBRANE BY INTERFACIAL POLYMERIZATION FOR  
NATURAL ORGANIC MATTER (NOM) REMOVAL

NURUL SUHADA BINTI DRAHIM

UNIVERSITI MALAYSIA PAHANG

STUDY ON POLYESTER COMPOSITE NANOFILTRATION (NF) MEMBRANE  
BY INTERFACIAL POLYMERIZATION FOR NATURAL ORGANIC MATTER  
(NOM) REMOVAL

NURUL SUHADA BINTI DRAHIM

A Thesis submitted in fulfilment of  
the requirements for the award of the degree of  
Bachelor of Chemical Engineering

Faculty of Chemical & Natural Resources Engineering  
UNIVERSITI MALAYSIA PAHANG

FEBRUARY 2013

**STUDY ON POLYESTER COMPOSITE NANOFILTRATION (NF)  
MEMBRANE BY INTERFACIAL POLYMERIZATION FOR NATURAL  
ORGANIC MATTER (NOM) REMOVAL**

**ABSTRACT**

The polyester composite nanofiltration (NF) membrane has been prepared by interfacial polymerization for natural organic matter (NOM) removal. The effect of reaction time on the production of thin film composite NF and its effect on the NOM and Sodium Chloride (NaCl) removal performance was conducted. The thin film composite membranes were synthesized through interfacial polymerization with monomer concentration of 2% w/v of triethanolamine (TEOA) and then react with organic solution of trimesoylchloride (TMC) at different reaction time to produce a new layer polyester on top of polyethersulfone (PES) microporous support. The fabricated thin film composite membranes were characterized in terms of water flux and permeability. It was found that the Polyester NF membrane with different reaction time (15, 25 and 35 minutes) which prepared through interfacial polymerization can reduce the humic acid concentration. Besides that, the variation of reaction time in interfacial polymerization technique improved the filtration performance of the membrane. The result shows that the flux and permeability were decreased as the reaction time increased while opposite trend for NOM and NaCl rejections were observed.

**KAJIAN BAGI PENURASAN NANO POLIESTER KOMPOSIT MEMBRAN  
OLEH PEMPOLIMERAN ANTARA MUKA UNTUK PENYINGKIRAN  
ORGANIK SEMULA JADI**

**ABSTRAK**

Penurasan Nano Poliester Komposit membrane disediakan melalui proses pempolimeran antara muka untuk penyingkiran organik semula jadi. Kesan masa tindak balas penghasilan Penurasan Nano komposit membrane dan kesan penyingkiran ke atas organik semula jadi dan natrium klorida (NaCl) telah dijalankan. Komposit filem nipis membrane disintesis melalui pempolimeran antara muka dengan kepekatan larutan 2% w/v trietanolamine (TEOA) dan seterusnya bertindak balas dengan larutan organik trimesoylchloride (TMC) pada masa tindak balas yang berbeza untuk menghasilkan lapisan poliester baru di atas permukaan mikro berliang polietersulfon (PES) membrane. Komposit filem nipis membrane yang telah dihasilkan dicirikan dari segi fluks air dan kebolehtelapan. Didapati Penurasan Nano Poliester membrane dengan tindak balas masa yang berbeza (15, 25 dan 35 minit) yang dihasilkan melalui proses pempolimeran antara muka boleh mengurangkan kepekatan humik asid. Selain itu, perubahan masa tindak balas dalam pempolimeran antara muka teknik boleh meningkatkan prestasi penurasan membran. Keputusan menunjukkan fluks dan kebolehtetapan menurun apabila masa tindak balas meningkat manakala bertentangan dengan hasil penyingkiran organik semula jadi dan garam (NaCl) telah diperhatikan.

## TABLE OF CONTENTS

	<b>PAGE</b>
<b>SUPERVISOR'S DECLARATION</b>	ii
<b>STUDENT'S DECLARATION</b>	iii
<b>DEDICATION</b>	iv
<b>ACKNOWLEDGEMENTS</b>	v
<b>ABSTRACT</b>	vi
<b>ABSTRAK</b>	vii
<b>TABLE OF CONTENTS</b>	viii
<b>LIST OF TABLES</b>	xi
<b>LIST OF FIGURES</b>	xii
<b>LIST OF SYMBOLS</b>	xiv
<b>LIST OF ABBREVIATIONS</b>	xv
<b>CHAPTER 1 INTRODUCTION</b>	
1.1 Research Background	1
1.2 Problem Statement	3
1.3 Research Objectives	4
1.4 Scope of Study	4
1.5 Significance of the Study	5
<b>CHAPTER 2 LITERATURE REVIEW</b>	
2.1 Introduction	6
2.2 Membrane Review	7
2.2.1 Definition of Membrane	7
2.2.2 Historical Development of Membranes	8
2.3 Concept of Membrane Process	9
2.3.1 Membrane Separation Process	9
2.3.2 Classification of Membrane Separation Process	10

2.3.3	Type of Membrane in Pressure Driven	11
2.3.3.1	Microfiltration	12
2.3.3.2	Ultrafiltration	13
2.3.3.3	Nanofiltration	13
2.3.3.4	Reverse Osmosis	14
2.4	Advantages and Applications of Membrane Processes	14
2.4.1	Advantages of Membrane Processes	14
2.4.2	Application of Membrane Processes	16
2.5	Nanofiltration Membrane	17
2.5.1	Introduction of Nanofiltration Membrane	17
2.5.2	Properties of Nanofiltration Membrane	18
2.5.3	Mechanism of Nanofiltration Membrane	19
2.5.4	Parameters Affecting the Performance of Nanofiltration Membrane	21
2.5.5	Applications of Nanofiltration Membrane	21
2.6	Membrane Limitations	23
2.7	Interfacial Polymerization	25
2.8	Natural Organic Matter (NOM)	27
2.8.1	Characteristic of Natural Organic Matter	27

## **CHAPTER 3 METHODOLOGY**

3.1	Research Design	29
3.2	Chemicals	30
3.3	Equipment	30
3.3.1	Amicon Stirred Cell	30
3.3.2	Nitrogen Gas	31
3.3.3	Ultrasonic Water Bath	31
3.3.4	UV-Vis Spectrometry	32
3.3.5	Fourier Transform Infrared (FTIR) Spectroscopy	32
3.3.6	Conductivity Meter and pH Meter	33

3.4	Preparation of Polyester Membrane	33
3.4.1	Preparation Solution for Interfacial Polymerization Process	33
3.4.2	Interfacial Polymerization Process	34
3.5	Membrane Characterization	36
3.5.1	Pure Water Flux	36
3.5.2	Rejection of Sodium Chloride (NaCl)	37
3.5.3	Removal of Natural Organic Matter (NOM)	38
3.5.4	Analysis of Membrane Surface	39
<b>CHAPTER 4 RESULTS AND DISCUSSION</b>		
4.1	Pure Water Flux and Permeability	40
4.2	Rejection of Sodium Chloride (NaCl)	43
4.3	Standard Curve of Humic Acid	47
4.4	NOM (Humic Acid) Removal	49
4.5	Analysis of membrane Surface	51
<b>CHAPTER 5 CONCLUSION AND RECOMMENDATION</b>		
5.1	Conclusion	52
5.2	Recommendation	53
<b>REFERENCES</b>		54
<b>APPENDIX A</b>		58
<b>APPENDIX B</b>		61

## LIST OF TABLES

		<b>PAGE</b>
Table 2.1	Classification of Membrane Process According Driving Process	11
Table 2.2	Application of Membrane Processes	16
Table 2.3	Applications of Nanofiltration Membrane	22
Table 4.1	Water Flux for 2% TEOA Membranes at Different Reaction Time	41
Table 4.2	Rejection of NaCl for M2-15	44
Table 4.3	Rejection of NaCl for M2-25	45
Table 4.4	Rejection of NaCl for M2-35	46
Table 4.5	Absorbance Value of Humic Acid	48
Table 4.6	Rejection of Humic Acid	49
Table B.1	Time Taken Water Flux Process	61
Table B.2	Water Flux at Different Membrane	61
Table B.3	Conductivity and Rejection of M2-15 Membrane at Different Concentration	63
Table B.4	Conductivity and Rejection of M2-25 Membrane at Different Concentration	64
Table B.5	Conductivity and Rejection of M2-25 Membrane at Different Concentration	65
Table B.6	The Absorbance (ABS) Value for M2-15, M2-25 and M2-35	67
Table B.7	Concentration of Feed, Retentate and Permeate Solutions	68
Table B.8	Rejection of Humic Acid	69



## LIST OF FIGURES

		<b>PAGE</b>
Figure 2.1	Basic Concept of Membrane Separation Process	9
Figure 2.2	Types of Membrane Separation Process	12
Figure 2.3	Relationship between the Solvent Flux, J with Pressure, $\Delta p$	19
Figure 2.4	Concentration Polarization	24
Figure 2.5	Fouling in Membrane Surface	25
Figure 2.6	Interfacial Polymerization Process	26
Figure 2.7	Fraction of NOM in Surface Water Based on DOC	28
Figure 3.1	Amicon Stirred Cell Model 8200	31
Figure 3.2	Fourier Transform Infrared (FTIR) Spectroscopy	32
Figure 3.3	Preparation of TEOA and TMC- Hexane Solution	34
Figure 3.4	Preparation Polyester NF membrane through Interfacial Polymerization	35
Figure 3.5	Water Flux Process	37
Figure 3.6	Equipments for the Water Flux, Rejection NaCl and Removal NOM Process	39
Figure 4.1	Graph Water Flux vs. Pressure of Three Different Polyester Membrane	42
Figure 4.2	Graph Rejection of NaCl vs. Pressure for M2-15 for Three Different NaCl Concentrations	44
Figure 4.3	Graph Rejection of NaCl vs. Pressure for M2-25 for Three Different NaCl Concentrations	45
Figure 4.4	Graph Rejection of NaCl vs. Pressure for M2-35 for Three Different NaCl Concentrations	46

Figure 4.5	Graph Absorbance vs. Concentration	48
Figure 4.6	Graph Rejection of Humic Acid vs. Pressure	50
Figure A.1	PES Membranes before Interfacial Polymerization Process	58
Figure A.2	Membrane was Immersed in The Ultrasonic Water Bath for 2 Minutes	58
Figure A.3	Three Polyester NF Membranes were Labeled as M2-15, M2-25 and M2-35 after The Coating Process	59
Figure A.4	The Filtration Process	59
Figure A.5	Samples for Analysis	60
Figure A.6	The Permeate, Retentate and Feed Samples	60

## LIST OF SYMBOLS

$A$	Area of Membrane
$C_p$	Concentration of permeate
$C_f$	Concentration of feed
$C_r$	Concentration of retentate
$g$	Gram
$hr$	Hour
$J$	Permeate flux
$L$	Liter
$M$	Meter
$mL$	millilitre
$P$	Permeability
$\Delta P$	Filtration pressure
$R$	Rejection
$\Delta t$	Filtration time
$V$	Volume

## LIST OF ABBREVIATIONS

ABS	Absorbance
DOC	Dissolved Organic Matter
ED	Electro Dialysis
FTIR	Fourier Transform Infrared Spectroscopy
IP	Interfacial Polymerization
MF	Microfiltration
NaCl	Sodium Chloride
NaOH	Sodium Hydroxide
NF	Nanofiltration
NOM	Natural Organic Matter
PES	Polyethersulfone
RO	Reverse Osmosis
TEOA	Triethanolamine
TMC	Trimesoylchloride
UF	Ultrafiltration

## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 Research Background**

Natural Organic Matter (NOM) is organic matter from plants and animals present in natural waters for examples in reservoirs, lakes and rivers. NOM is present in most surface waters that can affect the odor, colour and taste of waters. Therefore, the treatment needs to remove NOM to get the clear, clean and safe water which is can be used for others applications. NOM is the main component of organic carbon in aquatic systems. It is complex and difficult to separate mixture of similar macro- organic molecules. In addition, NOM can be categorized into hydrophobic and hydrophilic compounds, mono and multivalent ions, low molecular mass organics and inorganic colloids (Schäfer, 2001).

Membrane technology has been widely used in water and wastewater treatment and industrial separations process. Membrane processes have many advantages over conventional method such as it is simple in concept and operation, do not involve phase changes, low energy consumption, equipment size may be decreased and greater efficiency for raw materials use and potential for recycling of by- products.

Membrane filtration processes involving microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) in potable water production. These membranes use pressure as the driving force to separate out contaminants from water supplies. NF is a widely accepted process for the removal of particulate matter from surface waters. Nanofiltration (NF) membrane is a liquid separation membrane technology positioned between ultrafiltration and reverse osmosis (RO) (Schäfer et.al, 1998). NF membrane separations are widely used in various industrial fields such as water treatment, biochemical industries, pharmaceutical and others because NF has low pressure in operation, high permeate flux, low investment and high retention of multi-valent ion salts (Tang et.al, 2008). The NF membrane has the ability to remove NOM until certain standard quality.

Interfacial polymerization is widely used today for the production of ultra thin films for encapsulation, chemical separations, and desalination (Srebnik et.al, 2009). Most of NF membranes are thin film composite which can be prepared by interfacial polymerization. The NF membrane is prepared through interfacial polymerization of trimesoyl chloride (TMC) with the triethanolamine (TEOA) solution. The advantages of interfacial polymerization are the thin layer can be optimized for particular function by varying the monomer concentration in each solution, rapid reaction rates under ambient conditions and low requirement for reactant purity.

## **1.2 Problem Statement**

The high demand for clean water has led to the increasing development of membrane technology. Water is the backbone of the global economy that very important for agriculture, industry, energy production and domestic consumption. Natural organic matter (NOM) present in water not only affects the odour, colour and taste of water, but it can forms complexes with heavy metals and also can reacts with chlorine. Therefore, the sustainable manner should be considered to produce clean water and also protect the environment.

### **1.3 Research Objectives**

The objectives of this research are to identify Nanofiltration (NF) Polyester membrane for natural organic matter (NOM) removal and to study the effect of reaction time on the production of thin film composite NF and its effects on the NOM and Sodium Chloride (NaCl) removal performance.

### **1.4 Scope of Study**

In order to achieve the research objective, the scopes have been identified as follows:

- i. Production and characterization (flux and permeability) of thin film NF composite by interfacial polymerization method using 2% w/v of triethanolamine (TEOA) as monomer at different reaction time (15, 25 and 35 min).
- ii. Performance of salt, Sodium Chloride, NaCl removal.
- iii. Removal of NOM by the synthesized NF membrane.



## **1.5 Significance of Study**

The purpose of this research is to identify the polyester nanofiltration membrane which suitable for removal natural organic matter. If the NOM completely can be removed by this filtration method, the wastewater discharged could be minimized and reducing impact on environment. In addition can produce clean water when NOM removal completed which can be use for other application in daily days. The NF process becomes more important in water treatment for domestic and industrial water supply.

## **CHAPTER 2**

### **LITERATURE REVIEW**

#### **2.1 Introduction**

Water is the important sources for agriculture, industry, recreation, energy production, and domestic consumption. Therefore, it is important to improve the effectiveness and efficiency of water purification technology to produce clean water and protect the environment (Jeong *et.al*, 2007). This chapter will describe detail about the basic concept of membrane, types of membrane that usually used in industries, nanofiltration membrane, interfacial polymerization process and also information about natural organic matter (NOM) which present as humic acid.

## **2.2 Membrane Review**

### **2.2.1 Definition of Membrane**

The word of membrane is come from the Latin word *membrane* which means skin (Nath, 2008). According to Geankoplis (2003), membrane act as a semipermeable barrier and separation occurs by the membrane controlling the rate of movement of various molecules between two liquid phases, two gases phases or a liquid and a gas phase. Membrane is defined as a thin layer of material which acts as a semipermeable barrier that allows some particles to pass through it, while hindering the permeation of others components (Silva, 2007).

From the Soni *et.al*, (2009), membrane can be defined as a barrier which can separates two phases and limits the transport of various chemicals components to pass through that membrane. According to Nath (2008), membrane is defined as a structure having lateral dimensions much greater than its thickness that mass transfer occur under variety of driving forces. Also membrane can be homogeneous or heterogeneous, symmetric or asymmetric in structure, solid or liquid and carry a positive or negative charge.

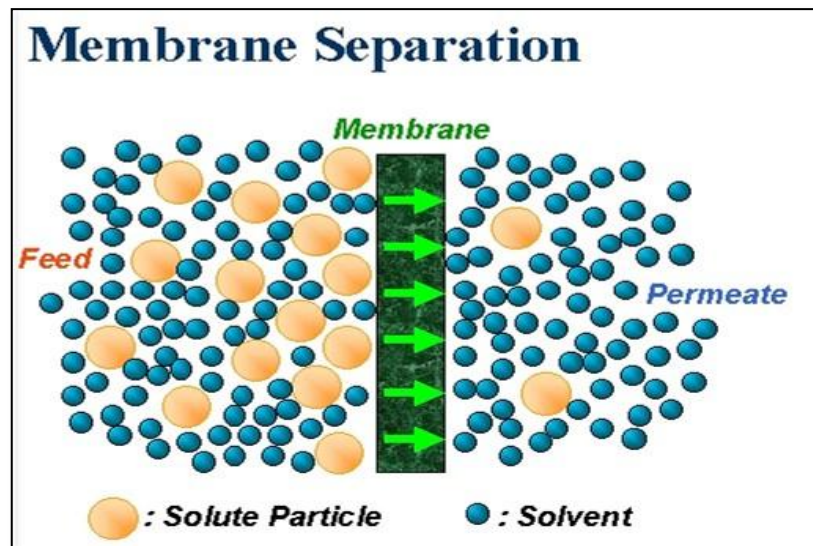
### 2.2.2 Historical Development of Membranes

The first studied of membrane was traced on eighteenth century philosopher scientist. The first recorded study of membrane was on 1748 by Abbé Nollet. He discovered quite accidentally that when a pig's bladder was brought in contact on one side with a water-ethanol mixture and the other side with pure water, the latter would pass preferentially. Nollet is the first recognize the relation between a semipermeable membrane, osmotic pressure and volume flux (Strathmann, 2000). According Baker (2004), the measurements of solution osmotic pressure made with membranes by Traube and Pfeffer were used by Van't Hoff in 1887 to develop the behaviour of ideal dilute solutions that work directly to the Van't Hoff equation. In 1907, Bechhold developed a technique to prepare nitrocellulose membranes for controlling the membrane pore size which he was determined by bubble test. Membranes first application in the testing of drinking water supply in Germany and elsewhere in Europe had broken down due to air raids at the end World War II. It is the first microfiltration membrane producer by Millipore Corporation (Nath, 2008). In 1944, Kolff was developed the artificial kidney as one of the first practical application of dialysis (Lee, 2009). In 1960, the modern membranes science was developed but membranes were used only in few laboratory and small industrial. And in 1980, microfiltration, ultrafiltration, reverse osmosis and electro dialysis were established process in large plant worldwide (Baker, 2004).

## 2.3 Concept of Membrane Process

### 2.3.1 Membrane Separation Process

Separation process is a process to transform a given mixture of chemicals into two or more composition end-use products. A membrane separation process is to separate an influent stream into two effluent streams known as permeate and retentate with the help of a membrane (Soni *et.al*, 2009). Figure 2.1 shows the basic membrane separation process:



**Figure 2.1** Basic Concept of Membrane Separation Process

According Nath (2008), porous membrane discriminate according to the size particles or molecules while non- porous membrane discriminate according to the chemical affinities between components and membrane materials. Membrane sharply can be change the rates of mass transfer because physical and chemical interactions between the membranes and separating components. The flux membrane depends on the membrane permeability and driving force of membrane as shown in Equation 2.1:

$$\text{Flux} = \frac{\text{Membrane Permeability} \times \text{Driving Force}}{\text{Membrane thickness}} \quad (2.1)$$

### **2.3.2 Classification of Membrane Separation Process**

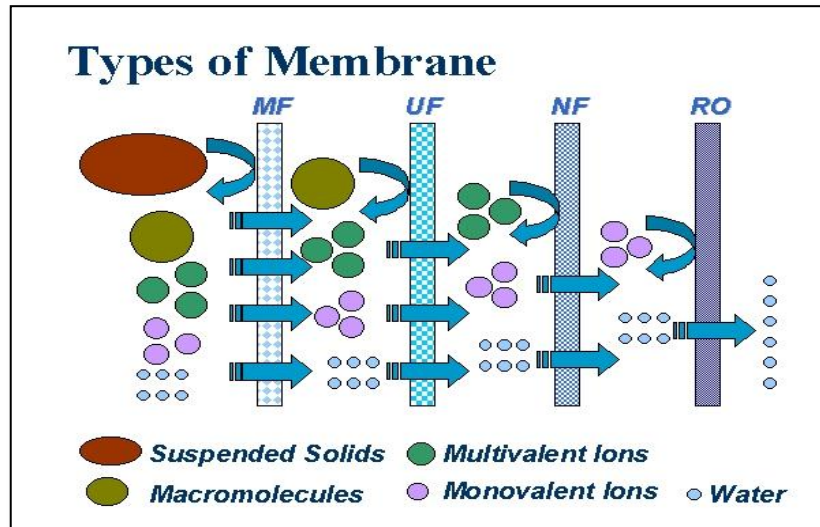
There are various types of membrane separation process. The processes in membrane can be classified according to the driving forces that involve in the process as shown in Table 2.1. Usually the most relevant processes is the pressure driven process such as reverse osmosis, ultrafiltration, microfiltration, pervaporation and gas separation (Nath, 2008). According Zularisam *et.al.* (2005) states that membrane filtration processes including microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF) have increased rapidly day by day especially in the water production.

**Table 2.1** Classification of Membrane Process according Driving Force  
(Sources: Nath, 2008)

Driving Force	Membrane Process
Pressure Driven	Reverse Osmosis (RO)
	Microfiltration (MF)
	Ultrafiltration (UF)
	Nanofiltration (NF)
	Pervaporation
	Membrane gas separation
Concentration Gradient Driven	Dialysis
	Membrane Extraction
Electrical Potential Driven	Electro dialysis (ED)
Temperature Different	Thermo Osmosis
	Membrane Distillation

### 2.3.3 Types of Membrane in Pressure Driven

There are various types of membrane based on the driving force which is applied to accomplish the separation process such as reverse osmosis, nanofiltration, ultrafiltration and microfiltration. However, all these membrane can be differentiated according to the size range of particles or solutes that are separated as shown in Figure 2.2. These processes are appropriate to different size of molecules where the microfiltration differentiates the largest size of molecules and reverse osmosis differentiating the smallest molecules that can pass through the membrane (Silva, 2007).



**Figure 2.2** Types of Membrane Separation Process

### 2.3.3.1 Microfiltration

Microfiltration is a filtration process which use porous membranes to separate suspended particles with diameters between 0.1 and 10  $\mu\text{m}$  and pressure below 2 bars. Thus, microfiltration membrane can categorize between ultrafiltration membranes and conventional filters (Baker, 2004). According to the Strathmann (2000), microfiltration membranes are used to separate macro molecule components or particles mostly in aqueous solution. Another concept of microfiltration is to remove particulate contaminants such as clay, algae and bacteria from drinking water (Haack *et.al*, 2002). Microfiltration is not suitable for removal of dissolved contaminants such as natural organic matter (NOM) (Taylor, 1996). Nath states that, a microfiltration membrane is generally porous that enough to pass molecules through the solution even if the large particles.