

**EFFECT OF TANNIC ACID-TRIMESOYL  
CHLORIDE ON THIN FILM COMPOSITE  
MEMBRANE**

**RIZA ASMA'A BINTI SAARI**

**UNIVERSITI SAINS MALAYSIA**

**2018**

**EFFECT OF TANNIC ACID-TRIMESOYL CHLORIDE ON THIN FILM  
COMPOSITE MEMBRANE**

**by**

**RIZA ASMA'A BINTI SAARI**

**Thesis submitted in fulfillment of the  
requirements for the degree of  
Master of Science**

**July 2018**



## ACKNOWLEDGEMENT

First of all, I would like to gratitude my praised towards our creator, Allah S.W.T for giving me strength, a peace mind and well-health during completion of the thesis. Alhamdulillah, I had able to complete my short thesis entitle, “Effect of Tanic acid-trimesoyl chloride on thin film composite membrane”. Although I had undergone many obstacles and queries throughout the completion, I am so glad that my project and report were carried out and conducted smoothly and successfully.

I would like to express my deepest appreciation to all those who provided me the possibility to complete my thesis. A special gratitude I give to my supervisor, Prof Abdul Latif Ahmad for giving me his continuous support, encouragement and helped me to coordinate my final year project especially in thesis writing. I would also love to acknowledge with much appreciation to my beloved parent, Mr.Saari Bin Mat Husin and Mrs.Hasnah Binti Ibrahim for their aspiring guidance, support, motivation and thoughtful advice during completing my lab work.

In the meantime, I would like to acknowledge my research fellows and friends for their cooperation and being supportive all this while. Last but not least, I also would like to thank technicians and staffs of School of Chemical Engineering, Universiti Sains Malaysia (USM) for their guidance, cooperation and assistance throughout the research.

## TABLE OF CONTENTS

	<b>Page</b>
<b>ACKNOWLEDGEMENT</b>	ii
<b>TABLE OF CONTENTS</b>	iii
<b>LIST OF TABLES</b>	viii
<b>LIST OF FIGURES</b>	ix
<b>LIST OF ABBREVIATIONS</b>	xii
<b>LIST OF SYMBOLS</b>	xiv
<b>ABSTRAK</b>	xv
<b>ABSTRACT</b>	xvii
<b>CHAPTER ONE : INTRODUCTION</b>	
1.1 Protein separation	1
1.2 Membrane separation process	1
1.3 Thin film composite membrane	3
1.4 Problem statement	5
1.5 Objectives of the study	8
1.6 Scopes of the study	8
1.7 Organization of the thesis	12
<b>CHAPTER TWO : LITERATURE REVIEW</b>	
2.1 Overview of membrane technology	14
2.2 Membrane classification	15
2.3 Types of feed flow	16

2.3.1	Dead end flow	17
2.3.2	Cross flow	18
2.4	Membrane separation process	19
2.4.1	Ultrafiltration (UF)	20
2.4.2	Factor affecting retentivity of UF membranes	22
2.5	Protein application	24
2.5.1	Bovine serum albumin (BSA)	25
2.5.2	Lysozyme	25
2.6	Development of Porous Support	26
2.6.1	Polymeric materials for ultrafiltration membrane	27
2.6.2	PES based membrane	27
2.6.3	Polymeric Additives	29
2.6.4	PES-NMP blend ultrafiltration	35
2.7	Surfactant	36
2.7.1	Anionic surfactant	37
2.7.2	Non-ionic surfactant	38
2.7.3	Membrane based surfactant	39
2.8	Development of active skin layer	39
2.8.1	Selection of monomer	41

### **CHAPTER THREE : MATERIALS AND METHODS**

3.1	Materials and chemicals	44
3.1.1	Chemicals	45
3.2	Membrane synthesis	46
3.2.1	Flowchart of the overall experimental work	46

3.2.2	Synthesis of ultrafiltration thin film composite membrane	48
3.3	Preparation of thin film composite membrane	50
3.3.1	Preparation of TFC membrane based on flat sheet membrane: Preliminary study	51
3.4	Parameter	52
3.4.1	Different reaction time	52
3.4.2	pH feed solution	52
3.4.3	Membrane point zero charge solution	53
3.5	Characterization of thin film composite membrane	53
3.5.1	Attenuated Total Reflectance-Fourier Transmitted (ATR-FTIR)	53
3.5.2	Scanning Electron Microscopy (SEM)	54
3.5.3	Atomic Force Microscopy (AFM)	55
3.5.4	Contact Angle (CA)	55
3.5.5	Membrane Pore Size	55
3.6	Performance evaluation of thin film composite membrane	56
3.6.1	Preparation of bovine serum albumin (BSA) and lysozyme buffer solution	56
3.6.2	Permeation system	57
3.6.3	Membrane permeation test for thin film composite ultrafiltration membrane	59
3.7	Membrane fouling analysis	60

## CHAPTER 4: RESULT AND DISCUSSION

4.1	Introduction	62
4.2	Pure water permeability	62
4.2.1	Performance of protein separation	65
4.3	Effect of tannic acid-trimesoyl chloride content on thin film composite membrane properties and performances	68
4.3.1	Effect of tannic acid-trimesoyl chloride (TA-TMC) on water permeability	69
4.3.2	Effect of tannic acid-trimesoyl chloride (TA-TMC) on protein rejection	76
4.4	Effect of post treatment reaction time on protein rejection	78
4.5	Effect of feed pH on membrane performance	82
4.5.1	Membrane point zero charge measurements	83
4.5.2	The influence of feed pH on permeate flux	85
4.5.3	The influence of feed pH on the rejection of BSA and lysozyme	87
4.6	Membrane fouling analysis	89
4.7	Molecular Orientation, Morphological and Physically Study	92
4.7.1	Molecular orientation study by using attenuated total reflectance-fourier transmitted infra-red (ATR-FTIR)	92
4.7.2	Morphological study by scanning electron microscopy (SEM)	97
4.7.3	Surface roughness analysis by atomic force microscopy (AFM)	101
4.7.4	Wettability analysis by contact angle (CA)	104

4.7.5	Membrane pore size measurement	106
-------	--------------------------------	-----

## **CHAPTER 5: CONCLUSION AND RECOMMENDATION**

5.1	Conclusion	108
-----	------------	-----

5.2	Recommendations	109
-----	-----------------	-----

	<b>REFERENCES</b>	<b>111</b>
--	-------------------	------------

## **APPENDICES**

Appendix A : Preparation of stock buffer solution

Appendix B: Standard curve of BSA and lysozyme

Appendix C: Calculation for water permeation equation

Appendix D: Calculation for protein rejection equation

Appendix E: Calculation for membrane fouling analysis

## **LIST OF PUBLICATION**

## LIST OF TABLES

		<b>Page</b>
Table 2.1	Overview of previous studies on the effect of additives on membrane properties	31
Table 3.1	Materials and chemicals used in the study	45
Table 3.2	Composition of casting solutions	49
Table 3.3	Tannic Acid and TMC Composite Ultrafiltration Membranes Prepared at Different Monomer Concentrations	51
Table 4.1	Pure water permeability for compaction test on the membrane	63
Table 4.2	Permeability of TFC membrane with different TA-TMC composition	69
Table 4.3	The root mean square roughness (Rq) for various type of membrane synthesized	103
Table 4.4	Contact angles value of PES support and TFC membrane with different TA-TMC composition	104

## LIST OF FIGURES

		<b>Page</b>
Figure 1.1	The schematic representation of the preparation of TFC membrane prepared via interfacial polymerization	5
Figure 2.1	Membrane based separation process	15
Figure 2.2	Schematic of dead-end flow through the membrane	17
Figure 2.3	Schematic of Cross Flow through the membrane	18
Figure 2.4	Membrane separation process	20
Figure 2.5	Illustration on ultrafiltration membrane process	21
Figure 2.6	Structure of surfactant	36
Figure 3.1	Flow chart of the experimental works	47
Figure 3.2	The schematic diagram of the dead-end filtration unit: nitrogen tank, pressure regulator, control valve, gauge, flat sheet membrane dead-end filtration, digital balance, computer	58
Figure 3.3	The schematic diagram of the dead-end filtration unit: nitrogen tank, pressure regulator, control valve, gauge, flat sheet membrane dead-end filtration, digital balance, computer Dead-end filtration setup for flat sheet membranes	58
Figure 4.1	PWP of PES composite membrane at different operating pressures	64
Figure 4.2	Effect of polymer concentration on PWP of the PES composite membrane at operating pressure of 200 kPa	65
Figure 4.3	Proteins permeation flux with different polymer concentration	66
Figure 4.4	Proteins rejection of PES composite membrane with different polymer concentration	67
Figure 4.5	The variation of Tannic acid-TMC composition with pure water flux	70

Figure 4.6	The chemical structure of (a) Tannic acid and (b) Trimesoyl chloride (TMC)	72
Figure 4.7	The variation of Tannic acid-TMC composition with permeate flux of proteins (BSA and Lysozyme)	74
Figure 4.8	The variation of Tannic acid-TMC composition with protein rejection (BSA and Lysozyme)	77
Figure 4.9	Effect of Tannic acid reaction time on the performance of composite membrane for BSA (The concentration of Tannic acid-TMC were fixed at 0.5g/L and 0.3g/L in solution; reaction time for TMC were fixed for 3 min)	79
Figure 4.10	Effect of TMC reaction time on the performance of composite membrane for BSA (The concentration of Tannic acid-TMC were fixed at 0.5g/L and 0.3g/L in solution; reaction time for Tannic acid were fixed for 10 min)	80
Figure 4.11	Effect of Tannic acid reaction time on the performance of composite membrane for Lysozyme (The concentration of Tannic acid-TMC were fixed at 0.5g/L and 0.3g/L in solution; reaction time for TMC were fixed for 3 min)	81
Figure 4.12	Effect of TMC reaction time on the performance of composite membrane for Lysozyme (The concentration of Tannic acid-TMC were fixed at 0.5g/L and 0.3g/L in solution; reaction time for Tannic acid were fixed for 10 min)	82
Figure 4.13	Plot of the variation in $\Delta \text{pH} = \text{pH}_f - \text{pH}_0$ vs. $\text{pH}_0$ in various pH solution for point zero charge (PZC)	84
Figure 4.14	Effect of feed pH on permeates flux during rejection of BSA and Lysozyme	86
Figure 4.15	Effect of feed solution's pH on protein rejection	87
Figure 4.16	Relative flux reduction, RFR (%) for the membrane fouling analysis on the membranes	90
Figure 4.17	Flux recovery ration, FRR (%) for the membrane fouling analysis on the membranes	91

Figure 4.18	FTIR spectrum of tannic acid (TA), PES substrate (#UF1) and TA-TMC composite ultrafiltration membrane	93
Figure 4.19	FTIR spectrum for various concentrations of Tannic acid-TMC composite ultrafiltration membrane	95
Figure 4.20	IR spectra of Tannic acid-TMC composite ultrafiltration membrane	97
Figure 4.21 (a)	Surface and cross-sectional morphology of TFC ultrafiltration membrane, (a) & (b) neat membrane UF1, (c) & (d) UF2, (e) & (f) UF4	99
Figure 4.21 (b)	Surface and cross-sectional morphology of TFC ultrafiltration membrane, (g) & (h) UF6, (i) & (j) UF8, (k) & (l) UF10	100
Figure 4.22	AFM Topography 3D-Image Comparison of PES substrate (a), and TFC membrane UF2 (b), UF6 (c), UF10 (d)	103
Figure 4.23	Water contact angle on surface of membrane, PES support membrane UF1 (a), UF2 (b), UF4 (c), UF6 (d), UF8 (e), UF10 (f)	105
Figure 4.24	Pore size measurement	106

## LIST OF ABBREVIATIONS

AFM	Atomic force microscope
ATR-FTIR	Attenuated total reflection infrared
BOD	Biological oxygen demand
BSA	Bovine serum albumin
CA	Contact angle analyzer
COD	Chemical oxygen demand
DMAc	Dimethylacetamide
DMP	Dimethyl phthalate
GA	Glutaraldehyde
HPE	Hydroxyl-ended hyperbranched polyester
HPEI	Hyperbranched polyethyleneimine
IP	Interfacial polymerization
IPC	Isophthaloyl chloride
MF	Microfiltration
MPD	Metaphenylene diamine
NF	Nanofiltration
NMP	N-methyl-2-pyrrolidone
PAN	Poly(acrylonitrile)
PEG	Polyethylene glycol
PES	Polyethersulfone
PSF	Polysulfone
PVAm	Polyvinylamine
PVDF	Polyvinylidene fluoride

RC	Regenerated cellulose
RO	Reverse osmosis
SDS	Sodium dodecyl sulphate
SEM	Scanning electron microscope
TEOA	Triethanolamine
TFC	Thin film composite
TMC	Trimesoyl chloride
UF	Ultrafiltration
UV-Vis	Ultra-violet spectrophotometer

## LIST OF SYMBOLS

MWCO	Molecular weight cut off
MW	Molecular weight
wt%	Weight percentage
rpm	Revolutions per minute
M	Molarity
R%	Percentage rejection
PWP	Pure water permeation ( $\text{Lm}^{-2}\text{h}^{-1}$ )
PWF	Pure water flux ( $\text{Lm}^{-2}\text{h}^{-1}$ )
A	Membrane area ( $\text{cm}^2$ )
$J_v$	Permeate flux of aqueous solution or pure water flux ( $\text{Lm}^{-2}\text{h}^{-1}$ )
$J_{w2}$	Water flux of clean membrane ( $\text{Lm}^{-2}\text{h}^{-1}$ )
V	Volume permeate collected (mL)
$C_p$	Concentration of permeate
$C_f$	Concentration of feed

# **KESAN ASID TANNIK-TRIMESOIL KLORIDA PADA KEPINGAN NIPIS FILEM KOMPOSIT MEMBRAN**

## **ABSTRAK**

Membran komposit filem nipis telah disediakan melalui proses sintesis antara larutan asid tannik dalam fasa cecair dan trimesoil klorida dalam fasa organik. Hasil kajian daripada penyelidik sebelum ini seperti Zhang et., al (2013) dan Tang et., al (20008) menunjukkan isu pengotoran dan kestabilan khususnya pada membran UF ketika proses penurasan protein. Oleh itu, teknik pempolimeran antara lapisan muka (IP) telah digunakan untuk mengkaji hubungan diantara kesan asid tannik dan trimesoil klorida terhadap prestasi rintangan kadar pencemaran, hidrofilik dan sifat pemisahan air pada membran komposit filem nipis. Fungsi asid tannik dan trimesoil klorida (TA-TMC) dengan tahap kepekatan berbeza pada sifat-sifat membran seperti ikatan kimia, morfologi, kekasaran permukaan, sifat hidrofilik dan prestasi ketelepan air serta penolakan protein (Albumin serum bovin dan Lisozim) juga turut dikaji. Keputusan menunjukkan bahawa peningkatan kepekatan asid tannik dan trimesoil klorida semasa proses pempolimeran antara muka dapat mengurangkan kekasaran permukaan dan mengurangkan kerosakan pada permukaan membran komposit akibat tindak balas pempolimeran yang berlebihan. Selain itu, pembentukan lapisan poliester juga didapati boleh mempengaruhi tahap sifat hidrofilik, tahap kadar pencemaran dan ujian prestasi membran. Secara keseluruhannya, keputusan prestasi terbaik keseluruhan telah dicapai menggunakan membran komposit yang dihasilkan dengan kadar kepekatan 0.5 g/L asid tannik dan 0.3g/L trimesoil klorida yang seterusnya membawa kepada fluks air tulen sebanyak 114.16 Lm<sup>-2</sup>h<sup>-1</sup> serta

penolakan BSA dan Lisozim masing-masing sebanyak 98% dan 94%. Dalam kajian ini, kesan kepekatan asid tannik dan trimesoil klorida (TA-TMC) pada sifat hidrofilik membran dikaji. Proses pempolimeran semakin meningkat ekoran daripada peningkatan kepekatan asid tannik dan trimesoil klorida (TA-TMC) yang seterusnya menghasilkan nilai hidrofilik dengan lebih baik iaitu  $29.7^0$  serta memberi penambahbaikan pada kekasaran lapisan dengan struktur yang lebih sekata dari 73.96 nm kepada 30.07 nm. Penggunaan kepekatan asid tannik dan trimesoil klorida (TA-TMC) yang berbeza juga memberi kesan kepada kadar tindak balas yang berlaku pada permukaan membran seterusnya menyumbang kepada pembentukan kumpulan ester dan regangan O-H yang dapat diperhatikan dengan lebih jelas apabila kepekatan asid tannik dan trimesoil klorida (TA-TMC) meningkat.

# **EFFECT OF TANNIC ACID-TRIMESOYL CHLORIDE ON THIN FILM COMPOSITE MEMBRANE**

## **ABSTRACT**

A thin film composite membrane was prepared by synthesized the reacting tannic acid aqueous solution and trimesoyl chloride in organic phase. Previous research shows that fouling and stability issue on the UF membrane particularly during filtration of protein. Therefore, interfacial polymerization (IP) technique was employed to investigate the effect of tannic acid and trimesoyl chloride on the performances of anti-fouling resistance, hydrophilicity and permeation properties of thin film composite membrane. The role of tannic acid and trimesoyl chloride (TA-TMC) with various concentrations on membrane properties such as chemical bonding properties, morphology, surface roughness, hydrophilicity, and performance in term of water permeability and protein rejection (Bovine serum albumin and Lysozyme) were investigated, respectively. The results revealed that the increasing on the concentration of monomer during interfacial polymerization process could reduce the surface roughness and reduce the defect on the surface of composite membrane due to the intense polymerization reaction. Furthermore, the formation of polyester selective skin layer was also found to influence the hydrophilicity, fouling property and membrane performances tests. The best overall performance result were achieved with composite membrane produced by 0.5 g/L tannic acid and 0.3 g/L trimesoyl chloride leading to a pure water flux of  $114.16 \text{ Lm}^{-2}\text{h}^{-1}$  and, BSA and Lysozyme rejection of 98 % and 94%, respectively. The effect of tannic acid and trimesoyl chloride (TA-TMC) on hydrophilicity of membrane is studied as well.

Further polymerization process with increasing the tannic acid concentration (TA) improved the hydrophilicity to  $29.7^{\circ}$  and improved the roughness of layer with a more uniform structure from 73.96 nm to 30.07 nm. Different concentration of monomers (tannic acid and TMC) used also affect the different rates of cross-linking occurred on the surface of membrane that contribute towards the formation peak of ester group and O-H stretch which more clearly observed as the concentration of tannic acid and trimesoyl chloride (TA-TMC) increased.

## **CHAPTER ONE**

### **INTRODUCTION**

#### **1.1 Protein Separation**

The rapid growth in the field of biotechnology has led to an increase in the demand for efficient, large-scale protein separation processes. Techniques used in research laboratories for protein separation, examples chromatography, electrophoresis, and affinity purification are excellent for small quantities of protein. Indeed, there are countless studies describing protein separation methods which can yield from a micrograms to a hundred milligrams of protein products. Besides that, the process are very difficult to scale-up, which limits protein separation process (Ghosh and Cui, 2000). Ghosh and Cui (2000) claimed that in term of scale-up problems, techniques such as chromatography and electrophoresis require complex instrumentation support to run efficiently and extremely high cost. For example, the high value of therapeutic proteins such as urokinase and t-PA, the separation cost can be high as 80% of the total cost of production. Hence, a separation technique which can yield a high separation at low process cost would certainly be beneficial to the biotech industry (Ghosh and Cui, 2000).

#### **1.2 Membrane Separation Process**

The issue on water quality always gain global concern due to its importance and widely used. The deterioration of water quality could be influenced by few factors such as advanced economic activities with the population which is gradually increasing, modernisation and urbanization (Kumar and Lee, 2012). Consequently, this impoverishment of water quality leads to critical water shortage. Various

solutions with the wastewater treatment technologies have been addressed to resolve the problems and attain the demand on clean water. Nevertheless, lack of existing conventional treatments is invariably retarded due to expensive cost, lack of the expertise, high maintenance, low yield, long duration of retention time, requirement of ample land, and most importantly, give a deficiency of a desirable quality on the safe discharge limits (Mohammadi *et al.*, 2010). Therefore, from the all weaknesses on the existing conventional technologies, it seems that membrane technology is a satisfactory method which can be used for wastewater application. Besides, the membrane technologies also provided better efficiencies in term of operation, cost of operating, and reduce energy consumption (Baker, 2004).

Generally, membrane processes which act as a selective barrier to control the movement of certain species in a mixture from pass through it, and the other side also retentate other species have been widely known and used in wastewater industries (Baker, 2004). It can be classified into different categories based on driving force used for filtration. In this regard, the pressure driven membrane filtration processes can be divided into four types known as ultrafiltration (UF) process, nanofiltration (NF) process, microfiltration (MF) process, and reverse osmosis (RO). Despite that, all these processes have gained more demand due to its advantages in term of minimal maintenance, operating pressure, energy consumption and high efficiency as well as ease of operation (Chen *et al.*, 2011). Nowadays, one of the most efficient processes which is consistently good in quality or performance, either domestic or industries is ultrafiltration (UF) processes. In addition to that, advanced development of UF membrane on the application of wastewater treatment

can be related to the higher demand from global due to the water shortage and environmental that becomes tougher.

Currently, UF has been widely applied as the most suitable low-pressure driven membrane process for various wastewater treatments. However, the details understanding on the required membrane properties for industry effluent application is significantly important in conjunction with attaining the optimized selectivity and exhibit a better performance to reduce fouling. In this scope of study, thin film composite ultrafiltration membranes were prepared. Tannic acid and Trimesoyl Chloride (TMC) which is one of the natural acid was used to undergo interfacial polymerization (IP) process. Even though there are only few studies were reported on the fundamental and practicality, yet selection of materials for the development of UF membrane with a vital role to reduce fouling resistance with a good hydrophilicity and separation performance is still inadequate.

### **1.3 Thin Film Composite Membrane**

Thin film composite (TFC) with interfacial polymerisation concept (IP) was introduced and established by Morgan in 1965 (Morgan & Kwolek, 1996). This IP then become an established method in the making of a barrier layer for macroporous substrate in TFC membrane synthesis. Cross-linking of aqueous and organic compound can also be performed using IP. The membrane with ultra-thin barrier layer has no definite structure; it can be built in any form as long as its permeability can give the best separation.

The most outstanding feature for thin film composite (TFC) membrane is the two main layers can be altered and tailor-made based on the specific characteristic required to achieve a higher flux, selectivity without neglecting the stability of operation in various ranges of temperature and resistance exerted during the process (Jeong et al., 2007). There are various approaches to fabricate TFC membranes, such as phase inversion, dip-coating, graft polymerization and interfacial polymerization (IP) (Li et al., 2013; Homayoonfal et al., 2010; Van der Bruggen, 2009). Among the aforementioned techniques, the interfacial polymerization is mostly investigated and employed to produce thin film composite membrane (Khorshidi et al., 2016; Ismail et al., 2015). Importantly, besides performed with higher water flux and higher solute rejection, the prepared membrane should also be considered for a few parameters such as chemically and mechanically stable for a long-term operation when high pressure is applied. Recently, TFC membrane with interfacial polymerization (IP) modification has gained more demand and attention due to their functional method that is able to produce an excellent properties of selectivity and fouling resistance by modifying the polymer membranes itself (Otitoju et al., 2016; Arribas et al., 2014).

This method was considered as one of the applicable methods in the membrane technology as the reaction occurs by self-inhibiting through the supply of monomers in aqueous and organic phase, which is very practical and accessible. Meanwhile, a thin film layer within 50 nm range can be produced through this method. The comprehensive on water permeability, solute rejection and performance efficiency of the membranes can influence the formation of this thin active layer (Mohammad et al., 2015). The modification was done with the purpose to minimize the defect formed on the film. Some researchers use the interfacial polymerization