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

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**by**

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# 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 ($Lm^{-2}h^{-1}$) |
| PWF | Pure water flux ($Lm^{-2}h^{-1}$) |
| A | Membrane area ($cm^2$) |
| $J_V$ | Permeate flux of aqueous solution or pure water flux ($Lm^{-2}h^{-1}$) |
| $J_{w2}$ | Water flux of clean membrane ($Lm^{-2}h^{-1}$) |
| 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 daripda 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 kesuluruhannya, 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 $Lm^{-2}$h-1 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 daripda peningkatan kepekatan asid tannik dan trimesoil klorida (TA-TMC) yang seterusnya menghasilkan nilai hydrofilik 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.

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**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 $Lm^{-2}h^{-1}$ 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 $29.7^0$ 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