

DEVELOPMENT OF POLYSULFONE /SILVER OXIDE MEMBRANES FOR
SEPARATION OF NATURAL ORGANIC MATTERS

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ABSTRACT

In this present work, the development of polysulfone (PSf)/silver oxide membrane was conducted with the used of silver oxide as hydrophilic additives, polyethylene glycol (PEG) as pore forming agent and 2,4,6-triaminopyrimidine (TAP) as a compatibilizer for separation natural organic matters (NOM). The PSf/silver oxide membranes were characterized based on their contact angle, thermal behaviour, tensile strength and morphology. The results were correlated with membrane performance for NOM separation. The NOM samples used in this study were collected from Sembrong river water in Parit Raja, Johor, Malaysia. The addition of silver oxide was found to increase membrane hydrophilicity and improved water permeability up to 323 liter per meter hour (LMH) for 1.5 wt. % silver oxide content. Silver oxide also has improved membrane antifouling properties. The effect of PEG as a pore forming agent in PSf/silver oxide membrane was investigated by manipulating PEG content from 8 wt. % to 16 wt. % at fixed concentration of PSf, silver oxide and TAP. It was observed that high PEG concentration improved the water permeation properties of the membrane. Tensile strength increment, silver oxide aggregation reduction, low silver loss during immersion and permeation confirmed that TAP had successfully enhanced compatibility between PSf and silver oxide. TAP has also improved rejection and antifouling of the membrane against NOM. The entrapment of silver oxide in PSf membrane was proved using Fourier transform infrared (FTIR) and X-ray diffraction (XRD). However, TAP was found to decrease membrane permeability. Therefore, the optimization of membrane formulation was carried out using response surface methodology (RSM), wherein the main responses were pure water flux and NOM rejection. The optimum amount of each component for membrane fabrication was found to be 10.58 wt. % PEG, 2.0 wt. % silver oxide and 0.3 wt. % TAP. The average confirmation run of experimental results for this optimum formulation was 356 LMH permeation and 94.38 % rejection, which was only 5.90 % and 1.48 % off respectively from predicted results.

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CHAPTER 1

INTRODUCTION

1.1 Research background

Natural organic matters (NOM) are one of the major pollutants in acid and low turbidity water sources. In Malaysia, most of water sources are contaminated with NOM, especially from peat soil. Natural organic matters such as humic acid and fulvic acid contribute to changes in the natural colour of water (from brown to black) and can reduce visibility if the dissolved organic carbon (DOC) is more than 5 mg/L. Therefore, the removal of NOM is usually known as colour removal. According to Thurman and Malcomlm [1], average surface water contains about 45% fulvic acid, 5% humic acid, 25% low molecular weight acid, 5% neutral compound, 5% bases and 5% contaminants. Although these compounds are relatively harmless, they can still lead to the formation of potentially carcinogenic disinfection byproducts, such as trihalomethanes, which form during the disinfection process [2,3]. In order to overcome these problem, ultrafiltration (UF) membrane is one of the approaches that has been highlighted in many articles due to its compactness, easy automation and high removal rate of NOM [4].

In preparation UF membrane, the most widely used polymer is polysulfone (PSf). PSf is known for its resistance in extreme pH conditions and high thermal stability [5]. However, one of the major problems of PSf is its hydrophobic character, which prevents spontaneous wetting in aqueous media. This hydrophobic

characteristic often results severe membrane fouling and decline membrane permeability.

Membrane fouling by proteins, NOM and other biomolecule adsorption reduces the membrane flux and prevents the wide scale application of UF membranes [6]. The current technique to counteract this problem is to clean the membrane with aggressive chemicals, such as hypochlorite, nitric acid, sodium hydroxide and oxalic acid at extreme pH [7,8]. However, these chemicals can only remove the adsorbed foulants. Therefore, after a period of time when the cleaning method becomes ineffective, the membrane must be replaced. Fouling is described as pore-blocking, solute aggregation or the adsorption phenomenon on membrane surface. Membrane fouling can be caused by surface characteristics, concentration polarisation, cake layer formation, foulant properties and, water chemistry [6,9,10]. Among all these causes, membrane surface is the most crucial. Thus, in order to produce membranes with high antifouling properties, membrane surface improvement was progressively being investigated in order to obtain high hydrophilicity and stable in extreme environment [11–13].

Membranes with good rejection and water permeability are usually prepared by combining suitable additives with an efficient method. Various types of additive, such as polymer, salts, non-solvents and inorganic particles, were incorporated using a variety of methods to improve membrane properties [14–19]. Typically, low molecular weight polymers are used as an additive to enhance membrane pores. Polyvinyl pyrrolidone (PVP) and polyethylene glycol (PEG) are the most common additives used in membrane formulation [20–22]. Investigation of PEG as an additive has attracted many researchers due to the ability of PEG to dissolve in water and organic solvents, its low toxicity and low costs [23–25]. Ma *et al.* have studied the effects of PEG in PSf membrane and found that PEG improved membrane hydrophilicity, porosity and water permeability [24]. The addition of PEG can also reduce the thermodynamic stability of dope formulation, which then leads to finger-like formation in the membrane structure [23].

The incorporation of inorganic particles in membrane matrix has been useful in the improvement of membrane performance. There are many inorganic particles which have been used to prepare polymeric membranes such as silver [26], alumina (Al_2O_3), titania (TiO_2) [27], zirconia (ZrO_2) [28] and, silica (SiO_2) [29]. Among

these materials, silver were one of the first inorganic additives that gained attention for membrane fabrication. It was found that incorporation of silver in polymer membranes could not only improve surface hydrophilicity, but also provide antibacterial properties. The toxicity of silver to bacteria is reported as due to interactions between ionic silver with thiol groups and formation of disulphide silver bonds which can destroys bacteria cells and dimerize their DNA. It also damage cytochrome-b of bacteria, which is used by bacteria for the replication process [30].

The addition of silver nanoparticles to the membrane using an in-situ synthesis method in dope solution has gained much interest. The synthesis of silver is easily accomplished using reduction agents such as PVP or dimethylformamide (DMF) [21,31]. Precursors, such as silver nitrate, are usually selected due to their ability to dissolve in solvents, such as N-methyl-2-pyrrolidone (NMP) or dimethylacetamide (DMAC). However, the problem with this method is that silver tends to leach out easily due to high interactions between the solvents and silver. Silver also tends to diffuse during phase inversion process [21]. Furthermore, the behaviour of nitrate ions in dope solution has still not yet been discovered.

The influence of silver nanoparticle sizes in the membrane was reported by Mollahoseini *et al.* [32]. The hydrophilic and antibacterial properties of the membrane were increased as the particle size of silver was reduced. Silver with smaller particle sizes provided large surface areas and high distributions in the membrane. They also reported that smaller silver particles enhanced membrane permeability and rejection properties.

The hydrophilic silver also improved membrane antifouling properties as reported by Zodrow *et al.* [33]. They applied the natural toxicity of silver to reduce bio-film formation on the membrane surface. The membrane has also demonstrated excellent rejection properties by completely removing 5×10^5 CFU/mL bacteriophage MS2 virus in water. The improvement of the anti-biofouling properties of the membrane was investigated by Koseoglu-Imer *et al.* [34]. They found that membrane fouling reduced as silver content increased due to the hydrophilic characteristic of silver in the PSf membrane. This hydrophilic characteristic was able to repel foulants' hydrophobic charges. Thus, the number of adsorption molecules on the membrane surface was reduced.

As far as this study is concerned, the investigations on the effect of silver oxide on the performance of membranes for NOM removal and fouling mitigation have rarely been studied. According to Yang *et al.* silver oxide has better hydrophilicity and antibacterial properties as compared to metallic silver. This is due silver oxide has higher valency state as compared to silver [35]. Hence it is expected that addition silver oxide in membrane can improve membrane hydrophilicity, rejection and antifouling properties. Therefore, in this work, the separation properties and fouling behaviour of PSf membrane with silver oxide as a hydrophilic additive, PEG as a pore forming agent and TAP as a compatibilizer was studied by using NOM source from river water. The microstructure, thermal behaviour and strength of each effect were presented and the fouling properties of the membrane were characterized.

1.2 Problem statements

NOM removal has become a serious that needs to be solved in most water treatment industry. The increased levels of NOM and changes in the quality of the water present a major challenge to drinking water industry. Recently, membrane filtration has been identified as one of the efficient in removing NOM. This is due to NOM separation via this method do not involves any extra chemical, which can influence the final quality of water [36]. Therefore, the need to fabricate membrane for NOM separation is very important in order to produce high NOM rejection values.

Although the membrane can highly separate NOM from water, however, tendency of NOM to adsorb on membrane surface and reduce membrane permeability resulted in fouling formation has create another problem for this membrane technology. Theoretically, fouling is complex process due to mechanism of pore plugging, pore narrowing and cake formation by NOM which is a major concern in water filtration [37]. However, the actual mechanism of membrane fouling that occurs due to NOM absorption is still not well understood. Since the negative effects on performance due to fouling are basically known, thus, it is important to understand the fouling pathways through a model of the behaviour of NOM interacting with the membrane polymer surface. Fouling can be controlled by

altering the operating conditions [38–40], chemical additions [41,42] and pre-treatments [43] or surface modifications of membrane [6,44].

Membrane surface modification by addition of hydrophilic materials such as inorganic metal oxide to the hydrophobic membrane to improve hydrophilicity has been studied in a number of papers [22,45]. The results show significance fouling reduction due to hydrophilic characteristic on membrane surface, which was able to repel hydrophobic foulant. In this study silver oxide was selected as hydrophilic additive in PSf membrane due to its chemical stability and hydrophilic properties which can reduce membrane fouling. Although it is reported that addition of silver and other inorganic additives such as TiO_2 and ZrO_2 improved permeability, this permeability increment is not satisfactory to be applied for ultrafiltration membrane separation [46,47]. Furthermore, high amount of inorganic additive in membrane will result in membrane pore blocking and reduce water permeability. Therefore, the addition of pore forming agent such as PEG or PVP is important to improve composite membrane structure and enhanced water permeability. Nevertheless, the influence of pore forming agent in composite membrane is rarely being studied. It is essential to discover the influence of pore forming concentration on composite membrane performance, as excess amount of pore forming agent will result in low separation properties. Another disadvantage of incorporation inorganic particle in membrane is its low compatibility between polymer which will lead to poor distribution and mechanical strength [22]. Thus, the addition of compatibilizer is one of the solutions to enhance membrane performance. Despite the achievement of membrane modification, it is reported that the membrane still follows the trade-off between the rejection and permeability. Hence, the optimization should be conducted using optimization tools to find the optimum concentration of additives to improve membrane water permeability and separation performance.

1.3 Objectives of study

The main objective of this study is to develop a new PSf/silver oxide membrane with optimized dope formulation that can achieve better NOM separation and antifouling properties. The sub-objectives can be further divided as follows:

1. To fabricate UF PSf membrane for NOM separation using PEG as pore forming agent.
2. To investigate the effect of incorporating silver oxide towards PSf membrane performance and antifouling properties.
3. To evaluate and investigate the effect of PEG concentration towards PSf/silver oxide membrane performance and antifouling properties.
4. To investigate the effect of TAP as compatibilizer towards PSf/silver oxide membrane performance and antifouling properties.
5. To optimize the silver oxide, PEG and TAP concentration in PSf membrane in respect to membrane permeability and NOM rejection.

1.4 Research scopes

In order to achieve the above objectives, the following scopes for the work have been drawn:

1. Fabrication of UF PSf membrane was studied using PEG 400, PEG 1500 and PEG 6000.
2. The concentration of PSf used was 18 wt. % and was fixed and applied to for all formulations.
3. Manipulation of silver oxide, PEG and TAP using the following ranges: silver oxide, 0 to 2.0 wt. %; PEG, 8 to 16 wt. %; and TAP, 0 to 0.4 wt. %.
4. Flat sheet PSf membranes were prepared and characterized in terms of membrane structure, hydrophilicity, thermal behaviour, antibacterial properties and strength.
5. Membrane performance was evaluated based on water permeability and NOM rejection.
6. Humic acid and Sembrong river water was used as NOM model for membrane rejection.
7. Sembrong river water was used as NOM model to estimate membrane fouling behaviour.
8. The optimization of additives was conducted using Design Expert (v. 7) software. The responses were membrane flux and rejection properties. The

optimum value obtained via Design Expert was confirmed experimentally by using five samples.

1.5 Novelty of work and significance of study

Although many studies have been focused on the effects of additives on membranes, investigations on the effects of silver oxide, PEG and TAP in a PSf mixed matrix membrane for NOM separation is not yet being reported. Furthermore, the used of nearby area water sources from Sembrong river as NOM model was considered as the first studied in this field. Thus, the aims of this work are to study the influence of each additive towards PSf membrane and to optimise membrane performance for NOM separation. The information from this study benefits in understanding the behaviour of silver oxide, PEG and TAP to improve PSf membrane performance. The fouling characteristic of each effect will help researchers and local professionals industrial to estimate membrane performance for NOM separations.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to membrane technology and separation

Membrane filtration was first developed by Professor Sigmund from University of Göttingen in Germany in 1935. The technology of membrane was found immediately after World War II bombing in Germany due to contamination of main source water. The membrane market continues to growth after the simplest and low cost method for membrane fabrication via phase inversion was found and introduced by Loeb and Sourirajan in 1959 [5].

Nowadays membrane has become dignified for water treatment technology as compared to conventional separation technology such as sedimentation, aggregation, adsorption and coagulation. It constitutes a growing market and provides enhanced separation capabilities in a wide variety of industries. According to McIlvaine Company, sales of membranes and equipment will exceed USD 10.4 billion in 2014, based to the latest projections in reverse osmosis (RO), ultrafiltration (UF) and microfiltration (MF) world market [48]. This is due to the increases volume of water that will be treated by membranes in ten market segments, including desalination, municipal water recycling, industrial process water and wastewater treatment, cooling tower and boiler water treatment, as well as in emerging market segments such as oil and gas extraction [49].

Membrane is defined as selective barrier between two phases [4]. A membrane separation process is given in Figure 2.1. Phase 1 is usually known as

feed and phase 2 is known as permeate. The separation is achieved when smaller molecule is transport trough membrane via driving force. This driving force can be pressure, concentration gradient or temperature.

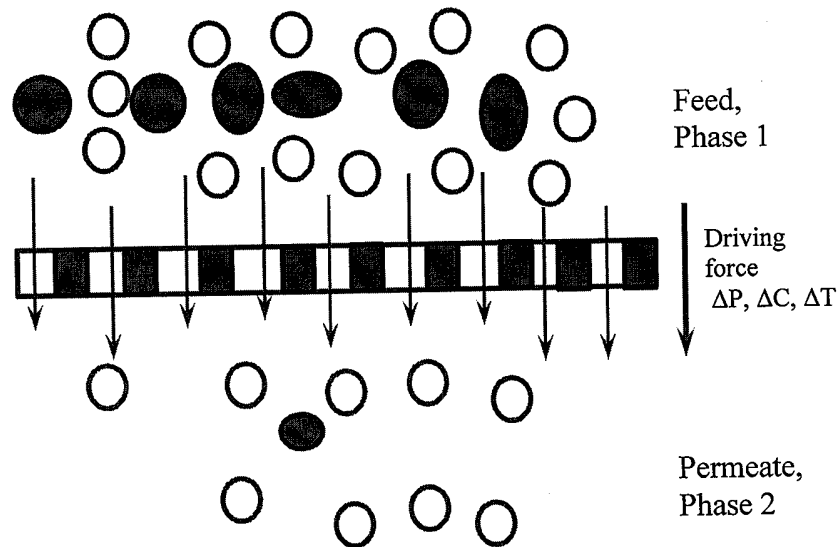


Figure 2.1: Two phase system separated by membrane

Basically, the membrane performance is determined by two parameters; its permeability or flux and rejection. Membrane flux is defined as volume flowing through membrane per unit area and time. In membrane separation for dilute aqueous mixture consisting water and a solute, the solute is partly or completely retained while the water molecules pass freely through membrane known as rejection. The higher rejection rate is desirable to accomplish particular separation [5].

Solute transportation via membrane occurs due to driving force applied in the feed. In water separation process using membrane the driving force usually applied using pressure. It is worth to mention that permeation rate trough membrane is proportional to driving force. Proportionality between flux and driving force given by

$$J = \alpha \times \Delta P \quad (2.1)$$

Where α is proportionality factors determines how fast the solute is transported through membrane and ΔP is driving force by pressure [4]. When membrane with smaller pore size is used or bigger solute species need to be retained, the higher pressure has to be applied in the operation system. Pressure driven membrane which are reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF) are now extensively used for natural and waste water purification. Table 2.1 shows the applications and the required membrane pore size to separate the solutes or particles.

Table 2.1: Overview of solute or particle dimensions and membrane separation process [36]

Size (μm)	Ions	Molecules	Macromolecules		Microparticles		Macroparticles
	0.001	0.01	0.1	1	10	100	1000
Solute/ Particle dimension	Mineral salts	Proteins		Algae Protozoa			
	Fulvic Acid	Red Blood Cells					
	Humic acid	Virus		Bacteria		Sand	
	Amino Acid						
	Pesticides	FeCl ₃ Floes					
	Metal Ions						
Membrane Separation process	RO						
	NF	MF					
	UF						
	Polysaccharides		Pollen				

As shown in the table, UF is a pressure driven membrane process whose nature lies between NF and MF membrane. UF membrane commonly can be used to

remove colloids and macromolecules. It can also be used as pre-treatment to a nanofiltration or reverse osmosis system. The purpose of this pre-treatment is to lengthen the filtration cycle of the process. Nowadays, UF has been recognised as an essential technology to water treatment and is becoming increasingly popular due to its ability to remove turbidity, microorganisms and viruses [50–52].

UF membrane possess assymetric porous structure with thickness around 150 μm and pore size in the range of 1 – 100 nm [4]. Most of UF membrane used commercially nowadays are prepared form polymeric materials by phase inversion process. Polyvinylidene fluoride (PVDF), polyetheretherketone (PEEK), polysulfone (PSf), polyethersulfone (PES), polyimide (PI), polyetherimide (PEI) and cellulose acetate are current commercial material that are suitable to be applied as UF membrane material [53–57]. Although UF has been commonly used in current market, the improvement on the available system is necessary.

2.2 Phase inversion

Membrane can be classified in different view of points such as the origin of membrane, applications or the preparation of membrane. Another way of classifying membranes is by their morphology or structure. According to Mulder [4], the classification based on structure is distinguished based on their structure whether it is dense, composite, asymmetry or symmetric as shown in the Figure 2.2.

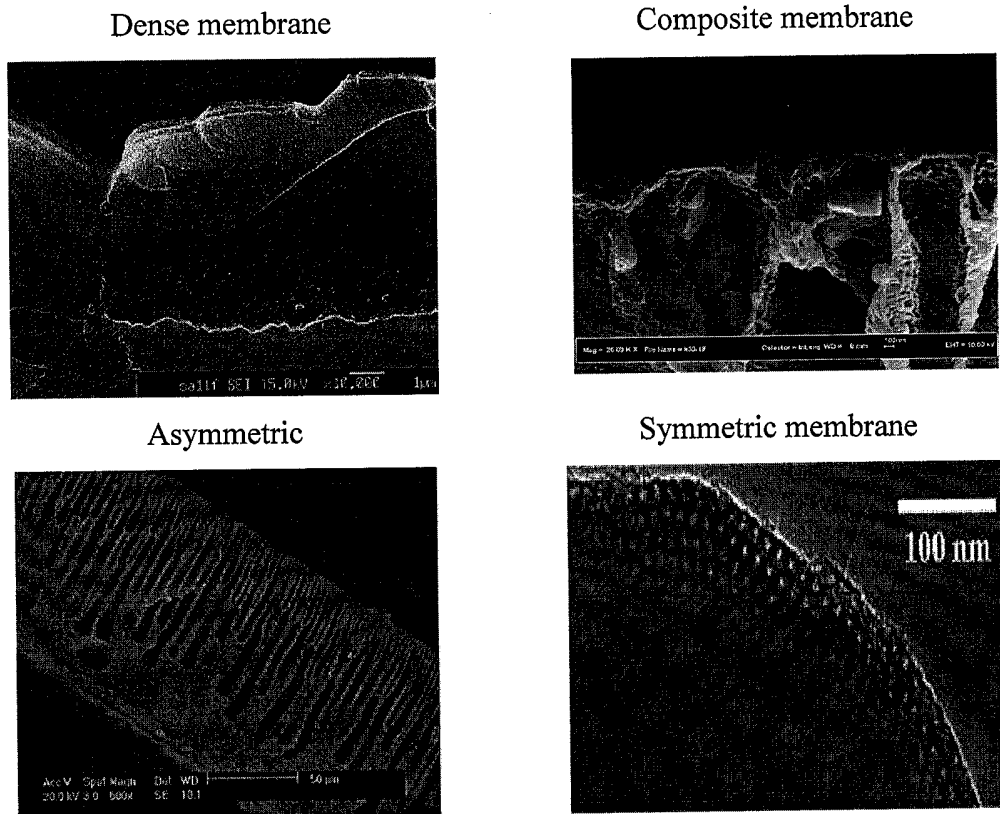


Figure 2.2: Different types of membrane cross section

Dense membrane is usually prepared either by solution evaporation or polymer extrusion. However, dense membrane can only be applied for high permeable material such as silicon or rubber materials [58,59]. Otherwise the transportation either liquid or gas through membrane seems impossible or very low. Most of the membranes nowadays are porous or has dense top layer on porous structure [60]. Even though the preparation of porous membrane is quite simple, but every aspect must be controlled to produce membrane with good quality. The composite membranes generally consist of two or more. In order to improve the membrane properties, the addition of new materials in composite membrane is commonly being investigated [4].

Current development of membrane is more convergent on asymmetric porous membrane. The asymmetric membranes combine high permeate flow and separation occurs on thin selective top layer. The underlying porous structure provides a

reasonable mechanical strength as well as the permeate flow. Asymmetric porous membrane can be generated via phase inversion [17], track etching [61], stretching [62] or template leaching [63].

The phase inversion process consists of the induction of phase separation in polymer solution. The phase separation can be done either by changing temperature, exposing to the nonsolvent atmosphere or immersing the solution in nonsolvent bath. The most important part in phase separation is thermodynamic stability of membrane solution which is subject to precipitation rate of membrane dope solution [64]. This precipitation behaviour can be explained using ternary diagram as shown in Figure 2.3. The ternary system consisting of solvent, nonsolvent and polymer is developed under this circumference. As shown in the figure, corners of the triangle represent the polymer, solvent and nonsolvent. Within the triangle represent the mixture of three components. Demixing will occur by the addition of such amount of nonsolvent to such an extent that the solution becomes thermodynamically unstable and reached binodal line [65].

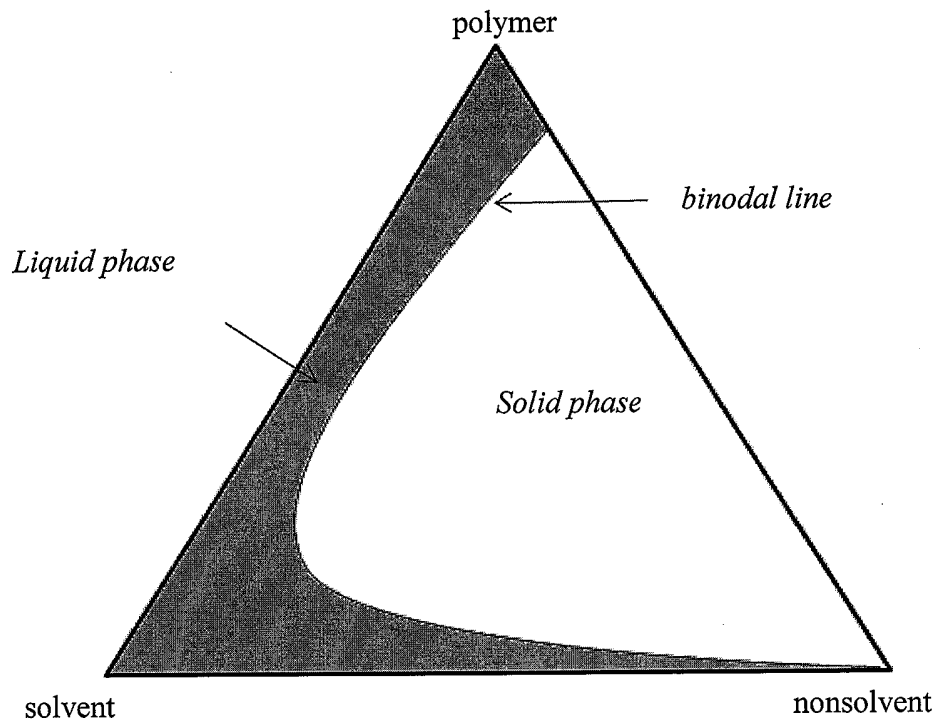


Figure 2.3: Ternary system with liquid-liquid demixing gap [65]

According to Bakeri *et al.*, the smaller liquid phase area, the fast phase inversion process will happen [66]. This is due to only small amount of nonsolvent were used for solidification process. In flatsheet membrane fabrication, the precipitation process started from the outer surface due to instability of thermodynamic between nonsolvent and the dope. Then solvent were diffused into nonsolvent bath and nonsolvent into the cast film. After external coagulant penetrates into the membrane depth, the droplets were formed and solidification occurred near the outer surface. These mechanisms drive the solidified walls to extend the droplets along the depth direction, which resulted in finger-like shapes formation. However when slow solidification occurred due to larger liquid phase area in ternary system, the wall between droplets was difficult to form. Thus, many small droplets combined to form larger droplets which results in sponge-like shape structure [4]. The structures of these two types of membrane are shown in Figure 2.4.

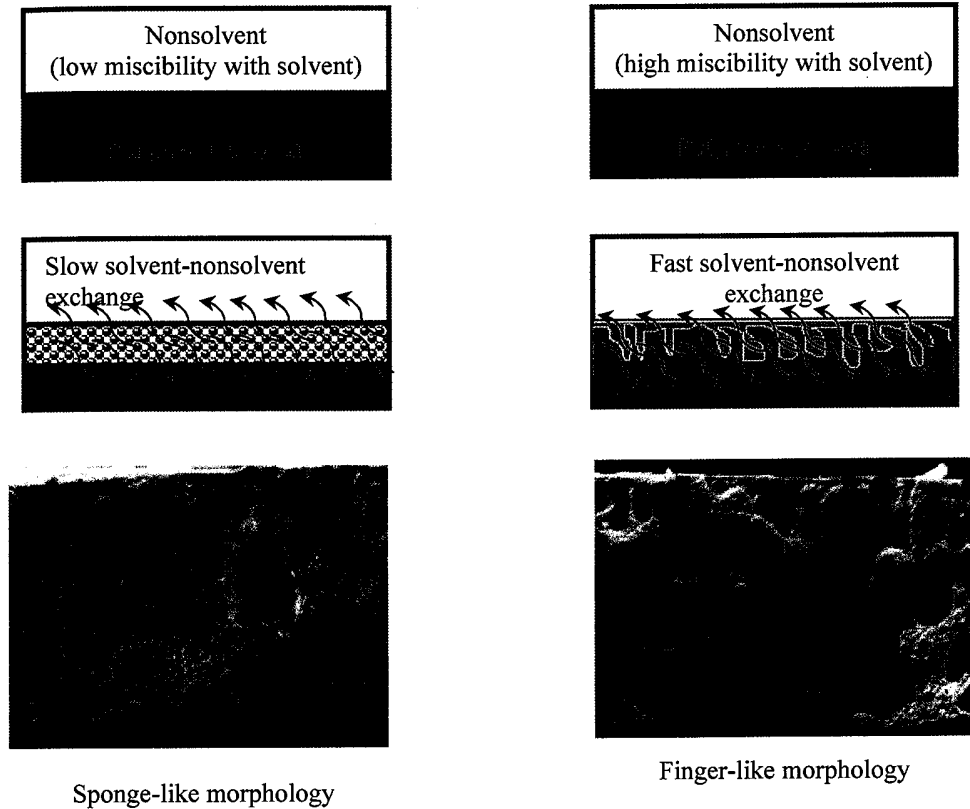


Figure 2.4: The influence of demixing rate on membrane morphologies

2.3 Natural organic matters (NOMs)

In Malaysia, most of water sources are contaminated with NOM, especially from peat soil. The amount and characteristics of NOM in surface water depends on climate, geology and topography. NOM such as humic acid and fulvic acid have contributed to changing the natural colour of water (brown to black). NOM becomes more visible if DOC is greater than 5 mg/L. Therefore, the removal of NOM is usually known as colour removal. According to Thurman and Malcolm, the average surface of water contains about 45 % fulvic acid, 5 % humic acid, 25 % low molecular weight acid, 5 % neutral compound, 5 % bases and 5 % contaminants [1].

Ahmad *et al.* has characterized the samples from water treatment plant at Parit Raja, Johor and the Sungai Sireh, Tanjung Karang using a fluorescence

technique. They found that NOM concentrations in the Parit Raja and Sungai Sireh water treatment plants are about 6.4 mg/L and 9.4 mg/L, respectively [67].

NOM removal is an important issue to solve in water treatment research. The increased levels of NOM and changes in the quality of the water present major challenges to the drinking water industry. The presence of NOM, as already indicated, creates serious problems to drinking water quality and its treatment processes. The major problem with NOM happen when excess addition coagulant and disinfectant such was reacted with NOM and produced disinfection by-product (DBP) [68].

DBP production has been of increasing concern due to their adverse health effects. New compounds have been discovered as detection methods and detection levels are improving. The most common, and among the first identified, were the trihalomethanes (THM) and haloacetic acids (HAA) [69]. More than 600 different compounds have already been identified in drinking water as a consequence of disinfection of water containing NOM [70]. All methods used for disinfection (chlorine, ozone, chlorine dioxide, chloramines, and UV-radiation) reportedly produce their own suite of DBPs and bio-reactive compounds in drinking water. Present knowledge and experience show that the hydrophobic compounds of NOM are the most important precursors for DBP formation [41,71,72]. Thus, the desired drinking water quality requires the removal of this organic matters to prevent DBP formation.

Designing and operating a drinking water treatment plant requires emphasis on the evaluation of removal technologies for NOM. A number of investigations discuss these NOM removal technologies. Among the various available technologies, the most common and economically feasible method is coagulation and flocculation, sedimentation/flotation and membrane filtration [2].

Recently, membrane filtration has been identified as one of the effective methods for the removal of NOM. This is because no extra chemical is needed to separate NOM, which can influence the final quality of water [36]. NOM filtration via PSf hollow fiber membrane was investigated by Zularisam *et al.* [73]. They

found that the membrane was capable of separating 99% of suspended solid at 120 kDA of membrane. Wei *et al.* have studied the effects of surface modification of polyether sulfone membrane on NOM separation performance. They reported that the retention of NOM increased from 77.7 % to 84.4 % after 2-acrylamido glycolic acid treatment [6]. NOM removal by cellulose acetate butyrate membrane has been studied by Hashino *et al.* using sodium alginate, humic acid and bovine serum albumin as their NOM model [74]. They found that the rejections of NOM model increased rapidly over a short filtration time and reached about 65%. The other membrane performance on NOM separation from literature is shown in Table 2.2. Thus, according to previous studies, it can be concluded that membrane filtration is effective in the removal of NOM.

Table 2.2: Membrane performance for NOM separation

Membrane	NOM model	Separation performance	Ref.
PES	Raw water from Kranji reservoir	60-85%	[6]
Cellulose acetate	Humic acid and tannic acid	60-90%	[75]
Polypiperazine amide	Raw water from Han river water	82-87%	[43]
Polyamide	Silver Lake surface water and Orange County groundwater	63-72%	[76]
PES	Trihalomethane, haloacetic acid	90-97%	[77]
PES	Humic acid	90-95%	[78]

2.4 Fouling of ultrafiltration membrane by NOM

Membrane fouling is referred to as the deposition or adsorption of the particles contained in the feed stream on the membrane surface or in the membrane pores. Membrane fouling has a negative impact on filtration performance as it decreases the permeate flux. According to Chan and Chen, membrane fouling manifests itself as flux decline and decreased transmission over time [79]. Fouling resulted from the reversible accumulation of solutes at the membrane surface, which is more commonly known as concentration polarisation. This accumulation also

leads to the progress of irreversible adsorption and cake built up as shown in Figure 2.5.

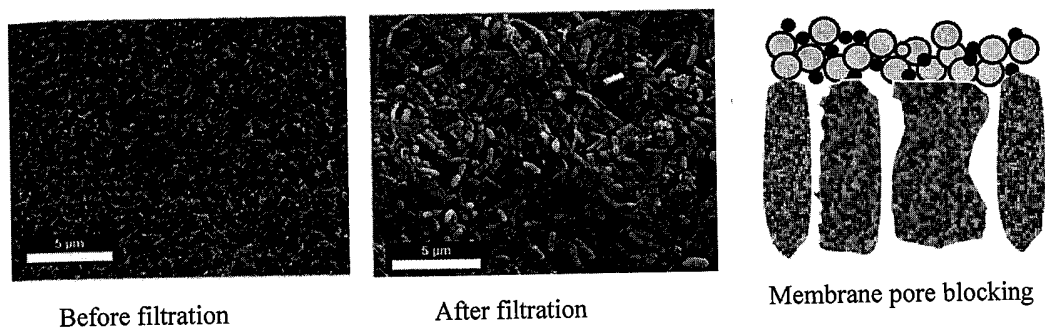


Figure 2.5: Membrane morphology before and after fouling [8]

The rate of membrane fouling is affected by many factors. The most important factors are the feed water characteristics, such as foulant types and concentration, ionic strength and pH. A higher foulant concentration naturally poses a greater fouling problem with the availability of a larger pool of foulants for deposition. The foulant type and composition influence the porosity of the fouling layer, which, in turn, determines the hydraulic resistance of the fouling layer. For example, a fouling layer that consists of organic matters and colloidal particles can have higher resistance than a fouling layer made up of only the same colloidal particles. The organic matters can fill up the voids between the colloidal particles, reducing the pathways for the feed water to reach membrane surface. Ionic strength and the pH of feed water affect the membrane-foulant and foulant-foulant interactions by altering the surface properties of the membrane and foulants [80]. Generally, a high ionic strength and low pH enhance the accumulation of foulants on a membrane surface. This problem can be overcome by selecting a membrane material that can resist low pH environments, such as PSf or polyethersulfone [37].

In the case of membrane fouling by NOM, both solution pH and ionic strength influence the properties of NOM and other feed components and consequently affects their filtration [36]. Hydrophobic interactions can lead to NOM aggregation and subsequently increase NOM-membrane interaction and membrane

fouling. In addition, NOM are most compact at their isoelectric points (IEP); when forming a fouling layer, they can pack more closely together due to the reduced electrostatic repulsion. Effects from compact form and packing density, lead to a denser fouling layer with increased hydraulic resistance.

The effects of NOM concentration and type of water on membrane fouling have been studied by Peter-Varbanet *et al.* [81]. Their results showed that the deposition of non-dissolved material induced structural changes in the fouling layer and development of irremovable fouling. They also reported that flux stabilization occurs when the decrease of resistance due to structural changes in the fouling layer balances the increase of resistance. Zularisam *et al.* [37] prepared cellulose acetate membrane for investigation of membrane fouling by NOM. They studied the fractions characteristics of NOM, which were divided into three components: hydrophilic, hydrophobic and transphilic. They reported that the hydrophilic component of NOM exhibited the worst flux decline compared to the hydrophobic and transphilic components. On the other hand, the hydrophobic fraction showed the highest NOM rejection. Thus, they conclude that the rejection-fouling mechanism depended on membrane-feed interaction instead of DOC concentration.

Generally, NOM such as humic acid change from linear to spherical when ionic strength increases due to neutralisation of anionic carboxylic acid and phenolic groups. This behaviour decreased NOM molecule size. Therefore, it is expected that rejection of NOM decreases as ionic strength increases. Rubia *et al.* have manipulated concentrations of ions in NOM solution [41]. They reported that both flux and DOC rejection decreased as ionic strength increased. The same trends were observed by Cho *et al.* [39].

The charge of an organic molecule can be changed by manipulating pH value. The increment of pH value caused NOM molecules to change their conformational isomerism and resulted in small sizes of NOM, as reported by Shaw *et al.* [82]. Meanwhile, the decrease of pH caused electrostatic repulsion to decrease and subsequently increased membrane fouling [83]. Wang *et al.* [84] proved this behaviour by studying the effect of pH on the diffusion coefficient of NOM. They

found that the diffusivity of NOM, such as humic acid, increased as pH value decreased and this led to membrane fouling.

2.5 Polysulfone membranes formation

PSf is an interesting materials which possesses good chemical property, easy to be processed and high thermal resistant [5]. PSf are copolymer of alkenes and sulphur dioxide (SO₂). According to patent US6548622, PSf can be synthesized by reacting sulphuric acid or sulphur trioxide to carboxylic acid anhydrate with an electron rich aromatic compound which behaves as a difunctional (bireactive) compound. It can also be produced using Friedel – Crafts chemistry which reacting 4-biphenylsulfonylchloride with a strong Lewis acid such as aluminium chloride or iron trichloride [85].

Nunes and Peneimann reported that the first development of PSf membranes appeared in the 1960s as an alternative to cellulose acetate membrane [5]. PSf offer high thermal stability and resistance in extreme pH conditions as compared to cellulose acetate. It has a T_g of 195 °C and soluble in aprotic solvent. Thus it can easily apply in conventional phase inversion processes.

In the preparation UF PSf membrane via phase inversion, the physico-chemical properties of the PSf dope solution influence the structure of the integrally skinned membranes. The dope solution consists of PSf and solvent, but can also contain other types of additives such as pore forming agent and hydrophilic inorganic additives. The choice of solvent is restricted by the polymer type. It determines the final membrane morphology via its interactions with the non-solvent in the coagulation bath. Increasing the initial polymer concentration in the casting solution, membranes with thicker and denser skin-layers are formed and results in higher rejection and lower permeances. However, by reducing the polymer composition membrane pore size increases due to rapid solvent/nonsolvent exchange rate [86]. This behaviour lead to reduce rejection and increase membrane permeability.

In the case of PSf membrane fabrication with at least 90% NOM rejection model such as bovin serum albumin or humic substance, the formulation of PSf resin is reported in the range of 15-18 % in solvent, such as dimethyl acetamide (DMAc) or N,N-methyl pyrrolidone (NMP) [24,87]. Table 2.3 reviews the percentage ranges of PSf, type of solvent, rejection model and flux in the development of PSf ultrafiltration membrane.

Table 2.3: Review on development of polysulfone ultrafiltration membrane.

Percentage of polysulfone in solvent	Solvent	Rejection model	Pressure (bar)	PWF (LMH)
18%[28]	NMP	Dextran	4	<1
18%[24]	DMAc	BSA, pepsin	2	0.81
17.5%[88]	DMF	Protein	3	16.8
15%[51]	DMAc	Oil	2	2.0
15%[89]	DMAc	Protein	2.95	5.0

The major concern for preparation PSf membrane is low flux and fouling. As shown in Table 2.3, membrane flux for PSf/solvent is around 0.81 – 16.8 LMH. This flux is too low to be applied in ultrafiltration system especially for NOM separation. The membrane that usually used to separate NOM fabricated by Milipore has flux around 150 LMH which is 9 times higher as compared to pristine PSf membrane developed by Arthanreewaran *et al.* [88]. Thus, it is important to enhance membrane flux by adding suitable additives such as pore forming agent.

2.6 Effects of PEG as pore forming agent on membrane properties

In order to obtain membranes with suitable structure and permeation properties, the introduction of suitable additives is necessary. The most important effects of additives are pore interconnectivity enhancement, suppression of macrovoid formation and increasing membrane surface hydrophilicity. Machado *et al.* [90] state that additives also change solvent capacity or the phase separation kinetics and thermodynamic properties of the membrane dope solution, which can jeopardize the

membrane's physical and mechanical properties. Therefore, the effects of additives must be studied to optimise membrane performance.

PEG is one of the commonly used additives in the preparation of porous membrane structure. It is used due to its hydrophilic property and its ability to dissolve easily in solvent. PEG can be used as an additive for membrane preparation using the phase inversion method. The addition of PEG in dope solution usually disturbed the miscibility between polymer and solvent. The binodal line of polymer, solvent and nonsolvent was found shifted to polymer solvent axis as PEG concentration and molecular weight increases, which means that less nonsolvent is needed for precipitation process and rapid phase inversion will occur [24,91].

Idris *et al.* reported PES membrane performance with PEG as an additive [45]. They observed that membranes permeation with PEG showed great increases up to 76.5 LMH in water permeation with addition 15 wt. % PEG. They also observed membrane MWCO enhanced with PEG addition. Chakrabarty *et al.* [92] reported that the molecular weight (MW) of PEG has significant effects on membrane performance. They found that as the MW of PEG increased, the porosity and water equilibrium content of the membrane also increased. However, the membrane sublayer seemed to have a dense structure with comparatively fewer macrovoids, which then led to pure water flux decrement. Ma *et al.* [24] also found the same behaviour in PSf membrane. The membrane porosity was enhanced greatly with the increment of PEG molecular weight and concentration. They reported that pure water flux increased up to 420 LMH for PEG 400 concentration 10 wt. %. They also observed that the increase in PEG 400 dosage does not change the molecular cut-off weight of the membrane, but can make the size finger-like pore structure increased. Therefore, they concluded that PEG could be regarded as a pore forming agent. Other researchers who studied the effect of PEG are summarized in Table 2.4.

Table 2.4: Effect of PEG to polymeric membrane

Base material	Additive(s)	Function of membrane
PSf [93]	PEG 400 Da	Function: to separate dextran aqueous solution; PEG makes the dope solution become thermodynamically less stable and improves membrane demixing rate. PEG also reduces membrane contact angles
PEI [94]	PEG (200 Da, 400 Da and 600 Da)	Function: to separate PEG 600 in ethanol; PEG small molecular weights (PEG 200 and PEG 400) work as pore reducing agents
CA [95]	PEG 400 Da	Function: to reject human serum albumin; PEG additive in the cast solution film can increase porosity/permeability and simultaneously increase the thermal/chemical stability of the prepared cellulose acetate membranes
PEI [96]	PEG 600 Da	Function: gas separation; Hydrophilic nature in PEG is used to improve membrane selectivity and is also used as a pore forming agent
PSf/SPEEK [88]	PEG 600 Da	Function: Ultrafiltration membrane for protein rejection; PEG 600 in the dope solution increased the exchange rate of the additive and non-solvent during the membrane formation process, resulting in macrovoid formation
PSf [97]	PEG (400 Da, 4000 Da, 6000 Da 10000 Da and 20000 Da)	Function: Separation of dextran solution; Hydrophilicity membrane increased with addition of PEG, tear drop like pattern was observed at low PEG concentration.
PVDF [98]	PEG(200 Da, 1000 Da, 6000 Da, 10000 Da, 20000 Da)	Function: BSA separation When PEG molecular weight was increased, the changes in the resultant membranes' morphologies and properties showed a transition point at PEG 6000. PEG was used as a pore-reducing agent at high molecular weight to result in pure water flux decreasing and solute rejection increasing.

2.7 Effects of inorganic additives and compatibilizer on membrane properties

Inorganic materials, such as silica, zeolite, zirconia, silver and titanium oxide are capable of resisting chemical attack and have high thermal stability. Blending these materials with polymer has major advantages due to their convenient operations, mild conditions and good and stable performances. Pinnau and He reported that the addition of inorganic particle can alter polymer chain packing in glassy, high-free volume polymers [99]. This was resulted in an increase of free volume, leading to a significant enhancement in permeability. Beside that that inorganic particle has the capability of improving the antifouling properties of membranes as reported by Hamid *et al.* [71]. They observed that the composite membranes were excellent in mitigating fouling, particularly in reducing fouling resistance due to concentration polarisation, cake layer formation and adsorption. Table 2.5 shows the improvement of membrane by incorporating with various types of inorganic particles.

As shown in table the function of silver in improving hydrophilicity and antibacterial properties is well studied. It can be concluded from the table that silver incorporated in membrane improved membrane hydrophilicity, permeability and antibacterial properties. Silver also reduced membrane biofouling as resulted from low foulant adsorption due to hydrophilic characteristic which is important when dealing with NOM separation. The influence of silver to improve membrane properties usually depend on silver size, method synthesised and concentration [32]. The smaller silver size is desirable, which is due to small sizes exhibits high distribution on the membrane surface and high hydrophilicity will be obtained. Different synthesis method will result different types of silver such as silver nitrate, silver oxide, Ag-SiO₂ and metallic silver [21,26,100,101]. These types of silver will influence the stability, hydrophilicity and antibacterial properties of membrane. Increasing silver concentration in membrane will improve membrane permeability, strength and antibacterial properties. However addition of excessive silver amount in membrane tend to create serious silver aggregation on membrane surface. This

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