SYNTHESIS, CHARACTERIZATION AND PERFORMANCE OF TRIETHANOLAMINE-BASED THIN FILM COMPOSITE NANOFILTRATION MEMBRANE

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ABSTRACT

Humic acid (HA) is one of the common NOM which contribute a major problem in treatment of surface water including (i) negative effect on water quality by colour, taste and odour problems, (ii) increased coagulant and disinfectant dose requirement (iii) promoted biological growth in distribution system and (iv) increased levels of complexes heavy metals and adsorbed organic pollutants. Thus, more efficient method for the humic acid removal has emerged. Among the membrane processes, nanofiltration (NF) has been increasingly used for wastewater and water treatments including natural organic matters (NOM). Nine membranes were prepared through interfacial polymerization of aqueous solution, triethanolamine (TEOA) and organic solution, trimesoyl chloride (TMC) on a polyethersulfone (PES) support film. The composite membranes were prepared under different TEOA monomer concentration (4, 6, 8 % w/v) and reaction times (15, 25, and 35 min). These membranes were characterized in terms of chemical properties (functional group and hydrophilicity) and morphological structures to verify polyester membrane formed on the top surface of PES (interfacial polymerization process). On top of that, membrane performance was also investigated in term of pure water permeability, rejection of charged (sodium chloride (NaCl) and sodium sulphate (Na_2SO_4)) and uncharged solutes (vitamin B_{12}). All nine polyester membranes showed NF characteristics which in between 12.98 L $m^2h^{-1}bar^{-1}$ until 1.25 L $m^2h^{-1}bar^{-1}$. Analysis done by attenuated total reflectance fourier transform infrared spectroscopy (ATR-FTIR) on top surface and field emission scanning electron microscopy (FESEM) on top and cross sectional membrane indicate a new polyester layer formed on the PES membrane support. Highest TEOA monomer concentration (8% w/v TEOA) and reaction time membrane (35 min) resulted as less hydrophobicity membrane when achieved the lowest contact angle measurement ($\theta = 34.0 \pm 0.35$) compared to unmodified membrane ($\theta = 62.6 \pm 0.33$). Using uncharged (Vitamin B_{12})/charged solute (NaCl) data, the changes in the morphological and electrical properties of the synthesized NF membranes were deduced by employing the combination of irreversible thermodynamic model, Steric-Hindrance Pore (SHP) model and Teorell–Meyer–Sievers (TMS) model. In NF membrane characterization, three important parameters have been identified as an effective pore radius (r_p), the ratio of effective thickness over porosity ($\Delta x/A_k$) and an effective charged density (X_d). In this study, it was observed that the variation of reaction times and TEOA monomer concentrations affect the properties of the membrane produced and affect water permeabilities and solute rejection as well. The salt rejection order of the membrane changed from 0.001 M $Na_2SO_4 > 0.1M$ $Na_2SO_4 > 0.001M$ NaCl $> 0.1M$ NaCl. Moreover, pH of humic acid solution plays an important role in flux reduction and fouling. HA filtration analysis was preferably chosen at pH 7 (4% 35 min) and pH 3 (4% 15 min) respectively It observes that all nine membranes able to removes humic acid with an efficiency of approximately 98% and were capable of reducing initial concentrations of 15 mg/L at the TEOA monomer concentration (6% w/v TEOA) and reaction time (35 min).

ABSTRAK

Asid humik adalah salah satu bahan organik yang menyumbang masalah utama dalam rawatan air permukaan termasuk (i) kesan negatif ke atas kualiti air dengan warna, rasa dan bau masalah, (ii) Keperluan kuantiti penggumpalan dan bahan cecair membunuh bakteria meningkat (iii) menggalakkan pertumbuhan biologi dalam sistem pengagihan dan (iv) meningkatkan kandungan logam berat kompleks dan bahan cemar organik terserap. Oleh itu, kaedah yang lebih berkesan untuk penyingkiran asid humik telah ditemui. Antara proses membran, nanofiltration (NF) banyak digunakan untuk rawatan air dan air sisa termasuk bahan organik semulajadi (NOM). Sembilan membran disediakan melalui pempolimeran antara muka larutan akueus, Triethanolamine (TEOA) dan pelarut organik, trimesil klorida (TMC) pada polyethersulfone (PES) filem sokongan. Membran komposit telah disediakan di bawah kepekatan TEOA monomer yang berbeza (4, 6, 8% w / v) dan masa tindak balas (15, 25, dan 35 min). Membran dicirikan dari segi sifat-sifat kimia (kumpulan berfungsi dan hidrofilik) dan struktur morfologi untuk mengesahkan membran poliester terbentuk pada permukaan atas PES (proses pempolimeran antara muka). Selain itu, prestasi membran juga diuji dari segi kebolehtelapan air tulen, penolakan dikenakan (natrium klorida (NaCl) dan natrium sulfat (Na2SO4)) dan bahan larut tidak bercas (vitamin B_{12}). Semua sembilan membran poliester menunjukkan ciri-ciri NF yang di antara 12.98 L $m^2h^{-1}bar^{-1}$ until 1.25 L $m^2h^{-1}bar^{-1}$. Analisis yang dilakukan melalui meletakkan sejumlah fourier pantulan mengubah spektroskopi inframerah (ATR-FTIR) di atas permukaan dan pelepasan laman mikroskopi elektron imbasan (FESEM) pada bahagian keratan rentas membran dan menunjukkan lapisan poliester baru terbentuk di atas membran sokongan PES. Kepekatan tertinggi TEOA monomer (8% w / v TEOA) dan tindak balas masa membran (35 min) mengakibatkan pengurangan sifat hidrofobik membran apabila mencapai ukuran sudut kenalan paling rendah ($\theta = 34.0 \pm 0.35$) berbanding dengan membran tidak diubahsuai ($\theta = 62.6 \pm 0.33$). Data bahan larut tidak bercas (Vitamin B_{12}) / bahan larut bercas (NaCl) , perubahan dalam sifat-sifat morfologi dan elektrik membran NF yang disintesis dengan menggunakan gabungan tak berbalik model termodinamik, model Sterik-Penghalang Liang (SHP) dan model Teorell-Meyer-Sievers (TMS). Dalam pencirian membrane NF, tiga parameter yang penting telah dikenal pasti iaitu jejari berkesan liang (r_p), nisbah ketebalan berkesan ke atas keliangan ($\Delta x / A_k$) dan ketumpatan yang berkesan dikenakan (X_d). Dalam kajian ini, ia telah diperhatikan bahawa perubahan masa tindak balas dan kepekatan monomer TEOA mempengaruhi sifat membran yang dihasilkan dan nilai kebolehtelapan air dan penolakan bahan larut juga. Perintah penolakan garam membran berubah dari 0.001 M Na_2SO_4> 0.1M Na_2SO_4> 0.001M NaCl> 0.1M NaCl. Selain itu, pH larutan asid humik memainkan peranan yang penting dalam pengurangan fluks dan pemendapan liang membran. Analisis penapisan asid humik yang terbaik iaitu pH 7 (4% 35 min) dan pH 3 (4% 15 min). Kesimpulannya, semua sembilan membran dapat membuang asid humik dengan kecekapan kira-kira 98% dan mampu mengurangkan kepekatan awal 15 mg/L pada kepekatan TEOA monomer (6% w/v TEOA) dan masa tindak balas (35 min).

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LIST OF SYMBOLS

α   Stokes radius (nm)
$A_k/\Delta x$ Ratio of porosity to thickness of a membrane (m)
C_p Concentration in the permeate solution, (g/L)
C_f Concentration in the feed solution, (g/L)
C_r Concentration in the retentate solution, (g/L)
C_b Concentration in the bulk solution, (g/L)
C   Mean concentration over the thickness of membrane (mol/m^3)
C_b Concentration of solute in the bulk solution (mol/m^3)
C_m Concentration of solute in the fluid at the feed/membrane interface (mol/m^3)
C_p Concentration of solute in the permeate solution (mol/m^3)
d_p Pore diameter (nm)
D_s Diffusivity of solute molecule in a dilute solution (m^2/s)
H_D Steric parameter related to wall correction factors in diffusion coefficient
H_F Steric parameter related to wall correction factors in convection coefficient
J_s Flux of solute (mol/m^2.s)
J_v Volume flux (m/s)
k   Boltzmann's constant (1.38×10^{-23} J /K)
P   Solute permeability (m/s)
P_s Solute permeability of salt (m/s)
r_p Pore radius (nm)
r_s Stokes radius (nm)
R   Rejection (%)
S_D Distribution coefficient of solute in diffusion condition
S_F Distribution coefficient of solute in convection condition
T   Absolute temperature (K)
Δx Membrane thickness (m)
X   Effective volume charge density (mol/m^3)
F_f Final pure water flux (L/ m^2.h)
F_i Initial pure water flux (L/ m^2.h)
J_w Pure water permeation flux (L/ m^2.h)
ΔP Transmembrane pressure (kPa)
P_m Permeability (L/m^2.h.bar)
m   Molecular mass (g/mol)
k_w permeability coefficient
$D(dC/dx)$ Back diffusion of the solute
JC Membrane surface
C_s Concentration of solute at the membrane

Greek letters

α Transport number of cation in free solution

σ Reflection coefficient

σ_s Reflection coefficient of salt

λ Ratio of solute radius to pore radius

ξ Ratio of effective volume charge density of membrane to the electrolyte concentration of feed solution

μ Solvent viscosity (water viscosity at 25 $^{\circ}$C, 0.8937×10^{-3} kg/ m.s)

$\emptyset X$ Effective fixed charge density (mol/m^3)

LIST OF ABBREVIATIONS

Abbreviations

Abs	Absorbance
AFM	Atomic force microscopy
ATR	Attenuated total reflectance
BPA	Bisphenol A
CA	Cellulose acetate
CN	Cellulose nanofibers
DABA	3,5-diamino-N-(4-aminophenyl) benzamide
DETA	Diethylenetriamine
DI	Deionized water
DOM	Dissolved organic matter
ENMs	Electrospun nanofibrous membranes
FA	Fulvic acid
FESEM	Field emission scanning electron microscope
FI	Fouling index
FO	Forward osmosis
FTIR	Fourier transforms infrared
HA	Humic acid
HS	Humic substances
IP	Interfacial polymerization
LMW	Low molecular weight
MF	Microfiltration
mPD	m-phenylenediamine
MWCO	Molecular weight cut-off
NaCl	Sodium Chloride
Na_2SO_4	Sodium Sulphate
NaOH	Sodium hydroxide
NF	Nanofiltration
NOM	Natural organic matter
PA	Polyamide
PAN	Polyacrylnitrile
PC	Polycarbonate
PEEK	Polyetherketone
PEI	Polyetherimide
PEI	Polyethyleneimine
PEO	Polyethylene oxide
PES	Polyethersulfone
PhACs	Pharmaceutically active compounds
PI	Polyimide
PIP	Piperazidine

PP	Polypropylene
PSf	Polysulfone
PSSS	Poly(styrene sulfonic acid) sodium salt
PVam	Polyvinylamine
PVC	Polyvinyl chloride
PVDF	Poly vinylidene fluoride
RO	Reverse osmosis
RSF	Rapid sand filters
SEM	Scanning electron microscope
SHP	Steric-hindrance pores
TEOA	Triethanolamine
TEPA	Tetraethylenepentamine
TETA	Triethylenetetramine
TFC	Thin film composite
TFNC	Thin-film nanofibrous composite
TMC	Trimesoyl chloride
TMS	Teorell-mever-sievers
TPC	Terephthaloyl chloride
UF	Ultrafiltration
UV	Ultra violet

CHAPTER 1

INTRODUCTION

1.1   RESEARCH BACKGROUND

Strict enforcement of rule and regulations and the requirement for a reliable potable drinking water supply has increase the interest in the using of membranes in drinking water treatment process. Membrane processes are using pressure as the driving force to separate out contaminant from water supplies. They are new alternative for many unit processes which are currently implemented such as sand filtration, carbon adsorption or ion exchange (Lowe and Hossain, 2008). One particular group of contaminants that is present in water supplies and which has brought about concern in the water industry is humic substances (HS). There are three substances which make up HS and they are humin, humic acid and fulvic acid. NOM is the organic material present in the surface or ground water. NOM interacts with all of the chemical components of natural water; these interactions change the behaviours of the pollutants in the surface and ground water (Sarathy and Mohseni, 2010). NOM in the surface water usually refers to the humic (HA) and fulvic acids (FA) that are decayed by-products of plants such as those found in the surface water. These substances plus the tannic acid are the major fractions of the dissolved organic matter (DOM) in water. These substances are oxidized very slowly and their solubility in water may differ with pH. The dissolved fractions of NOM may not be fully removed using the conventional water treatment practices (i.e. flocculation, coagulations and chlorination) and have been shown to produce carcinogenic by-products such as trihalomethane and haloacetic acid are formed during the disinfection (Lowe and Hossain, 2008). Other conventional methods in removal of HA in drinking water treatment plants are chemical oxidation using chlorination, ozonation, activated carbon adsorption and coagulation (Alborzfar et al., 1998). The organic compounds in the surface water and ground water arise from the natural and anthropogenic sources (i.e. storm water runoff and leaking sewer lines from surrounding land). NOM in water also caused bacterial re-growth in water distribution.

The growth in population and development in urbanization, industrialization and irrigated agriculture cause growing demands and pressure on the water resources, besides contributing to the rising water pollution. The costs are rising and rigorous scrutinization from the environmentalists and conservationists need to be faced because of the new development of water resources. Enforcement from Ministry of Health Malaysia stated that drinking water quality standard for trihalomethane is 1.0 mg/L for maximum acceptable value. This maximum acceptable value must followed by all drinking water manufacturers and suppliers. .HA will form very toxic disinfection byproducts (DBPs); *i.e*. chlorinated organic compounds, for example, trihalomethanes (THMs), which exhibit mutagenic properties during chlorination step in tap or drinking water production or water treatment. The guideline values for DBPs in drinking water announced by the World Health Organization should not exceed 100 μg L (Mahvi et al., 2012). But, reaction of humic acid in surface water can formed trihalomethane, thus greater research efforts being put into the improvement of the membrane processes. Membrane technology can provide a continuous operation and better water quality with the potential to remove the targeted contaminants in one stage. The effective removal of NOM such as humic substances with membranes is a significant challenge in the water industry. Our study emphasize on improvement of filtration system in water treatment process. Conventional method of filtration system consist filters with varying sizes of pores, and is often made up of sand, gravel and charcoals. The diameter of a grain of fine sand is approximately 0.1 millimeters, so only particles with diameters less than 0.1 millimeter would pass through the fine sand layer. This kind of filter would not be able to produce safe drinking water, because many contaminants are much smaller than 0.1 millimeters (i.e humic acid). The surface water treatment with the nanofiltration (NF) membranes has become an attractive alternative to the conventional treatment for the removal of the humic substances.

The NF membrane separation is widely used in the various industrial fields. Water and wastewater treatment are one of the fields that use this kind of technology to treat the water until the water reaches the quality that it can be discharged to the environment or reusable for other processes. This NF is known to have the properties in between the

reverse osmosis (RO) and the ultrafiltration (UF) (Mansourpanah et al., 2010). Because of that, it has the significant advantages including low operation pressure, higher permeation flux, high retention of multivalent salt, compound more than 300 of molecular weight compound, and low investments, operation and maintenance costs (Tang et al., 2008).

NF membrane could be an asymmetric or a thin film composite (TFC) membrane. However, the most commercial available membrane in the market is a TFC membrane produced by the interfacial polymerization (IP) method. IP process is well known as diffusion-control and self-limiting process. Thus, determination extent reaction of IP is major influenced by the reaction time (Ahmad and Ooi, 2005 and Mohammad et al., 2003). When the polymerization time increase, top skin layer thickness of the composite membrane will increases too until polymerization process complete and water flux will constant. Then, short reaction time have low extent of cross-linking is low and the permeability of the membrane is high. However, the membrane surface layer will be improved by increasing of reaction time and the membrane will gradually become integrated. The NF membrane is produced through two preparation steps which are the polymer phase inversion resulting a microporous support membrane and the IP of a TFC layer on top of a microporous support membrane or other porous substrate (Mohammad et al., 2003). The common NF membrane is based on the polyamide (PA) membrane which uses the amine group monomer for IP process. On top of that, there are several research studies focused on other monomers such as bisphenol-A (BPA) in order to produce the polyester NF membrane (Abu Seman et al., 2010; Mohammad et al., 2003; Jayarani and Kulkarni, 2000).

Moreover, IP has significant advantages which involve the rapid reaction rates under the ambient conditions, no requirement for the reactant stoichiometric balance and a low requirement for the reactant purity (Li et al., 2008).The reaction rate of IP is very high, so that reactants diffuse to the interface and combine almost stoichiometrically to form high molecular weight polymer. The high reaction rate is required otherwise diamine will have time to penetrate through the polymer to start new polymer chains in the organic phase. Interfacial polymerization occurs at room temperature. Polymers that are unstable at high

temperatures can go through this pathway. High molecular weight polymer is made without matching the stoichiometric ratio The IP technique is an adequate method for the preparation of thin film composite membranes with an ultra thin polyester active layer.

1.2   PROBLEM STATEMENT

IP is a common technique used for a preparation of NF and RO composite membranes either in the lab scale or commercial scale. In general, the produced membranes exhibit high water permeation flux and high salt rejection (Ahmad et al., 2004).Most commercial NF and RO membranes produced by the IP method have a polyamide (PA) thin layer on top of the membrane support. The polyamide is produced from the reaction of amine monomer with acyl chloride in organic phase (n-hexane). One of the common amine monomers used is *m*-phenylenediamine (*m*PD) and other amine monomers for production of polyamide are included.

Besides the PA membrane, a few researchers have explored this technique to produce the other polymeric thin film polyester and polyester amide membranes, where BPA was used as the primary monomer during the IP (Abu Seman et al., 2010; Mohammad et al., 2003; Jayarani and Kulkarni, 2000). Even their membranes could exhibit very good performances (high rejection and low organic fouling); however, in the last few years, BPA toxicity has become a big issue as it may strongly contribute to some negative effects to human health. For instance, manufacturers used polycarbonate (PC) plastic (reaction between BPA and $COCl_2$) as the materials for baby bottles because it is rigid, has shatter resistant and clear in colour. Plastic baby bottles have received many attentions recently as research came to light showing many models leach BPA, a suspected endocrine disruptor (Beverly, 2011). Concerning this issue, BPA as monomer of IP process to form polymeric membrane from previous research also can cause toxicity to human health.

Studies demonstrated that BPA migrated faster from polycarbonate bottles which were in turn over by a few (3–7) years and were exposed to high temperature (Michałowicz, 2014). BPA is able to bind to several kinds of receptors that are associated

with hormones of the endocrine system and other systems of the body causing endocrine disruption activity, oxidative and mutagenic potential.

Instead of using BPA as monomer, previous studies show that polyester TFC membranes produced by triethanolamine (TEOA) have the ability to be used in the desalination at different environmental pHs. TEOA is an organic compound that is both a tertiary amine and a triol. A triol is a molecule with three alcohol groups. TEOA is a strong base and have potential to produce hydrogen bond. The similarities between TEOA and BPA are from their functional group (Figure 1.0). Both can react with multifunctional acid chloride to form cross-linked network structure because of multi-hydroxyl existence in their molecular structure (Tang et al, 2008). In addition, the tertiary amino group in its molecule can be transferred into quaternary ammonium group to improve the membrane performance by adjusting pH of the feed solution. On top of that, TEOA is an active monomer which is environment-friendly, economical and easy to be obtained (Tang et al., 2008).
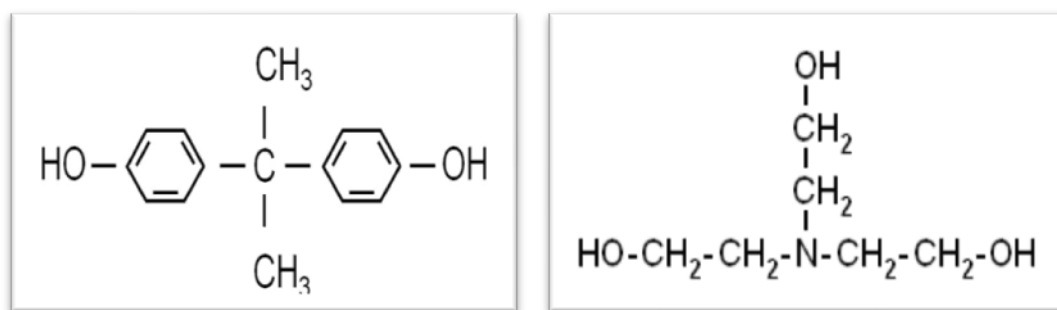
Figure 1.0 Molecular formula for Bisphenol-A (left) and Triehanolamine (right)

In this study, TEOA was selected as the main monomer for producing polyester TFC NF membrane for NOM removal (i.e. humic acid). Previous research done by Tang et al., (2008) found from their premier experiment that the TEOA polyester composite nanofiltration membrane can be efficiently applied in separating multi-valent anion from mono-valent anion in neutral electrolyte solution because the TFC membrane presents negative charge at pH higher than the isoelectric point of the membrane (between pH 4 and 5).When pH in the feed solution decrease, then the flux for NaCl solution increased. It shows that the TFC polyester membrane is also particularly suitable for treating acidic feed.

On top of that, this study was focused on how the TEOA monomer concentration and reaction time may affect on the structure properties (pore size; active layer thickness) and electrical properties (effective membrane charge) and indirectly to the membrane performance (i.e. permeability, salt rejection and HA removal, fouling).

The presence of natural organic content (NOM) have big impact on aesthetic quality, as NOM imparts a yellowish tinge to water that many people find unpalatable (Crittenden and Montgomery Watson Harza (Firm) 2005). Therefore, the content of NOM in water is an indicator of the true colour in water, since the true colour is caused by NOM and is used to define the aesthetic quality of water. NOM may result in the formation of trihalomethanes (THM's) during chlorination and impedes the removal of iron and manganese from the water (Alborzfar et al., 1998)

1. 3   RESEARCH OBJECTIVES

The main objective of this research is to synthesis thin film composite polyester nanofiltration membrane by triethanolamine-based interfacial polymerization process. .

1.4   SCOPES OF STUDY

In order to achieve the objective mentioned previously, there are a few scopes:

1.   Synthesis TFC polyester NF membrane on the polyethersulfone (PES) as micro porous support and investigating the effect of TEOA concentration ($4\%w/v - 8\%w/v$) and reaction time (15-35 min) which influences the membrane properties.

2.   Characterization of physical/chemical properties of the membranes such as morphology, surface chemistry and hydrophilicity by using FESEM, ATR-FTIR and contact angle, respectively.

3.   Determination of the structure properties including the pore radius (r_p), ratio of membrane thickness to porosity ($\Delta x/A_k$) and electrical properties such as the membrane charge (X_d).

4.   Membrane performance testing for the removal of HA and antifouling properties at different pHs.

CHAPTER 2

LITERATURE REVIEW

This chapter will describe in details the general overview of the membrane processes, the application of the NF membrane technology, the application of the NF in the water treatment, the membrane fabrication and the TFC formation, the characterization of the NF membrane and also the information on the HA and as well concentration polarization.

2.1   General Overview of the Membrane Process

The development of the NF membrane was started from year 1960s until the early year 1990s. It has introduced NF technology to its current technology.. The origin of UF membrane can be recall back at late 1950s and the development of Loeb-Sourirajan anisotropic or asymmetric cellulose acetate (CA) membranes for seawater desalination. These membranes constituted the origin for the membrane development in RO and UF process.. The progress in RO and UF technology has formed another type of membrane which is NF membrane. This greater research and development effort spanned a very short period of time of about 15 years, starting in year 1960. And by the early 1970s a full range of CA asymmetric (or anisotropic) membranes including the entire spectrum, from RO through NF to UF, were available. Then, Today, NF has the ability to resolve many separation problems, but such actual applications are small in number compared to the potential applications that still await improvements in the membrane stability, flux and selectivity. The characteristics of UF membrane separation covered by this definition are currently known as NF. This term was being categorized as open RO, loose RO, intermediate RO/UF, selective RO, or tight UF membranes.

A membrane can be defined as a thin barrier which permits selective mass transport, a selective barrier between two phases, and a phase that functions as a barrier that prevents the mass movement but allows a regulated passage of one or more species (Wang et al., 2011). Generally, membrane process involve of two or more operations of separation. A membrane operation can be explained as an operation where a feed stream is divided into two streams (permeate containing material which has passed through the membrane and retentate containing the non-permeating species. The membrane operations can be used to concentrate or to purify a solution or a suspension (solvent-solute or particle separation) and to fractionate a mixture (solute-solute separation).

Additionally, it includes the definition of the permselective membrane and implies that a chemical potential difference exists between two phases. In other words, even if the (permselective) membranes may be characterized by their structures, their performances in term of fluxes and selectivity are mostly dependent on the characteristics of the elements contained in the two phases and on the driving force applied. This becomes the reason on the classification of the membranes according to the types of separation. New examples of materials that have semi-permeable qualities at some scales have been shown through earlier research papers on the polymer and membrane science. However, these potential candidates make it to the commercial environment are limited (Mohanty and Purkait, 2011; Nunes and Peinemann, 2006).

The development of the abundant materials has been carried on after that to improve the ability and performances of the current membrane technology. Generally, polymeric membrane and inorganic membrane are two main categories of the membrane and there are differences between both categories since they are made up from two different materials. Polyamide, polyacrylonitrile, cellulose acetate and polypropylene are the polymeric membranes which are composed from the polymer materials (Coulson and Richadson, 2002). The non-organic (inorganic) such as silica, zirconia, alumina and titania have made up the part of the micro and ultra-membrane. The production of the membrane process occurs through two main techniques: (i) the precipitation of the colloidal metal oxide on a support material such as carbon, (ii) heat exposure process, spray dried oxide microsphere

to the pure ceramic materials. The benefit of using this membrane to be compared to the polymeric membrane is a high temperature stability which contributes to its suitability in the steam sterilization in the biotechnology field, the application in the food technology without changing the physical properties of the membrane and the increase of the resistant to clog and restrict pore distribution.

Other than that, the membranes can also be grouped by nature as biological and synthetic membranes Synthetic polymer has a high chemical stability and better barriers towards the microbial reduction. Synthetic membranes are separated into organics membrane represented by polymeric or liquid, while the inorganic membrane is represented by the ceramic or metal membranes. There are different between biological membrane, which are part of the living organism, and synthetic membranes that are man-made

Biological membranes carry out very complex and specific transport tasks in living organisms for example in kidney and integumentary (skin) system. They accomplish them quickly, efficiently and with minimal energy expenditure, frequently using active transport. Synthetic membranes are not nearly as complicated in their structure or function as biological membranes. They have only passive transport properties and are usually less selective and energy efficient. In general, however, they have significantly higher chemical and mechanical stability, especially at elevated temperature. The selectivity of synthetic membranes is determined by a porous structure according to their size or through a homogeneous structure according to their size or according to the solute solubility and diffusivity. The permeability of the membrane for different components, however, is only one parameter determining the flux through the membrane.
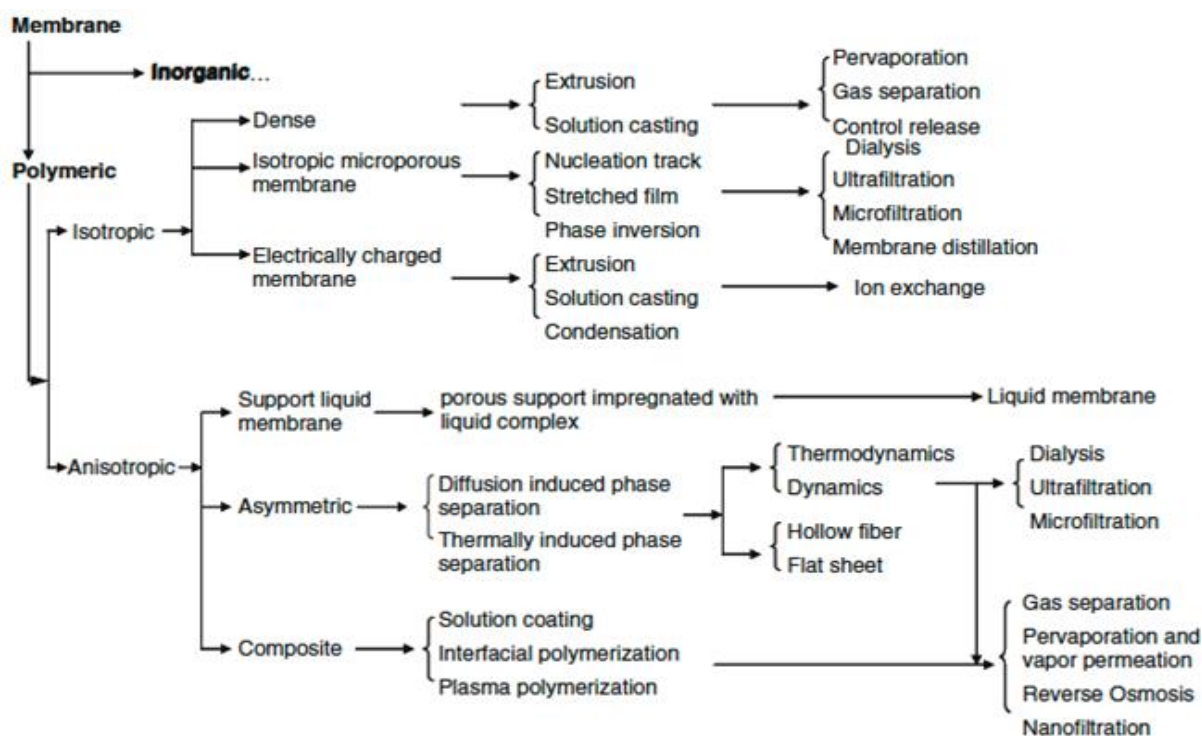
Figure 2.1 Classification of Polymeric Membrane (Wang et al., 2010)

From Figure 2.1, the structural classification actually determines the separation mechanisms and membrane application by categorizing the membranes as symmetric and asymmetric. A membrane which is porous, cylindrical porous and homogeneous (nonporous) can be symmetrical, while a membrane which is porous, porous with the top layer and composite that consists of a porous membrane part and a dense top layer can be asymmetrical. The thickness of the top layer in the asymmetric membranes is 0.1 to 0.5 μm which is supported on a porous sub layer with a thickness of about 50 to 150 μm.

Various polymers and organic materials could yield the hydrophobic and hydrophilic surfaces. There are ways to determine whether a polymer is hydrophillic or hydrophobic. Firstly, determination if a polymer is inherently hydrophillic or hydrophobic by looking at the chemical structure of the polymer repeat unit. Hydrophilic contain polar or charged functional groups, rendering them soluble in water. Functional group that made hydrophilic polymer are hydroxyl, carbonyl or carboxyl meanwhile for hydrophobic polymer which the hydrocarbons without any functional group (C-C) bonds. Polyethylene

oxide (PEO) and crystallizable polyamide, polyurethanes and polyester are made into common commercial hydrophilic copolymers and they make a hydrophobic polymer more hydrophilic. Hydrophobic materials like cellulose esters, PC, polysulfone (PSf), polyethersulfone (PES), poly vinylidene fluoride (PVDF), polyimide (PI), polyetherimide (PEI), aliphatic polyamide (PA) and polyetherketone (PEEK) are also common polymeric materials (Wang et al., 2010; Mulder, 1996).

Among the separation operations, a membrane offers basic advantages in which it takes place at an ambient temperature without the phase change, which offers an energetic advantage to be compared to the distillation. Then, the process will take place without an accumulation of products inside the membrane. Membranes are well-adapted to be run continuously without a regeneration cycle as in the ion-exchange resin operations or without an elution cycle as in the chromatography.

The addition of chemical additives is not needed, as in the case of azeotropic distillation or in the water clarification by settlement or conventional filtration. Because of that, it contributes to the quality of the product and leads to less pollutant wastes, besides explaining the success of pervaporation for the fractionation of azeotropic mixtures and UF for the water clarification.

This membrane system actually gives more economic benefits to be compared to the conventional methods. In addition, there are other advantages of the membrane system which are the flexibility and versatility; in which the technology application has more spectrums of separation ranges than the conventional methods (Mustaffar, 2004). It also can be operated in the combination with the conventional methods or on its own. Moreover, the simplicity of the operation is reflected when the membrane process is relatively less complex and sophisticated.

Due to the low energy consumption, membrane systems consume less energy since the separation does not include the phase change. Thus, the pressure becomes the system driving force for the membrane process. Additionally, the overall membrane system is (30-

CHAPTER 1

INTRODUCTION

1.1   RESEARCH BACKGROUND

Strict enforcement of rule and regulations and the requirement for a reliable potable drinking water supply has increase the interest in the using of membranes in drinking water treatment process. Membrane processes are using pressure as the driving force to separate out contaminant from water supplies. They are new alternative for many unit processes which are currently implemented such as sand filtration, carbon adsorption or ion exchange (Lowe and Hossain, 2008). One particular group of contaminants that is present in water supplies and which has brought about concern in the water industry is humic substances (HS). There are three substances which make up HS and they are humin, humic acid and fulvic acid. NOM is the organic material present in the surface or ground water. NOM interacts with all of the chemical components of natural water; these interactions change the behaviours of the pollutants in the surface and ground water (Sarathy and Mohseni, 2010). NOM in the surface water usually refers to the humic (HA) and fulvic acids (FA) that are decayed by-products of plants such as those found in the surface water. These substances plus the tannic acid are the major fractions of the dissolved organic matter (DOM) in water. These substances are oxidized very slowly and their solubility in water may differ with pH. The dissolved fractions of NOM may not be fully removed using the conventional water treatment practices (i.e. flocculation, coagulations and chlorination) and have been shown to produce carcinogenic by-products such as trihalomethane and haloacetic acid are formed during the disinfection (Lowe and Hossain, 2008). Other conventional methods in removal of HA in drinking water treatment plants are chemical oxidation using chlorination, ozonation, activated carbon adsorption and coagulation (Alborzfar et al., 1998). The organic compounds in the surface water and ground water arise from the natural and anthropogenic sources (i.e. storm water runoff and leaking sewer lines from surrounding land). NOM in water also caused bacterial re-growth in water distribution.

The growth in population and development in urbanization, industrialization and irrigated agriculture cause growing demands and pressure on the water resources, besides contributing to the rising water pollution. The costs are rising and rigorous scrutinization from the environmentalists and conservationists need to be faced because of the new development of water resources. Enforcement from Ministry of Health Malaysia stated that drinking water quality standard for trihalomethane is 1.0 mg/L for maximum acceptable value. This maximum acceptable value must followed by all drinking water manufacturers and suppliers. .HA will form very toxic disinfection byproducts (DBPs); *i.e.* chlorinated organic compounds, for example, trihalomethanes (THMs), which exhibit mutagenic properties during chlorination step in tap or drinking water production or water treatment. The guideline values for DBPs in drinking water announced by the World Health Organization should not exceed 100 μg L (Mahvi et al., 2012). But, reaction of humic acid in surface water can formed trihalomethane, thus greater research efforts being put into the improvement of the membrane processes. Membrane technology can provide a continuous operation and better water quality with the potential to remove the targeted contaminants in one stage. The effective removal of NOM such as humic substances with membranes is a significant challenge in the water industry. Our study emphasize on improvement of filtration system in water treatment process. Conventional method of filtration system consist filters with varying sizes of pores, and is often made up of sand, gravel and charcoals. The diameter of a grain of fine sand is approximately 0.1 millimeters, so only particles with diameters less than 0.1 millimeter would pass through the fine sand layer. This kind of filter would not be able to produce safe drinking water, because many contaminants are much smaller than 0.1 millimeters (i.e humic acid). The surface water treatment with the nanofiltration (NF) membranes has become an attractive alternative to the conventional treatment for the removal of the humic substances.

The NF membrane separation is widely used in the various industrial fields. Water and wastewater treatment are one of the fields that use this kind of technology to treat the water until the water reaches the quality that it can be discharged to the environment or reusable for other processes. This NF is known to have the properties in between the

reverse osmosis (RO) and the ultrafiltration (UF) (Mansourpanah et al., 2010). Because of that, it has the significant advantages including low operation pressure, higher permeation flux, high retention of multivalent salt, compound more than 300 of molecular weight compound, and low investments, operation and maintenance costs (Tang et al., 2008).

NF membrane could be an asymmetric or a thin film composite (TFC) membrane. However, the most commercial available membrane in the market is a TFC membrane produced by the interfacial polymerization (IP) method. IP process is well known as diffusion-control and self-limiting process. Thus, determination extent reaction of IP is major influenced by the reaction time (Ahmad and Ooi, 2005 and Mohammad et al., 2003). When the polymerization time increase, top skin layer thickness of the composite membrane will increases too until polymerization process complete and water flux will constant. Then, short reaction time have low extent of cross-linking is low and the permeability of the membrane is high. However, the membrane surface layer will be improved by increasing of reaction time and the membrane will gradually become integrated. The NF membrane is produced through two preparation steps which are the polymer phase inversion resulting a microporous support membrane and the IP of a TFC layer on top of a microporous support membrane or other porous substrate (Mohammad et al., 2003). The common NF membrane is based on the polyamide (PA) membrane which uses the amine group monomer for IP process. On top of that, there are several research studies focused on other monomers such as bisphenol-A (BPA) in order to produce the polyester NF membrane (Abu Seman et al., 2010; Mohammad et al., 2003; Jayarani and Kulkarni, 2000).

Moreover, IP has significant advantages which involve the rapid reaction rates under the ambient conditions, no requirement for the reactant stoichiometric balance and a low requirement for the reactant purity (Li et al., 2008).The reaction rate of IP is very high, so that reactants diffuse to the interface and combine almost stoichiometrically to form high molecular weight polymer. The high reaction rate is required otherwise diamine will have time to penetrate through the polymer to start new polymer chains in the organic phase. Interfacial polymerization occurs at room temperature. Polymers that are unstable at high

CHAPTER 3

METHODOLOGY

This chapter covers the materials and methods used in the present study. The first part concerns on the IP method and membrane characterization. In the IP method, the formation of the active layer was manipulated by the variation of the monomer concentration and reaction time. The second part describes the direct method used for the morphology studies. For the direct method, FESEM was used to view the membrane structure while ATR-FTIR is used for the surface chemistry characterization, respectively. The last part describes the equipment used in the filtration studies and supporting analytical equipment. Meanwhile, the solutes rejection test was also conducted in order to characterize the membrane by using the solute transport model.

3.1   Materials

The commercial flat sheet UF PES membrane was supplied by AMFOR INC (China) and the membrane details are shown in Table 3. 1. TEOA purchased from R & M Marketing (Essex, UK) was used as an active monomer of aqueous phase. TMC was used as an active monomer of organic phase was obtained from Alfa Aesar (UK). Sodium hydroxide (NaOH) was used as base to be mixed with TEOA purchased from Merck (Germany), while n-hexane was used as the organic phase solvent, which was obtained from Merck (Germany). Glycerol and sodium disulphite were purchased from R & M Marketing (Essex,UK)for membrane preservation. HA was purchased from Sigma Aldrich (Switzerland) to represent NOM in the surface water. Additionally, in structural or charge parameters characterization Vitamin B_{12} and salts (NaCl and Na_2SO_4) were obtained from by Merck (Germany) and Systerm, respectively.

Table 3.1 Properties of UF Membrane (AMFOR INC, CHINA)

| Membrane	UF PES50
Material	PES
Nominal MWCO	50,000 Da
Water flux @ 25°C & 50PSI	260 L/m^2. h^{-1}

3.2   Equipments

3.2.1   Amicon Stirred Cell

For the membrane permeability, fluxes, fouling and rejection study, Amicon Stirred Cell (model 8200, Amicon Inc. USA) was used in this experiment as shown in Figure 3.1. It had the volume capacity of 200 ml and held a membrane disc of 62 mm in diameter with an effective area of 28.7 cm^2. The maximum operating pressure of the cell is 500 kN m^{-2}. The cell is in the cylindrical shape and it has a membrane holder, elastomeric tubing to flow out the permeate, the base (supports membranes holder and body)magnetic stirrer is mounted in a cell, cover the container with cap assembly and pressure relief valve to retain cap assembly that hold the Amicon when the pressure be charged. O-ring gasket made from the silicone was used to hold the membrane and avoid leakage when the pressure was charged.

When the filtration process started, the solution was poured to the cell body until it reached 180 ml. Then, the cap assembly was placed on the body and cell, and mounted inside the stand assembly. This Amicon was used in conjunction with a stirring table. The table was magnetically coupled to a stirring bar, which maintained the fluid movement during the operation, thereby reducing the negative effects of the concentration polarization (i.e. the build-up of the concentrated solutes on the membrane). A magnetic stirrer had been mounted inside and the cell had had the diameter of 48 mm. Pressure relief valve was closed by turning it from the counter clockwise to a vertical position before the experiments started. The cell was allowed to equilibrate at least 10 minutes before conducting any experiment. All of the filtration processes were carried out with 180 ml of feed solution and a stirrer speed of 300 rpm.

After the filtration process had completed, the pressure relief valve was released. The excess pressure inside the cell was released by turning the pressure relief valve to the horizontal position. The cap assembly was removed and conductivity measurement was made by the conductivity meter.
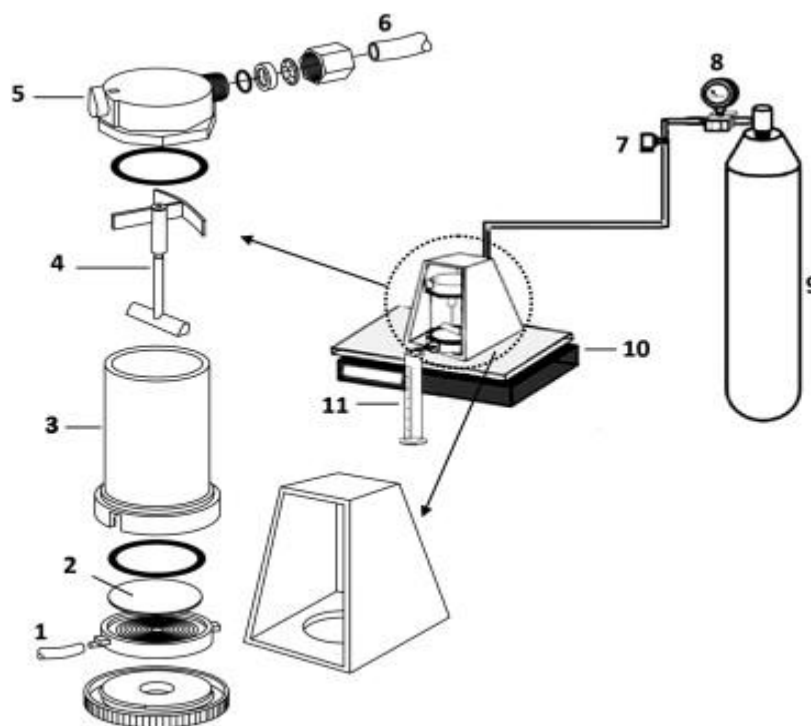
Figure3.1 Amicon stirred celland experimental set-up used for the NF (1) Permeateoutlet, (2) Membrane disc, (3) Body, (4) Stirrer assembly, (5) Pressure relief valve, (6) Nitrogen inlet pressure, (7) Valve, (8)Manometer, (9) Nitrogen cylinder, (10) Magnetic stirrer and(11) graduated cylinder
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