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Membrane Fouling Reduction by the Incorporation of Hydrophilic Surface Modifying Macromolecules in Ultrafiltration Membrane Manufacturing

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MEMBRANE FOULING REDUCTION BY THE INCORPORATION OF HYDROPHILIC SURFACE MODIFYING MACROMOLECULES IN ULTRAFILTRATION MEMBRANE MANUFACTURING

by

Hai Anh Nguyen

M.A.S.c Thesis

Submitted to the School of Graduate Studies and Research

Under the supervision of Dr. Roberto M. Narbaitz

In partial fulfillment of the requirements for the degree of M.A.S.c in Environmental Engineering

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ABSTRACT

Ultrafiltration membranes have been increasingly used for drinking water disinfection and the removal of natural organic matter (NOM) to avoid the formation of toxic disinfection by-products (DBPs). A key feature of membranes is their decreasing water yield with time or fouling. This study investigates polyethersulfone (PES) ultrafiltration membrane surface modification as a fouling reduction strategy for drinking water treatment applications. The key features of our surface modification are the addition of hydrophilic surface modifying macromolecules (LSMMs), specially developed in our lab for this purpose. Flat sheet membranes were prepared with different PES concentrations, polyvinylpyrrolidone (PVP) and with different concentrations of three types of LSMMs (LSMM200, 400, and 600) via a single-step casting process. The surface hydrophilicity of the membranes was quantified via contact angle analysis. Their bench-scale filtration performance was then evaluated using pure water permeation rate monitoring, molecular weight cut-off (MWCO) determinations, and long-term filtration test with Ottawa River Water (ORW). This water was chosen because it is fairly typical of Northern Canadian waters with high NOM content (TOC = 7 mg/l) and color, which also should accelerate fouling and help assess if the modified membranes are better. The surface modification produced slightly more hydrophilic membranes (contact angle reductions of up to 8^{o}) and improved membrane performance. Varying the PES concentration and the presence of PVP did not have a significant impact on LSMM migration. Compared to the unmodified membranes, LSMM200 modified membranes achieved almost the same fluxes with more stable organic removals (the MWCO was reduced by a factor of 2).

LSMM400 and LSMM600 modified membranes achieved up to 33% higher fluxes. The best membrane contained LSMM600; it improved the long-term flux even though it had a smaller MWCO. In all cases, surface modification resulted in significantly decreased flux reductions and NOM deposition, which indicated fouling reduction. Regardless of differences in the MWCOs, dissolved organic carbon (DOC) removals very similar for all types of membranes (ranging from 66 to 74%). These high DOC removals were enhanced by fouling. There was a clear trend of increasing long-term flux and decreasing flux reduction with increasing contact angle. The addition of PVP did not have any significant impact on the modified membranes' characteristics and performance.

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GLOSSARY

a_{PEG}	Stokes radius of PEG (nm)
a_{PEO}	Stokes radius of PEO (nm)
C_f	Feed concentration (mass/volume)
$C_{p(t)}$	Permeate concentration at time t (mass/volume)
d_p	Pore diameter (nm)
f_i	Fraction of pores with diameter d_i (dimensionless)
J	Total flux (m^3/m^2-s)
J_i	Solvent flux for pores with diameter d_i (m^3/m^2-s)
N	Number of pores per unit area
N_i	Density of pores with diameter d_i (dimensionless)
$PR_{(t)}$	Permeate flux (product rate) of ORW at time t ($l/m^2.h$)
ΔP	Pressure difference across the pores (Pa)
S	Surface porosity (%)
T_g	Glass transition temperature (^oC)
δ	Length of the pores, considered equivalent to the thickness of the skin layer (no tortuosity) (m)
η	Solvent viscosity ($N\text{-}s/m^2$)
μ_p	Geometric mean of the pore diameter (dimensionless)
σ_p	Geometric standard deviation (dimensionless)

Abbreviations

AFM	Atomic Force Microscopy
BA-L	Oligomeric fluoroalcohols
Cl_2	Chlorine
D/DBPs	Disinfectant/Disinfectant-by-products
DBPs	Disinfection by-products DBPs
DEG	Diethylene glycol

DMAC	N,N-dimethylacetamide
DOC	Dissovled Organic Carbon
DPS	Hydroxyl diphenyl sulfone
DSC	Differential scanning calorimetry
ED	Electrodialysis
EDR	Electrodialysis reversal
FTIR	Fourier transform infrared
HAA	Haloacetic acids
HDI	Hexamethylene diisocynate
LSMMs	Hydrophilic Surface Modifying Macromolecules
MDI	Methylene bis-p- phenyl diisocyanate
MF	Microfiltration
MW	Molecular weight
MWCO	Molecular Weight Cut-off
NF	Nanofiltration
NMP	N-methyl pyrrolidone
NOM	Natural organic matter
ORW	Ottawa River Water
PA	Polyamide
PAN	Polyacrylonitrile
PC	Polycarbonate
PCL	Polycaprolactone diol
PEG	Polyethylene glycol
PEO	Polyethylene oxide
PES	Polyethersulfone
PP	Polypropylene
PPO	Polypropylene diol
PS	Polysulfone
PTFE	Polytetrafluoroethylene
PTMO	Polytetramethylene oxide
PVDF	Poly(vinylidene-fluoroethylene)

PVP	Polyvinylpyrrolidone
PWP	Pure Water Permeation
RO	Reverse osmosis
SEM	Scanning Electron Microscopy
SMMs	Surface modifying macromolecules
TDS	Total dissolved solids
THMs	Trihalomethanes
TOC	Total organic carbon
UF	Ultrafiltration
VOCs	Volatile organic compounds
XPS	X-ray photoelectron spectroscopy

CHAPTER 1

INTRODUCTION

1.1 Background

Membranes have been increasingly used in water treatment to comply with stringent laws on water quality. Besides desalination, membranes are used to remove microorganisms, particles, hardness and natural organic matter (NOM). NOM removal from surface waters is especially critical to drinking water treatment because NOM reacts with chemical disinfectants to form toxic disinfection by-products (DBPs). In general, membrane treatment has many advantages over conventional water treatment processes. Their key advantages are: limited use of chemicals, disinfection without forming DBPs, more reliable viruses and protozoa removal, lower operational requirements, lower space requirements, and potential for fully automated operation. However, one of the disadvantages of membranes is fouling, which results in a decrease in the permeate flux (i.e. the amount of water produced per unit area) with time. One of the important foulants in drinking water treatment is NOM (Amy et al., 2001). There have been many initiatives to reduce membrane fouling via different approaches, such as pretreating the feed solution, optimizing system operation, optimizing flow configuration within the membrane systems, cleaning fouled membranes, and changing membrane properties (Mulder, 1996).

For the past twelve years, our research group (Dr. Paul Santere at the University of Toronto, Dr. Takeshi Matsuura, Dr. Roberto Narbaitz and collaborators at the University of Ottawa) has been developing tailor-made surface modifying macromolecules to act as

additives in the manufacturing of polyethersulfone (PES) membranes. During membrane manufacturing process, due to the surface energy properties of these additives, these polymers migrate to the membrane surface, creating surface modified membranes, which should be less susceptible to fouling. For the first ten years, the work concentrated on hydrophobic surface modifying macromolecules (SMMs). The surface modified membranes have demonstrated to have somewhat better performance in the separation of volatile organic compounds (VOCs) from aqueous solutions via pervaporation (Fang et al., 1994; Mahmud et al., 2001), for ethanol and water separation (Minnery, 2000); ultrafiltration of oil/water emulsions (Hamza et al., 1997); biomedical ultrafiltration and microfiltration applications (Ho et al., 2000). One of the main advantages of this new technology is that the PES-SMM membranes have superior strength and perform for much longer than PES membranes (Suk et al., 2002b). However, the addition of hydrophobic SMM did not result in a significant impact on NOM fouling reduction (Mosqueda-Jimenez et al., 2004c). This was not totally surprising given that in general fouling resistance increases with membrane surface hydrophilicity.

1.2 Objectives

This thesis approaches fouling reduction by modifying PES membranes to make them more hydrophilic by the addition of hydrophilic **S**urface **M**odifying **M**acromolecules (LSMMs).

Therefore it is hypothesized that the use of LSMMs will alter polyethersulfone (PES) surface characteristics that will reduce membrane susceptibility to fouling and improve membrane performance.

The specific objectives of this thesis are:

- To evaluate the effect of LSMM type and concentration on their migration to the membrane surface.
- To analyze the incorporation of LSMMs and surface hydrophilicity on:
    - The final characteristics of the membrane, and
    - The membrane performance including fouling reduction.

This thesis is organized as a paper-format thesis; the main results, presented in Chapter 4 and 5, were prepared in a journal manuscript format.

CHAPTER 2

LITERATURE REVIEW

The following literature review will discuss current problems in drinking water treatment, membrane applications in water treatment, ultrafiltration, membrane fouling, and surface-modified membranes.

2.1 Current problems in drinking water treatment

In the last century, there have been vast developments of all types of technology; and drinking water treatment technology has been no exception. Still, in the quest for a better quality product, many more issues on water treatment have been identified.

With the population growth, there is a greater need for water. The water quality from new sources (to satisfy the additional demand) tends to be of lower quality so it requires the use of more expensive treatment technology to make it meet health standards. The conventional methods with chemical flocculation, filtration, and chemical disinfection create toxic disinfection by-products (DBPs). Moreover, even with chemical disinfection, a large number of waterborne outbreaks were still reported. Between 1972 and 1981, 50 waterborne outbreak of Giardia involving 20,000 cases were reported in the US. In 1993, approximate 403,000 became ill during a Cryptosporidiosis outbreak in Milwaukee, Wisconsin (USEPA, 2001). The following subsection will discuss more in detail the microbial threats and the formation of DBPs.

2.1.1 The microbial threats

During the early part of the twentieth-century, there were remarkable achievements in water treatment. Many typical acute waterborne diseases were virtually eliminated with the application of filtration and chlorination. However, waterborne diseases continue to occur. In 1990, the USEPA Science Advisory Board concluded that exposure to microbial contaminants was likely the greatest remaining health risk associated with drinking water supply (USEPA, 2001). Between 1980 and 1996, more than 500,000 waterborne disease cases were reported in the United States, and it is suspected that there were many more unreported cases (Pontius and Clark, 1999). A number of responsible microorganisms included bacteria, protozoa and viruses including pathogenic Escherichia coli, Helicobacter pylori, Giardia lamblia, Cryptosporidium parvum, Hepatitis A, and Rotavirus. In Canada, the most recent outbreak happened in Walkerton in May, 2000 where 7 people died and over 2,000 became ill as a result of E. Coli 0157 contamination of the drinking water system.

In general, chemical disinfection is able to inactivate almost all microorganisms. However, a number of cyst forming bacteria and protozoa (Giardia lamblia and cryptosporidium parvum) is quite resistant to chlorine. To control many of the latter, it is necessary to increase in the dose of disinfectant added and the contact time.

2.1.2 The formation of disinfection by-products

DBPs are formed when chemical disinfectants react with organic matters present in water. The principal type of organics in waters used to create drinking water are mixtures referred to as natural organic matter (NOM), and because of their role in the above

reaction, they are also called DBP precursors. NOM is frequently quantified in terms of total organic carbon (TOC) concentrations, and surface waters generally have TOC concentrations ranging from 1 to 20 mg/l, while ground waters generally have TOC concentrations below 2 mg/l (Montgomery, 2005).

NOM comprise mainly of fulvic acid (~40%), humic acid (~10%), hydrophilic acids (~30%) and other substances (~20%) (Schafer, 2001). It is formed from the chemical and biological degradation of plant and animal residues (Montogomery, 1985). The origin of NOM in a surface water depends on the origin of the water and the environment surrounding the water. NOM from different water sources, therefore, varies in characteristics, concentration, and molecular weight, which lead to different treatment approaches.

The use of disinfectants such as chlorine and ozone, although inactivates pathogens and reduce the risk of water born diseases, creates toxic DBPs. Epidemiological studies have shown some adverse impacts of DBPs include cancer, cardiovascular diseases, and adverse reproductive outcomes such as neural birth defects (Pontius and Clark, 1999).

Depending on the types of disinfectants used, different types of DBPs are formed. With chlorine (Cl_2), the major concerns are chlorinated by-productss. Among of which, trihalomethanes (THMs) and haloacetic acids (HAA) occur most consistently and have the highest concentrations (Cohn et al., 1999). With ozone, the major concern is the formation of bromoform and bromate (BrO_3^-) when bromite ions are present in the water source. Alternative disinfectant such as chloramines, chlorine dioxide can also react with source water organics to form other organic by-products at lower concentrations. Due to

its low cost, chlorine or hypochlorite by far is the most popular disinfectant; it is in use in more than 90% water treatment plants in the United States (Haas, 1999). Even if not used as the main disinfectant, chlorine is still added after disinfection to maintain a residual throughout the distribution system. Since many DBP formation reactions are very slow, many of the DBPs are actually formed within the distribution system via reactions involving the chlorine residual. Thus, it is important to remove as much NOM as economically feasible prior to residual chlorination.

Due to the high health risk and the toxicity of DBPs, in 1998, USEPA finalized the Disinfectant/Disinfectant-by-products (D/DBPs) rules which require water treatment plants to achieve new limits of DBPs and certain percent reductions of TOC prior to disinfection. The D/DBPs rule was promulgated into two stages. Stage 1 D/DBPs balancing the risks between microbial pathogens and DBPs became effective for all U.S community water systems in January 2004. Phase I of stage 2 required all water treatment plants to comply with local running annual average of 120 and 100 μg/l for THMs and HAA respectively at each monitoring locations in stage one D/DBPs rule. Phase II of stage 2 promulgated a lower value of 80 and 60 μg/l for THMs and HAA, respectively at new monitoring locations representative of long residence times and high DBPs concentrations (USEPA, 2001). These stricter rules put pressure on water treatment plants to reduce DBPs concentrations.

2.1.3 Microbial versus DBP risks

The higher disinfectant doses and longer contact times within the plant in order to inactivate some resistant protozoa and microorganisms have increased the formation of

disinfection by-products (DBPs) in the plant and within the distribution systems. Thus, using alternative disinfectants, removing NOMs or delaying the contact of NOM with disinfectant are crucial in controlling the formation of DBPs.

The competing risks of microbial threats and the formation of DBPs set new challenges for water engineers. In the effort to resolve the two problems, membranes have been considered to be a good candidate. Membranes are physical barriers capable of separating materials and particles (such as microorganisms), so they can disinfect without adding chemical disinfectants and do not form any DBPs. In addition, some membranes can achieve substantial NOM removal and thus reduce DBP formation associated with residual chlorination. Membranes have many advantages over conventional water treatment processes. A key advantage of membrane water treatment units is that they can consistently produce excellent quality water regardless of the water quality variations of the raw water while in conventional water treatment plants, the quality of the water produced is a function of the raw water quality. In addition, membrane units are more compact, require lower energy than conventional water treatment units, and capable of automation. In the long run, membranes might be the proactive approach to deal with potentially stricter water quality laws.

2.2 Membrane processes

Mallevialle et al. (1996) defined membranes as physical barriers capable of separating materials as a function of their physical and chemical properties when a driving force is applied across the membrane. Depending on the types of membranes, the driving forces can be the gradient of pressure, such as in microfiltration (MF), ultrafiltration (UF),

nanofiltration (NF), and reverse osmosis (RO); while in electrical dialysis, the driving force is an electrical potential. The membrane's material and structure characteristics are the principal factors determining whether it will separate a given particle or contaminant.

Although observations of membrane phenomena started in the late 19^{th} century, the application of membrane processes at the laboratory scale did not start until early 1920s and this was solely used for the development of physical/chemical theories of membrane processes (Baker, 2004). The first industrial-scale membrane application was in 1955 in the USA to desalt brackish water (Mulder, 1996).

The development of asymmetric membranes in the early 1960s consisting of a very thin dense toplayer (thickness < 0.5 μm) supported by a porous sublayer (thickness 50-200 μm) (Mulder, 1996) was a breakthrough in industrial membrane applications. The top layer determines the transport rate, which is inversely proportional to its thickness, while the supporting layer acts more like a mechanical support and possesses negligible resistance to mass transfer.

Later, in 1972, another type of asymmetric membranes with a top layer originating from different polymeric materials to that of the support layer was developed (Matsuura, 1994). They are called composite membranes. Composite membranes have the advantage of optimizing each layer separately but also are more complicated to manufacture. Figure 2.1 presents schematic drawings of asymmetric and composite membranes. More details in asymmetric membrane materials and their preparation will be presented in section 2.2.2.

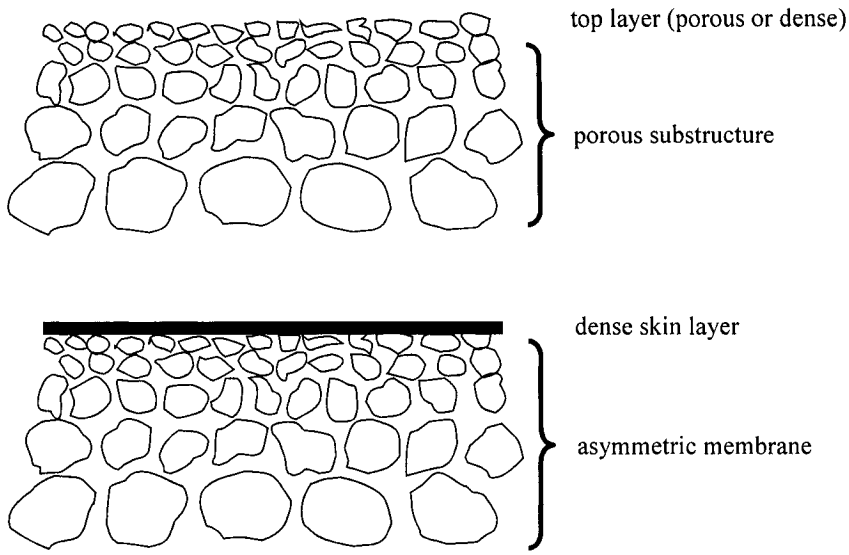


Figure 2.1 Schematic drawing of an asymmetric membrane and a composite membrane (Aptel and Buckley, 1996)

The following subsection discusses in more details the membrane processes employed in drinking water treatment.

2.2.1 Membrane processes in drinking water treatment

In addition to some electrodialysis (ED) units, several pressure-driven membrane types are used in water treatment: reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF), presented in Figure 2.2. Table 2.1 summarizes membrane processes used in water treatment with values of operating pressure ranges, fluxes, and applications, etc.

MF has the largest pore size, ranging from 0.1 μm to several μm. MF therefore can just remove large particulates (turbidity, microorganisms including Giardia and Cryptosporidium protozoa, bacteria, and under some circumstances, viruses). MF has operating pressure ranging from 30 to 210 kPa (5 to 30 psig).

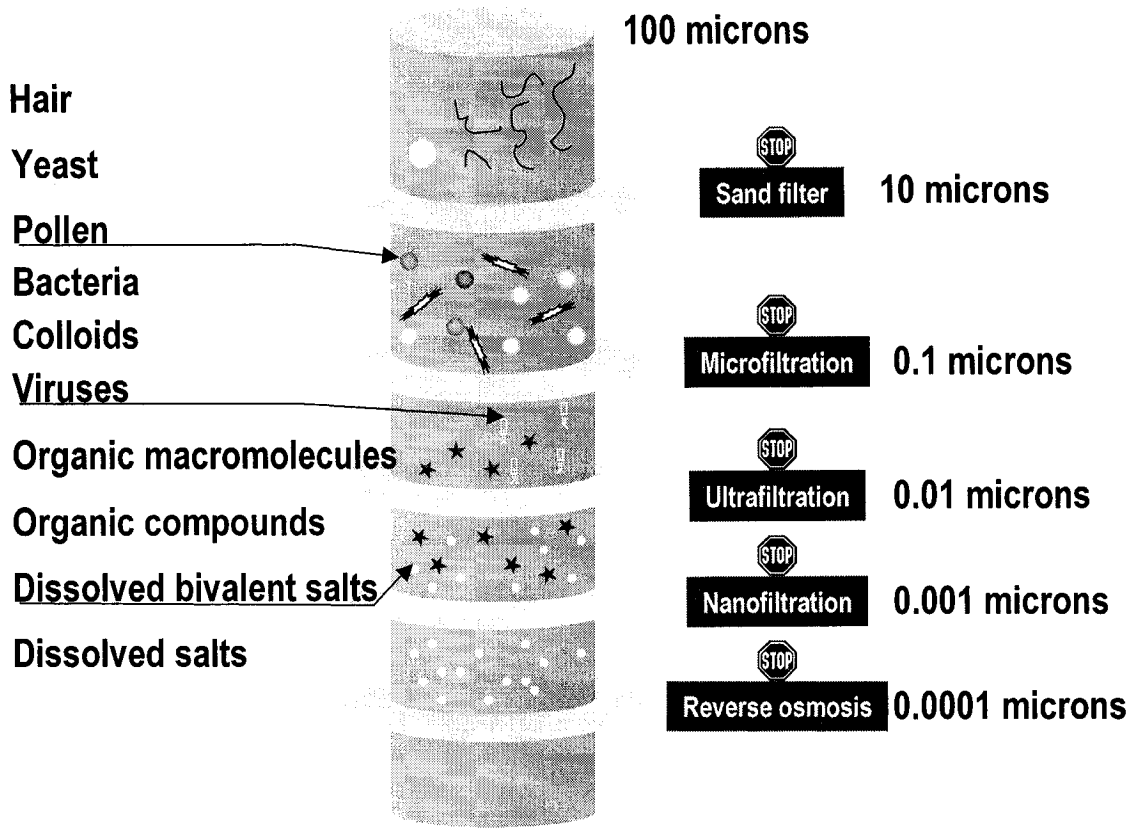


Figure 2.2 Ranges of separation (Buckley and Hurt, 1996)

UF membranes have smaller pore sizes than those of MF, ranging from 1 to 100 nm. In addition to removing large particulates as MF, ultrafiltration membranes are also used for the separation and concentration of macromolecules and colloidal particles. Aptel and Buckley (1996) defined UF as a clarification and disinfection membrane operation in water treatment. UF operating pressures range from 140 to 520 kPa (20 to 75 psig). UF membranes are primarily prepared from polymeric materials such as polysulfone (PS), polyethersulfone (PES), polyacrylonitrile (PAN), and cellulosic polymers.

Table 2.1 Summary of the membrane operations in water treatment (after Mosqueda-Jimenez, 2003)

Membrane operation	Driving force	Flux (LMH = L/m^2-h) (gfd = gal/ft^2-day)[b]	Pores	Molecular Weight Cut-off[h]	Water Treatment Application	Capacity of largest facility
Microfiltration	Pressure difference 34 – 207 kPa (5 – 30 psi[a]) 69 – 345 kPa (10 – 50 psi[b])	170 – 1700 LMH 100 – 1000 gfd[b]	>50 nm[c]	> 500,000 MW[d]	Sterile filtration clarification[c]	0.9 m^3/s (21 mgd) Chester, GB
Ultrafiltration	Pressure difference 138 – 517 kPa (20 – 75 psi[a]) 345 – 689 kPa (50 – 100 psi[b])	35 – 160 LMH 20 – 300 gfd[b]	2 – 50 nm[c]	> 5,000 MW[d]	Macromolecules and all types of microorganisms and particles[c]	1.1 m^3/s (25 mgd) Olivenhain, CA
Nanofiltration	Pressure difference 345 – 862 kPa (50 – 125 psi[a]) 689 – 1379 kPa (100 – 200 psi[b])	25 – 40 LMH 15 – 25 gfd[b]	< 2 nm[c]	> 400 MW[a]	Softening operations and NOM control[c]	1.8 m^3/s (40 mgd) Boca Raton, FL
Reverse osmosis	Pressure difference 689 - 8271 kPa (100 – 1200 psi[a]) 1379 – 4136 kPa (200 – 600 psi[b])	5 – 35 LMH 3 – 20 gfd[b]	Dense media[e]	> 50 MW[d]	Desalination and many low molecular-weight organics removal[c]	1.1 m^3/s 24 mgd Jubail, Saudi Arabia[g]
Pervaporation	Activity (partial pressure)[c]		>50 nm[c]		VOC removal from water and wastewater[f]	Experimental/ Bench Scale
Membrane stripping	Activity (partial pressure)[c]		>50 nm[c]		Radon removal[f] VOC removal	Experimental/ Bench Scale

[a] Bergman and Lozier, (1993)
[b] Taylor et al. (1989)
[c] Aptel and Bucley (1996)
[d] Lonsdale (1986)
[e] Dense media, the diffusion of species takes place in the free volume that is present between the macromolecular chains of the membrane material.
[f] Aptel and Semmens (1996)
[g] Dupont (1995)
[h] Molecular Weight Cut-off (MWCO): smallest molecular weight species for which the membrane has more than 90% rejection.

NF membranes have pore sizes ranging between those of RO and UF. NF is used for the removal of multivalent ions (calcium and magnesium) in softening operations and recently in the removal of NOM. NF systems have operating pressures ranging from 340 to 860 kPa (50 to 125 psig).

Of all the above membranes, RO are the tightest membranes with pore radius smaller than 1 nm (Matsuura, 1994). Water molecules with radius about one tenth of 1 nm can pass through RO membranes freely but electrolyte solutes cannot due to the preferential sorption of water molecules at the solvent-membrane interface, which is responsible for the separation. Cellulose acetate and aromatic polyamide are typically used in the preparation of reverse osmosis membranes. RO are mostly used in desalination of brackish and seawater. The operating pressure typically ranges from 689 to 4136 kPa (100 to 600 psi) when treating fresh or brackish water (total dissolved solids (TDS) up to about 10,000 mg/L) and from 5514 to 8271 kPa (800 to 1,200 psi) for seawater desalting applications (TDS > 35,000 to 45,000 mg/L). RO is also used to produce ultrapure water for the manufacture of semiconductors.

Other than pressure driven membranes, electrical potential driven membranes such as ED or electrodialysis reversal (EDR) are also used in water treatment. In ED and EDR, it is the electrical potential that induces ions to pass through anion and cation permeable membranes, leaving a demineralised dilute stream.

Pervaporation, whose driving force is the activity difference across the membrane, is another process increasingly used for the dehydration of alcoholic azeotropes and

recently for the removal of VOC from drinking water and wastewater (Aptel and Buckley, 1996).

The next section will discuss more in detail about membrane materials and preparation.

2.2.2 Membrane preparation and materials

Membrane can be made from a wide range of different materials and can be divided into two groups: inorganic and organic (polymeric). Organic membranes are far more commonly used than inorganic membranes.

Currently, there are four main types of membranes based on their base materials. They are ceramic membranes, glass membranes, metallic membranes (including carbon) and zeolitic membranes. Ceramic membranes formed by the combination of a metal (aluminium, xirconium, or titanium) with a non-metal (in the form of oxides, nitrides, or carbides) are presently the main class of inorganic membranes (Mulder, 1996). Although inorganic membranes generally possess superior chemical and thermal stability relative to polymeric membranes, they are less popular due to their high cost and brittleness.

For organic (polymeric) membrane, the choice of a membrane polymer is not arbitrary, but rather based on very specific properties, originating from structural factors (Mulder, 1996). According to Zeman and Zedney (1996), polymers are chosen for membrane manufacturing generally possess the following characteristics:

i) It must have suitable properties for the targeted applications. For example, cellulose-type polymers are usually chosen for biotechnology applications due to their low protein binding characteristics.

ii) The polymer has to be compatible with the selected membrane formation technology. For instance, in immersion or air casting, the polymer has to be soluble in a practical and safe solvent.

iii) It has to be readily available and affordable and with constant characteristics to maintain a constant quality and supplies.

iv) It has to be a good membrane former. New developed membrane polymers should outperform a comparable product made from established polymers.

Polymers used in MF membrane manufacturing are crystalline polymers, which exhibite good thermal and chemical resistance. Mulder (1996) presented a list of polymers usually used in MF manufacturing including polycarbonate (PC), poly(vinylidene-fluoroethylene) (PVDF), polytetrafluoroethylene (PTFE), polypropylene (PP), polyamide (PA), cellulose-esters, polysulfone (PS), poly(ether-imide), polyetheretherketone. Among these relatively hydrophobic materials, PTFE, PP, PVDF are used more often. PTFE is highly crystalline and exhibits excellent thermal stability and chemical resistance. PVDF also shows good thermal and chemical (including chlorine) resistance, but not as good as PTFE.

Despite some of the advantages of hydrophobic polymers, hydrophilic polymers are used more frequently because of their lower adsorption tendencies or reduced fouling. The best-known hydrophilic polymers are cellulose and its derivatives. They are relatively resistant to temperature, to biological degradation and to chlorine, but very sensitive to acid or alkaline hydrolysis. However, aromatic polyamides are preferred because of their

outstanding mechanical, thermal, chemical and hydrolytic stability but their free chlorine tolerance is almost zero (Cheryan, 1986).

Polymers used for UF membranes are very similar to those used in MF membrane manufacturing. However, due to their smaller pore size, UF membranes are generally prepared by the phase inversion technique, (as opposed sintering, track-etching used in MF manufacturing). Polymers used in UF membrane manufacturing are therefore generally amorphous polymers because they facilitate generating, regulating, and controlling the size of small pores. A very important class of polymers consists of polysulfones (PS) and polyethersulfones (PES), which are not only used as basic materials for UF membranes but also as support materials for composite membranes. These polymers possess very good chemical and thermal stability indicated by their glass transition temperature (PS: T_g = 190° C, PES: T_g = 230° C). PS polymers are more hydrophobic and more suitable when mechanical strength and thermal stability are prime requirements, since water molecules act as plasticizers for hydrophilic materials. PS, however, has low pressure limit and thus can only be used to prepare membranes operating at low pressure such as MF or UF membranes.

PES is slightly more hydrophilic than PS and possesses higher glass transition temperature. PES also shows high compatibility with other polymers (Zeman and Zedney, 1996). Esters, ketones, polar aromatic solvents, and methylene chloride attack PES, however, it has good resistance to inorganic chemicals, oils, greases, aliphatic hydrocarbons and gasoline (Minnery, 2000). PES can withstand chlorine contact to 200mg/l for short period of time for cleaning, pH values between 1 to 13 and temperature up to 75°C (Montgomery, 2005). In addition, PES is commercially available and

relatively inexpensive. Thus, PES is the most widely used polymers for manufacturing UF membranes (Hamza et al., 1997). However, due to its hydrophobic characteristics, membranes manufactured from PES are easily fouled (Wavhal and Fisher, 2002).

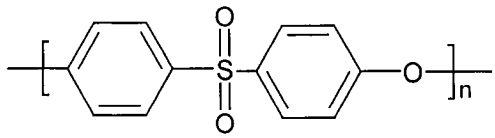


Figure 2.3 Chemical structure of PES

Depending on the material used and the desired membrane structure, a preparation technique would be chosen. The available methods are sintering, stretching, track-etching, phase inversion, sol-gel process, vapour deposition and solution coating. Sintering, stretching, track-etching are only used to prepare MF membranes because these methods can just produce membranes with large pore sizes. Stretching method can produce very porous membranes (up to 90%) but can be applied to only (semi) crystalline polymeric materials. Track-etching can produce membranes with uniform dimension but the membrane porosity is very low (less than 10%) (Mulder, 1996). The most popular method is phase inversion because it allows the generation of all kinds of morphologies. Most commercially available membranes are obtained from phase inversion (Mulder, 1996). Coating is also popular and used to produce composite membranes. The phase inversion and methods used in manufacturing composite membranes can produce membranes with active dense top layers. This thesis will focus on discussing these two methods.

Mulder (1996) explained that in the phase inversion technique, a polymer is transformed from a liquid to a solid state in a controlled manner. The process of solidification or gelation is initiated by the transition from one liquid state into two liquids (liquid-liquid demixing). At a certain stage, during demixing, one liquid phase (the high polymer concentration phase) solidifies and forms a solid matrix. By controlling the initial stage of the phase transition, membrane morphology can be controlled. Matsuura (1994) described the method as followed: a polymer is dissolved in a solvent and the polymer solvent is cast on a suitable support, for example a glass plate. The solvent is allowed to evaporate at the surface increasing the polymer concentration at the solution/air interface, thus the polymer forms the skin layer. The concept of phase inversion covers a range of different variations including solvent evaporation, precipitation by controlled evaporation, thermal precipitation, precipitation by vapor phase, and immersion precipitation. The first three methods are dry methods where the casting solution containing base polymer and a solvent is diluted and the solvent is allowed to evaporate completely (Kesting, 1985). Immersion precipitation is the most popular method and it is used to produce most commercial membranes (Mulder, 1996). The other techniques are sometimes incorporated in immersion precipitation, i.e., solvent evaporation or controlled evaporation is first introduced, followed by immersion precipitation to produce membranes with smaller pore size. Matsuura (1994) described how to prepare an asymmetric membrane by incorporating several techniques. First, a polymer solution containing base polymer (and possibly some additives) and solvent is prepared. Then, a film is cast on a glass plate followed by an evaporation step where solvent is allowed to evaporate partially. The glass plate then is immersed into ice-cold water, which causes

gelation to occur. The film detaches from the glass plate within a few minutes. After one hour standing in cold water, the film is subjected to post treatment by gradually increasing the water temperature to about 80^{o} C and holding for ten minutes before the water is cooled rapidly. Pressure treatment may also follow. The post treatment would decrease pore size and porosity. Immersion precipitation is a wet method and the membranes have to be kept wet all the time or have to be dried by a special method. During gelation, water diffuses out and solvent diffuses in. Water therefore forms an integral part of the membrane and if it evaporates in the air, the asymmetric porous structures would collapse due to capillary forces generated during drying. Commercial membranes are dried before shipping.

As described above, it is evident that there are many variables involved in the immersion precipitation technique including casting solution composition, solvent evaporation temperature, evaporation period, nature and temperature of the gelation media (Matsuura, 1994). By controlling these factors, membranes with different pore size, pore structure and morphologies can be prepared.

While the above asymmetric membranes are prepared from the same material, composite membranes, on the other hand, have the top layer and the support layer consisting of different materials (figure 2.1). Usually, the support layer is prepared by phase inversion technique while several methods are available to apply an (ultra)thin top layer upon the support. The main methods are lamination, dip coating, plasma coating, and in-situ polymerization.

The first type of composite membranes was prepared by spreading a thin layer of a very dilute polymer solution on a liquid (water or mercury). The solvent was allowed to evaporate to form a very thin polymeric film. The porous substrate was then placed carefully below this thin top layer. As can be seen from the above description, this lamination technique is not suitable for large-scale production.

Dip-coating is a simple method; usually used in the preparation of RO, gas separation and pervaporation membranes. The substrate is dip-coated in a polymer, monomer or prepolymer solution (the concentration is usually less than 1%), followed by curing with heat or radiation (Mulder, 1996). The solution is therefore must not dissolve the substrate. This is a disadvantage which somehow limits the use of dip-coating.

In plasma coating, plasma is obtained by the ionization of a gas by means of a high frequency (up to 10 MHz) electrical discharge (Mulder, 1996). Plasma reactions include polymerization, depolymerization and modification of functional groups. A very thin layer with a thickness in the range of 50 nm can be obtained. To control the thickness of the coating, the concentration of the monomer in the reactor must be carefully monitored. Thicknesses can also be altered by changing the polymerization time, gas flow and pressure, and electrical discharge frequency.

In in-situ polymerization or interfacial polymerization, a polymerization reaction occurs between two very reactive monomers (or one pre-polymer, for example hexanediamine, octanedicarbonyl chloride) at the interface of two immiscible solvents. Heat treatment is often applied to complete the interfacial reaction and to crosslink the water-soluble monomer or prepolymer. The first polymerized layer offers a great resistance to the

diffusion of the reactants, causing the formation of an extremely thin film (Aptel and Buckley, 1996).

As can be seen from the above description, composite membranes have the advantage of optimizing separately the substrate and the top layer. However, the techniques are much more complicated than the phase inversion technique. Ideally, changing the top dense layer of asymmetric layer without applying complicated treatment would tremendously reduce the cost of asymmetric membranes.

2.3 Ultrafiltration membrane performance

This section discuss in detail about UF membranes, process design, their application, especially in drinking water treatment.

As mentioned in section 2.1, UF membranes are capable of separating microorganisms, such as protozoa (Giardia and Crypstosporidium), bacteria, and viruses. UF membranes operate within the 20 to 75 psig pressure range, producing fluxes ranging from 9.4 to 37.7 x 10^{-6} m^3/m^2-s (20 to 80 gfd or 36 to 126 l/m^2.h) (Singh, 1997). Other factors of concerned are average pore size (1 to 100 nm), MWCO (in the range of 5000 to 500,000 Dalton), porosity, etc. Rejection in UF membranes, however, is not simply due to a sieving mechanism but rather a combination of physical rejection (i.e., sieving) and membrane-solute interaction. In many cases, the particles to be separated are adsorbed onto the surface of the pores, resulting in a significant reduction in pore size (Matsuura, 1994). For that reason, membrane rejection characteristics are often assessed through challenge studies in which the ability of a membrane to reject a specific contaminant is demonstrated. In this manner, the actual exclusion characteristic of the membrane is

empirically determined and accounts for all of the factors that impact performance (USEPA, 2001).

Materials used for UF membrane preparation are PS, PES, PAN, PVDF, cellulosic polymers, as well as inorganic materials. Most polymeric UF membranes are prepared by the phase inversion technique.

In industrial application, there are four basic designs of UF equipment: tubular, hollow fibers, plate and frame units and spiral wound modules. Most commercially available MF and UF membranes currently used for drinking water treatment are constructed in the hollow fibre configuration (USEPA, 2001) due to its high flux/surface area ratio and it permits hydraulic backflushing to reduce the impact of fouling.

Cheryan (1986) listed laboratory-scale apparatus used for testing UF membranes as being dead-end cells, stirred UF cells, or thin-channel devices. Dead-end cells have almost no polarization control and only suitable for separating very dilute solutions of macromolecules in small volumes. Stirred cells (such as Amicon stirred batch UF cells) are most popular, they are also used in studying UF membrane fouling. Thin channel devices include cross-flow cells such as Millipore's MiniTan cells, Millipore's cells and Osmonic's SEPA cells, which are also used in UF fouling evaluations (Mosqueda-Jimenez et al., 2004a).

UF membranes are used in many industrial applications including textile industry, food industry, diary processing, biotechnology, medical and therapeutic, wastewater treatment. The use of UF in drinking water treatment has received a lot of attention recently.

2.3.1 Ultrafiltration in municipal drinking water treatment and NOM removal

The use of UF membranes instead of conventional chemical coagulation, filtration and disinfection in drinking water treatment has proven to have many advantages, especially in the removal of pathogens and NOM. MF and UF membranes can achieve up to 7 log removal of pathogens and particles. USEPA (2001) listed 120 membrane-based drinking water treatment plants in the United States, of these 27% use UF membranes to remove pathogens. These are loose UF membranes with MWCO ranging from 100,000 to 500,000 Daltons (USEPA, 2001). In addition to removing pathogens, UF membranes can remove a fraction of NOM as opposed to MF membranes, which are used mainly to remove particles and pathogens. The mean capacity of these water treatment plants is 6500 m^3/d (1.71 MGD). Most of the membranes were provided by five main manufacturers including Aquasource, Koch, Pal, US Filter and Zenon (USEPA, 2001).

NF and some UF membranes are used increasingly to remove NOM thus avoiding the formation of DBPs. Thorsen (1999) described how the use of membranes in removing NOM increased, especially in northern countries including Northern America, Northern Great Britain, Scandinavia, Russia and Norway where organics are the main cause of the brownish color of the water. By 1996, the number of plants especially for removal of humic substances worldwide was estimated to about 50, most of them in Norway (Thorsen, 1999). Thorsen (1999) estimated that by 1999 there were 110 plants utilizing membranes for colour removal (including UF and/or NF membranes); about 70% of these plants were located in Norway and the rest in Scotland and Sweden.

Pilot studies and full-scale units have demonstrated that NF membranes may achieve NOM removals greater than 90% (see Table 2.2). However, NF membranes have lower fluxes and require higher operating pressures. The possibility of replacing them by UF that has higher water production rates and lower operating pressure seems very attractive. Recently, Osmonics introduced a new series of UF elements (thin-film membranes), specially designed to be used in colour and/or TOC reduction. Table 2.4 presents the performance claims made by Osmonics with up to 93% removal. However, their fluxes are very low (ranging from 7 to 26 $l/m^2.h$) with TOC removals ranging from 70 to 93%. However, published results of pilot studies with other types of UF membranes have generally shown NOM removals of less than 50% (see Table 2.3), when they are not combined with some kind of pretreatment. If pre-treatment (coagulation or PAC) is combined, removal rates of almost 90% may be achieved (Jacangelo et al., 1994). The use of additional treatment however has additional costs plus additional waste material (i.e., sludge). In addition, the use of pre-treatment though increases removal, may also have a negative impact on membrane performance. Li and Chen (2004) found that PAC enhance the organic removal but at the same time increase membrane fouling.

The use of UF in NOM removal is especially hindered because of the decline of flux with time or fouling. This thesis concentrates on UF without pretreatment and reducing NOM fouling.

Table 2.2 NOM removal by NF membranes (Mosqueda-Jimenez, 2003)

Reference	Membrane brand	Scale	Water treated	%Removal
Blau et al. (1992)	201117 (A15s), DuPont	Pilot	Daytona Beach, Florida	>93% NPDOC
Chellam et al. (1997)	NF-70, Film Tec	Pilot	Occoquan Reservoir in northern Virginia	>95% TOC
Chellam et al. (1997)	NTR7450, Hydranautics	Pilot	Occoquan Reservoir in northern Virginia	90% TOC
Fu et al. (1993)	NF70, Film Tec	Pilot	Orange County (Cal.)	94% TOC
Fu et al. (1993)	PVD1 Hydranautics	Pilot	Orange County (Cal.)	92% TOC
Fu et al. (1993)	Desal 5, Desalination Systems Inc.	Pilot	Orange County (Cal.)	98% TOC
Fu et al. (1993)	TS80 Tri-Sep	Pilot	Orange County (Cal.)	96% TOC
Fu et al. (1993)	TFCS Fluid System	Pilot	Orange County (Cal.)	96% TOC
Fu et al. (1993)	7450 Nitto Denko	Pilot	Orange County (Cal.)	93% TOC
Fu et al. (1994)	NTR7450, Nitto Denko	Pilot	Dyer Road Well Field	>94% TOC
Fu et al. (1994)	TS80, TriSep	Pilot	Dyer Road Well Field	>97% TOC
Jacangelo et al. (1994)	Zenon crossflow hollow fiber, Zenon Environmental Inc.	Pilot	Mokelumme River and the Sacramento-San Joaquin Delta in northern California	<70% TOC
Jacangelo et al. (1994)	Moustic transverse-flow hollow fibre, Zenon Environmental Inc.	Pilot	Mokelumme River and the Sacramento-San Joaquin Delta in northern California	~80% TOC
Jacangelo et al. (1994)	SU-620 spiral wound, Toray, Tokyo	Pilot	Sacramento-San Joaquin Delta in northern California	<70% TOC
Jacangelo et al. (1994)	Moustic transverse-flow hollow fibre, Zenon Environmental Inc.	Pilot	Ottawa River, Ottawa, Ontario	>80% TOC
Pedersen et al. (1991)	Zenon Environmental Inc.	Pilot	Lac Vail (Québec)	84% TOC
Siddiqui et al. (2000)	NF70, Filmtec	Pilot	Silver Lake, Colorado	>82% DOC
Siddiqui et al. (2000)	NF45, Filmtec	Pilot	Silver Lake, Colorado	>82% DOC
Siddiqui et al. (2000)	DL254, Desal	Pilot	Boulder Reservoir, Colorado	>94% DOC
Siddiqui et al. (2000)	MX07, Osmonics	Pilot	Boulder Reservoir, Colorado	>89% DOC
Tan & Sudak (1992)	BW30, Film Tec	Pilot	Orange County (Cal.)	98.5% TOC
Tan & Sudak (1992)	CALP, Desalination Systems Inc.	Pilot	Orange County (Cal.)	97.9% TOC
Tan & Sudak (1992)	NF70, Film Tec	Pilot	Orange County (Cal.)	95% TOC
Tan & Sudak (1992)	NTR729HF Nitto Denko	Pilot	Orange County (Cal.)	95.7% TOC
Tan (1993)	NF40, Film Tec	Pilot	Orange County (Cal.)	84% TOC
Tan (1993)	Desal 5, Desalination Systems Inc.	Pilot	Orange County (Cal.)	88% TOC
Tan (1993)	NF70, Film Tec	Pilot	Orange County (Cal.)	90% TOC
Tan (1993)	NTR729HF Nitto Denko	Pilot	Orange County (Cal.)	95% TOC
Taylor et al. (1987)	N50, Film Tec	Pilot	Groundwater, Village of Golf	90% DOC

Table 2.3 NOM removal by UF membranes as cited in the literature (adapted from Mosqueda-Jimenez, 2003)

Reference	Membrane brand	Scale	Water treated	% Removal
Chellam et al. (1998) and Chellam et al. (1997)	Aquasource, Lyonnaise des Eaux	Pilot	Occoquan Reservoir (North Virginia)	5-10% TOC
Crozes et al. (1997)	DN100 M258, Aquasource, Lyonnaise des Eux	Pilot	Boise river, (Idaho)	20% TOC
Crozes et al. (1997)	XM-50 Romicon	Pilot	Seine river, France	20% TOC
Jacangelo et al. (1994)	DN100 M258, Aquasource	Pilot	Mokelumme River and the Sacramento-San Joaquin Delta in Northern California, Ottawa River Water, Ottawa, Ontario	<16% TOC
Laîné et al. (1989)	XM100, Amicon Inc.	Lab	Lake Decatur (Ill.)	42% TOC
Laîné et al. (1989)	YM100, Amicon Inc.	Lab	Lake Decatur (Ill.)	43% TOC
Laîné et al. (1989)	PM30, Amicon Inc.	Lab	Lake Decatur (Ill.)	47% TOC
Laîné et al. (1989)	YM5, Amicon Inc.	Lab	Lake Decatur (Ill.)	41% TOC
Laîné et al. (1991)	Cellulosic Derivative	Pilot	Boise River (Idaho)	23% TOC
Laîné et al. (1991)	Acrylic polymer	Pilot	Boise River (Idaho)	20% TOC
Siddiqui et al. (2000)	192-PT3, Osmonics	Pilot	Silver Lake, Colorado	25 – 32% DOC
Tan & Amy (1991)	Desal 5, Desalination Systems Inc.	Pilot	Orange County (Cal.)	51% TOC > 88% Colour
Tan (1993)	Desal G5, Desalination Systems Inc.	Pilot	Orange County (Cal.)	73% TOC
Taylor et al. (1987)	G10, DeSalination Systems Inc.	Pilot	Groundwater, Village of Golf	40% DOC
Taylor et al. (1987)	UFP4040, Film Tec	Pilot	Groundwater, Village of Golf	16% DOC
Taylor et al. (1987)	G50, DeSalination Systems Inc.	Pilot	Groundwater, Village of Golf	16% DOC
Taylor et al. (1987)	PT2, Osmonics	Pilot	Groundwater, Village of Golf	5% DOC
Taylor et al. (1987)	PT4, Osmonics	Pilot	Groundwater, Village of Golf	5% DOC
Taylor et al. (1987)	G10, DeSalination Systems Inc.	Pilot	Groundwater, Village of Golf	57% DOC
Mosqueda-Jimenez (2003)	PES modified membranes	Lab	Ottawa River Water, Ottawa, ON	77% TOC

Table 2.4 Commercial Osmonics Ultrafiltration elements designed for colour and/or TOC removal (Osmonics, 2001)

Membrane element	MWCO, Daltons	Average flux LMH (GFD)	Average pressure, kPa (psig)	% Recovery	TOC removal, %
G-10	2,500	6.8–10.2 (4-6)	483 – 827 (70-120)	70-90%	93
G-20	3,500	12-26 (7-15)	483 – 621 (70-90)	70-90%	70
G-50	8,000	25.5 (15)	724 (105)	70-90%	78
G-80	10,000	25.5 (15)	724 (105)	70-90%	78

2.4 Fouling

Membrane fouling is the reduction of flux with operation time when all operating parameters are kept constant. The reduction of flux can be caused by several mechanisms including: membrane compaction (the membrane compression under pressure), concentration polarization and fouling. Membrane compaction is a function of the membrane physical characteristics. Concentration polarization causes flux reduction by forming a boundary layer (Figure 2.4) that may be eliminated by increasing the turbulence adjacent to the membrane. This layer arises from a localized increase of the solute concentration at the membrane surface and/or increase of hydrodynamic resistance in the boundary layer and thus lowers the flux.

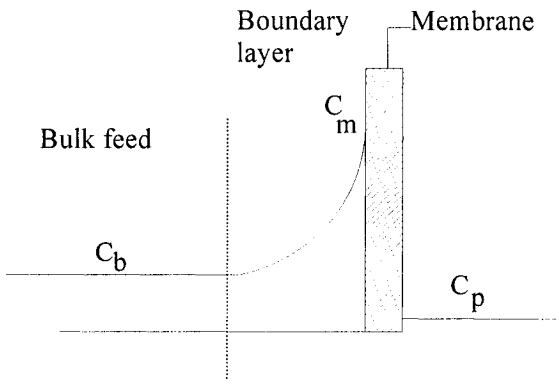


Figure 2.4 Concentration Polarization (Mulder, 1996)

The impact of concentration polarization is minimized by using systems with large hydraulic shears near the membrane surface. Fouling is flux reduction (if the operating pressure is kept constant) due to the deposition and accumulation of submicro particles on the membrane surface or the precipitation of smaller solutes on the surface and within the pores of the membrane itself (Cheryan, 1986). It is hard to differentiate between concentration polarization and fouling because concentration polarization may start fouling (Mulder, 1996).

The consequences of fouling are lower water production, higher energy costs, higher cleaning costs, and shorten membrane life if harsh chemicals are used for the cleaning fouled membrane. The cleaning process itself increases the operational cost for hiring personnel, purchasing chemicals, and managing the waste and wastewater generated. Cleaning cannot recover the original flux, for MF/UF membranes, the flux recovery can be as high as 85 to 97% but with high-pressure membranes, only significantly lower recoveries (70 to 90%) can be obtained (USEPA, 2001). During cleaning period, the system has to stop, causing a loss in production. If membrane poisoning (i.e. irreversible fouling) occurs, even after cleaning, flux cannot be recovered to produce the desired water quantities or result in very high-energy cost; membranes have to be replaced with new ones. Normal membrane life is generally five to ten years (Montgomery, 2005).

Due to their bigger pore sizes, fouling is more serious in MF, UF, and loose NF than in tight NF and RO systems. Fouling is very complex, because each component of the feed stream will react differently with the membrane and affect the membrane-solute interaction. In addition to the complicated physico-chemical interactions of feed components and membranes, operating parameters such as temperature, flow rate,

pressure and feed concentration, together with the module design, have great impact on membrane fouling. The following section will discuss more in detail the various fouling mechanisms.

2.4.1 Fouling mechanisms

Since fouling is the result of specific interactions between the membrane and the various solutes in the feed stream, it is difficult to establish a general rule that can be universally accepted (Cheryan, 1986). However, it is useful to have an understanding about how different types of solute blocking that lead to fouling. Bowen et al. (1995) described four different fouling mechanisms, according to their physical causes: complete blocking of the pores (pore plugging); intermediate blocking or long term adsorption; cake filtration or boundary layer resistant; and standard blocking or direct adsorption (internal adsorption). The first three fouling mechanisms occur when solutes are bigger than the membrane pore sizes; whereas the last one occurs when solutes are smaller than membrane pore sizes. Pore plugging occurs when each particle arriving to the membrane causes total blocking of a pore or pores with no superposition of particles. When each particle settles on a previously-arrived particle that already blocks pores or directly blocks some membrane area, intermediate blocking occurs. In cake filtration, particles attach or locate on each others already arrived and already blocking some pores and there is no room for directly obstructing some membrane area. In internal adsorption, particles are deposited inside pore walls, leading to pore size decrease (Figure 2.5).

Given the different pore size distribution of asymmetric membranes and the different solute sizes of the feed solution, it is reasonable to say that membrane fouling is the succession or combination of different mechanisms (Bowen et al., 1995).

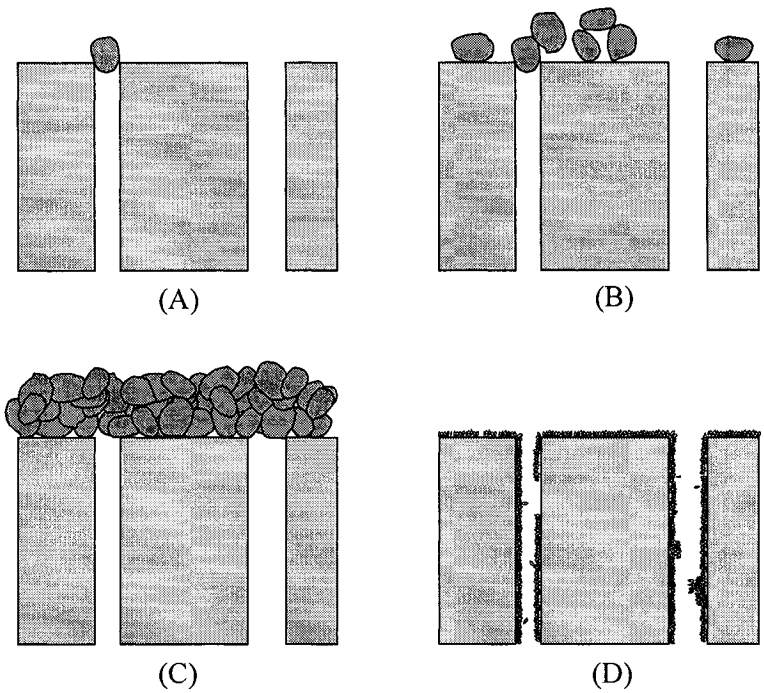


Figure 2.5 Fouling mechanisms according to Bowen et al. (1995)

(A) complete blocking, (B) intermediate blocking, (C) cake filtration, (D) standard blocking

Unfortunately, fouling does not occur as a result of one physical mechanism, but rather the complex interaction between membrane surface and solutes. There have been many studies trying to identify the fouling mechanisms, factors affecting fouling including solute properties (size, charge, functional group), and membrane properties (morphology, surface roughness, charge).

Zeman and Zedney (1996) considered two types of fouling in MF and UF membranes: macrosolute adsorption, which refers to the specific intermolecular interactions between the macrosolute and the membrane that occur even in the absence of filtration; and filtration-induced macrosolute or particle deposition, which is over and above that observed in a static system. In their intermolecular interaction studies, they found that the covalent interactions between different feed components rather than the covalent interaction between feed components and membrane surface, lead to the formation of large aggregates or particulates that readily foul membranes. They also studied about the electrostatic interactions between membranes and charged solutes and found that the magnitude of the interactions is a strong function of the total ionic strength (salt concentration). Their flux reduction due to particle deposition studies identified three fouling mechanisms: pore blockage, pore constriction, and cake filtration that correspond to a reduction of number of accessible pores, a decrease in the effective pore radius, and an increase in the resistance provided by a deposited particle cake on the upper surface of the membrane, respectively.

In his study of a cross-flow UF membrane, Song (1998) found that the degree of pore blockage depends on the shape and the relative size of the particles and the pores and the blockage is more serious if particles and pores are similar in both shape and size. This agrees well with the studies conducted by Baker (2004).

Other studies on factors affecting fouling are specific for each type of solutes (Cheryan, 1986; Laine et al., 1989; Jucker and Clark, 1994; Ridgway and Flemming, 1996; Nilson and DiGiano, 1996; Zeman and Zedney, 1996; Anselme and Jacobs, 1996; Wiesner and Aptel, 1996; Amy and Cho, 1999; Cho et al., 1999a, Cho et al., 1999b; Cho et al., 2000;

Carroll et al., 2000;; Amy et al., 2001; Fan et al., 2001; Schafer et al., 2001; Cho et al., 2002; Lee et al. (2003); Lee et al., 2004). The following section will look at factors affecting fouling in term of types of solutes including inorganic, organic (especially NOM) and biofouling.

2.4.2 Fouling by different types of foulants

Foulants are substances that cause fouling including inorganic solutes, organic solutes, microorganisms, and microalgae.

2.4.2.1 Fouling by Inorganic substances

Zeman and Zedney (1996) presented a list of a wide range of inorganic species that can cause fouling. They include calcium sulphate, calcium carbonate, calcium phosphate, silica, metal oxides and hydroxides (particularly of iron and aluminum), colloidal sulphur, and other inorganic particulates. Fouling by salts and metal compounds generally occurs by precipitation or flocculation on or within the porous structure of the membrane.

Anselme and Jacobs (1996) identified other inorganic fouling phenomenon frequently found in operating treatment plants. That includes dissolved metal precipitation, which leads to the formation of an iron oxide and manganese cake on the membrane. In UF, the formation of iron oxide and manganese is often related to the use of an oxidant during a previous process step. This fouling, however, is reversible by backwashing.

In controlling inorganic fouling, temperature and pH play a very important role because they relate directly to the salt solubility and precipitation. For example, the solubility of

calcium salts, the most prominent inorganic foulants in many systems, decreases slightly with increasing temperature. Calcium precipitation can be prevented by acidifying the water, i.e., lowering the pH. The solubility of silica, that is presented in many natural waters, is also a function of temperature and pH. Thus adjusting the pH, which controls the solubility of the salts, decreases the chance of deposition on the membrane and increases the chance of permeating through the membrane (Cheryan, 1986).

Aluminum and iron coagulants are often added to surface waters prior to hollow fibre MF or UF to improve particle and organics removal. These systems operate with frequent backwashing steps, which minimize the impact of inorganic fouling. However, coagulation with ferric chloride in water containing NOM has been reported to result in severe fouling in flat sheet MF membranes, and slightly less severe fouling in UF membranes (Schafer et al., 2001).

2.4.2.2 Fouling by organic substances

Two types of organic foulants have been studied extensively: protein and NOM. Protein fouling remains a very controversial topic and most of the protein studies used bovine serum albumin. Since proteins are rejected by the membrane, they tend to have high concentrations at the membrane surface (Cheryan, 1986), which lead to the significant increase in hydraulic resistance. Zeman and Zedney (1996) found that hydraulic resistance of MF membrane after protein filtration increased significantly due to the formation of a relatively thick protein deposit on the upper surface of the membrane. They also mentioned that the hydraulic resistance caused by the protein deposit is a function of solution, pH, and ionic strength. This is because pH and ionic strength relate

to changes in the protein packing density associated with electrostatic repulsive forces between charged proteins within the deposit. The feed environment also alters the interactions of the individual proteins and develop electroosmostic counterflow through these charged protein layer (Zeman and Zedney, 1996).

Another organic substance that has been identified as a significant foulant in drinking water treatment is NOM. Since NOM is a very complex solute and their characteristics vary from site to site, it is hard to have a general conclusion about NOM fouling. However, there have been extensive studies on the impact of specific properties of NOM on fouling. In their study on NOM fouling of MF/UF membranes, Lee et al. (2003) identified fouling mechanisms associated with NOM including reduced pore size, pore blockage, and/or surface (gel layer) coverage.

The interaction of NOM with a membrane depends on both the NOM characteristics (molecular weight (MW), MW distribution, charge, structure: functional group, aromatic versus aliphatic or hydrophobic versus hydrophilic (Laine et al, 1989; Jucker and Clark, 1994; Nilson and DiGiano, 1996) and the membrane surface (charge, membrane morphology, hydrophobicity/hydrophilicity). The membrane hydrophobicity is determined by contact angle, zeta potential is measured to determine the membrane surface charge, and fourier transform infrared (FTIR) spectroscopy is used to measure surface functional group. Wiesner and Aptel (1996) gave an example of negatively charged function groups on organic polyelectrolytes (such as fulvic and humic acids) that can be electrostatically repulsed by negatively charged membrane surfaces. This agrees with the studies done by Carroll et al. (2000) on MF membranes. They found that the major contribution to fouling was attributed to the NOM fraction comprising neutral

(uncharged) hydrophilic compounds. To study the impact of hydrophobic/hydrophilic NOM fraction on fouling, Cho et al. (1999b) separated hydrophobic and hydrophilic fractions of NOM by using XAD-8 resin. Amy and Cho (1999) showed that the nature of foulants was of a hydrophilic character, particularly polysaccharide-like material. For highly humic feedwaters, hydrophobic NOM was found to contribute to fouling and flux decline (Amy et al., 2001). Cho et al. (2000) later found that non-charged NOM fractions (including both hydrophilic and hydrophobic neutrals/bases) to be significant founlants for negatively charged membranes. Fan et al. (2001) identified potential foulant in order as hydrophilic neutrals>hydrophobic acids>transphilic acid. Amy et al. (2001) reported that the electrostatic repulsion between NOM acid components and the membrane surface was an influential factor in increasing NOM rejection and decreasing fouling and flux decline.

The inorganic water quality, including pH and ionic strength may also affect NOM-membrane interactions. Calcium ions and protons may associate with NOM functional groups rendering the molecule more or less stable. Higher calcium concentrations and lower pH values tend to increase the hydrophobicity of humic materials and favour their adsorption (Wiesner and Aptel, 1996)

Cho et al. (2002) later identified a hydrodynamic factor f/k (f is the permeate flux and k is the back-diffusional mass transfer coefficient) as a major influential factor in terms of flux decline and NOM rejection. They also found that when keeping the same f/k ratio, the effect of membrane hydrophobicity on flux decline, the difference in flux decline with different NOM –source waters (different aromaticity (hydrophobicity) and charge density), was not significant.

Lee et al. (2004) recently looked at the impact of membrane morphology on NOM fouling and they found that membrane roughness may be considered as a more important factor in membrane fouling by controlling interaction between molecules and the membrane surface, compared to the hydrophobic/hydrophilic character of membranes. They also confirmed that a high content of NOM hydrophilic fraction (31 and 35% of the total DOC) resulted in more significant flux decline.

All the above studies have shown that fouling due to NOM adsorption depends on the characteristics of NOM and membranes, the feed solution environment as well as operating parameters. Thus, NOM fouling is complex and difficult to predict.

2.4.2.3 Biofouling

Ridgway and Flemming (1996) defined biofouling as a biofilm formation resulting in an unacceptable degree of system performance loss. Thus, biofilm formation invariably precedes biofouling, and a biofilm may exist in the absence of detectable biofouling.

Biofilm formation involves the accumulation of microorganisms like bacteria, fungi, and microalgae at a phase transition interface. The transport of microorganisms to an interface may occur passively by diffusion, gravitational settling, or bulk fluid convection (Ridgway and Flemming, 1996). Bacteria then accumulate on membrane surface by two processes: (1) attachment, i.e., adhesion, adsorption, which is prerequisite for biofilm formation; and (2) growth or cell multiplication using nutrients transported to the surface from the bulk fluid.

The adhesion mechanisms of bacteria to membranes surface are elaborate and virtually, all natural and synthetic materials are susceptible to bacterial attachment and colonization, even the materials exhibiting low surface energy like Teflon and hydrophobic plastics.

There are several factors that favor biofouling including reduced feed water cross-flow velocities, elevated operating pressures and temperatures, high feed water concentrations of organics, small feed channel dimensions, and membrane polymers with enhanced bacterial affinities (Ridgway and Flemming, 1996).

Membrane biofouling has been reported for nearly every type of feed water including brackish surface water, ground water, but especially in food and beverages industries where process streams contain high content of nutrients.

Biofouling not only results in flux decline but also some bacteria may even chemically degrade certain polymeric materials. In addition, the bacteria within the biofilm are resistant to some bacteriocidal agents, and they are considerably more difficult to remove from the membrane surface by either chemical or mechanical cleaning (Zeman and Zedney, 1996).

2.4.3 Fouling reduction

Due to the complexity of fouling phenomenon, each separation problem requires its own specific approach. Mulder (1996) mentioned four general methods of reducing membrane fouling: (i) pretreating the feed solution; (ii) changing membrane properties; (iii) optimizing module and process conditions; (iv) cleaning fouled membranes. Pretreating

the feed can involve heat treatment, pH adjustment, chemical clarification, etc. but it is only the most effective way to minimize fouling when it results from specific membrane-solute interactions and some pretreatment methods (coagulation) resulted in more severe fouling (Schafer, 2001; Li and Chen, 2004). The use of various kinds of turbulence can reduce fouling, however fluidized bed systems and rotary module systems are not economically feasible, especially for large-scale applications (Mulder, 1996). Cleaning can only reduce fouling to some extent and not a proactive way of reducing fouling. There have been many attempts to change the membrane properties to reduce fouling; for example use hydrophilic instead of hydrophobic materials or use negatively charged membrane (Nyström and Järvinen, 1991; Brink et al., 1993; Combe et al., 1999; Kull et al., 2005). One potential way is to modify the membrane surface while keeping the supporting layer properties the same.

2.5 Membrane surface modification

There have been many initiatives to modify membrane surfaces at a laboratory scale. Most of the work attempted to make the membrane surface more hydrophilic, which should be less susceptible to fouling.

According to Zeman and Zydney (1996), almost 50% of all MF/UF membranes marketed today are surface-modified. The common membrane surface modification strategies involve: (1) addition of a compatible modifier into the casting solution; (2) adsorption of modifier onto the membrane surface; (3) chemical or physicochemical post-treatment of the surface via hydrolysis or gas plasma treatment; (4) grafting or cross-linking a modifier on the surface. While method (2) to (4) involve more than one step and the

additional steps are performed after the main membranes are formed, in method 1, surface modification can be achieved using a single casting step. The methods (2) to (4) literature will be discussed in more detail below, that for method (1) will be discussed in the subsection that follows.

Trying to make the membrane surface more hydrophilic by surface adsorption of modifier, Brink et al. (1993) preadsorbed two water-soluble polymers, methylcellulose and poly(vinyl methylether) to several MF and UF polycarbonate and polysulfone membranes. They observed less protein (solute) internal adsorption (pore narrowing was more severe in unmodified membranes) of protein in UF membranes and attributed it to the partly sealing of the pore entrance by the preadsorped polymers. However, this preadsorption technique could not reduce protein adsorption in MF and UF membranes with pore sizes larger than 30 nm because the adsorbed polymer could not cover the pore opening.

Combe et al. (1999) studied the effects of surface modification (modifying pore, hydrophobicity, charge, and porosity) of cellulose acetate membranes on humic acid adsorption. The surface modification was achieved via several methods. Annealing (i.e., immersing membranes in a water bath at temperatures ranging from 40 to 80^{o}C) was conducted to modify porosity and pore size. Hydrolysis and oxidation was to modify hydrophilicity-hydrophobicity nature; and contacting membranes with a dilute solution of "Colloid 189" (vinyl acetate/acrylic acid copolymer) was to obtain a surface charge. They found that annealing has a great effect on membrane permeability, without changing pore charge or hydrophobicity. Hydrolysis greatly increases membrane porosity, increases hydrophilicity, but decreases the charge of the membranes, which might explain why it

has little effect on adsorption of humic acids. Oxidation had a small effect on porosity, but significantly increased hydrophilicity and the negative membrane charge but still adsorption of humic acid increased on the oxidized membranes. They explained this behavior by the role of calcium in adsorption, and the measurement and interpretation of charge by zeta potential. Only by pre-adsorption of an anionic polymer on the membrane surface is adsorption of humic acid on the membrane surface decreased.

Surface modification was also accomplished by UV irradiation (Nyström and Järvinen, 1991); by grafting (Lindau and Jönsson, 1999; and Belfer et al., 2004); and plasma treatment (Wavhal and Fisher, 2002).

Nyström and Järvinen (1991) studied UV irradiation of polysulfone UF membranes in an aqueous solution alone or together with hydrophilicity increasing agents, i.e., dextrans. They observed an increase of the water flux (PWP) up to 4 times compared to the unmodified membranes. However, after one hour of filtration of a whey solution, the flux reduction for the UV-irradiated membranes was very similar to that of the unmodified membranes).

Lindau and Jönsson (1999) presented an example of unsuccessful membrane surface modification. They attempted to modify PVDF membranes by grafting cellulosic polymers onto the membrane surface and blending a hydrophilic copolymer with polyamide (PA) in the casting solution. The modification of PVDF membrane surface did not result in fouling reduction. They attributed this due to the fact that the octanoic acid molecules, used as the test solution, were not retained by the membrane. Instead, they passed into the membrane pores where they can be adsorbed on the pore walls. In the

case of polyamide-modified membranes, only for octanoic acid concentrations less than 60%, they observed lower flux reduction. However, for these successful modifications, when rinsed with distilled water, they can not recover their initial fluxes.

Wavhal and Fisher (2002) used plasma treatment to modify PES membrane surfaces. Modification was achieved argon plasma treatment followed by polyacrylic acid grafting in vapor phase. They attributed that with plasma treatment times greater than 120 seconds, PES membrane surfaces were rendered completely hydrophilic due to the fact that the water drop (used in contact angle measurement) immediately disappeared. However, they disregarded the impact that porosity might have on water adsorption which might also explain why they observed significant higher (6 times higher) pure water flux in modified membranes compared to the unmodified counterparts (more porous membranes have higher PWP). However, the plasma modified membranes showed slightly improved performance (with higher (9%) flux ratio after protein fouling) and higher flux recovery after cleaning (~10%).

Though the surface modification by using technique (2) to (4) generally resulted in some improvements, unexpected results can still occur. In addition, all these surface modifications involve multiple steps before the membrane surface can be finally modified. Moreover, plasma techniques and surface fluorination cannot be easily controlled, and scale-up of an experimental set-up to a large production reactor is not a simple process (Chan, 1994). Plasma treatment also requires a vacuum system, which increases the cost of operation. Cross-linking is only useful for producing solvent resistant surfaces; its use in modifying the surface energies is not common. Chemical coating and grafting require specific conditions which somewhat limit their use (Pham,

1995). The next section looks at surface modification in a simpler way by the addition of surface modifying macromolecules. Membrane surface can be modified via a single casting step.

2.5.1 Surface Modifying Macromolecules (SMMs)

The addition of a compatible modifier into the casting solution is an excellent option that can modify membrane surface using one step. This method has some characteristics including: a) modification is limited to the surface without damaging it, b) the bulk properties of the polymer are kept relatively intact, c) the surface-active additive is blended with the casting solution. This technique has been successfully used by Kasemura et al. (1993); Hester and Mayes (2001) as well as Matsuura, Santere, Narbaitz and coworkers.

Since the early 90s our research group has been involved in the manufacture and application of surface-active polymeric additives capable of modifying surfaces, called "**S**urface **M**odifying **M**acromolecules" or SMMs. SMMs are polymers tailor-made to be compatible with PES, have lower surface energy than PES, and are endgrouped with either hydrophobic or hydrophilic tails. The key features of SMM are: SMM is blended with the casting solution containing the base polymer PES and solvent (other additives may also be added); membrane is cast in air using the casting solution; during casting, SMMs preferably migrate to membrane surface to minimize the total free energy of the system. The migration modified membrane surface either more hydrophobic or hydrophilic, depending on hydrophobicity-hydrophilicity of the types of SMMs added. Thus, the membrane surface can be modified via a single casting step. Figure 2.6

illustrates the migration of SMM to the membrane surface with time. The dark circles represent SMM molecules while the white circles represent base polymer and solvent.

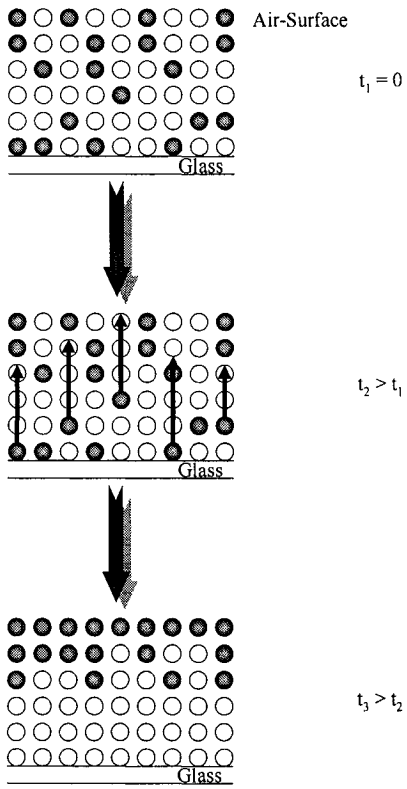


Figure 2.6 Migration of SMM to the membrane surface (Fang, 1997)

For almost ten years, the work involved various applications using many hydrophobic SMMs containing fluorocarbon tails. The SMMs were synthesized by a two-step solution polymerization method. The initial step involved the reaction of a diisocyanate with a polyol in a common solvent to form a urethane prepolymer solution. The reaction was then terminated by the addition of an oligomeric fluoroalcohol resulting in a polymer that needed to be precipitated. The precipitated polymer is then washed in 30 v/v % acetone-water mixture to leach out unreacted monomer before being dried in the oven at 50° C. Figure 2.7 presents a schematic of SMM synthesis and a hypothetical structure.

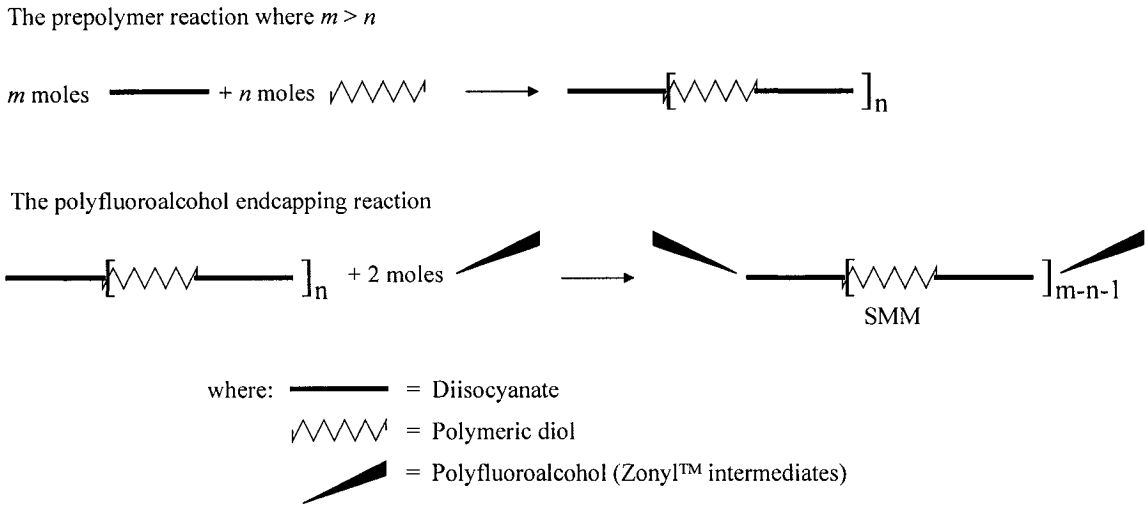


Figure 2.7 Scheme for SMM synthesis (Pham, 1995)

Khayet et al. (2003) presented a review of the pre-2004 SMM research. Until now, the main diisocynanates used for SMM preparation have been methylene bis-p- phenyl diisocyanate (MDI) used by Pham (1995), Ho et al. (2000), Mandeep (2001), Mosqueda-Jimenez (2003); and hexamethylene diisocynate (HDI) by Tang et al., (1996). The polyols employed were polypropylene diol (PPO) by Pham (1995), Ho et al. (2000), Mandeep (2001), Mosqueda-Jiminez (2003), Tang et al. (1996). In addition to PPO, other polyols and groups were also used including polytetramethylene oxide (PTMO) by Tang et al. (1996), polycaprolactone diol (PCL) by Ho et al. (2000), diethylene glycol (DEG) and hydroxyl diphenyl sulfone (DPS) by Mandeep (2001) and Mosqueda-Jimenez (2003). The most commonly used solvent is N,N-dimethylacetamide (DMAC). The oligomeric fluoroalcohols used are fractions of the commercial products Zonyl (BA-L) and Zonyl (FSO-100) purchased from Dupont Chemical (Rockville, MD).

To evaluate the reproducibility of the SMM manufacturing procedure, Pham (1995) synthesized eight different types of SMMs prepared by varying the reactant mole ratio,

the prepolymer reactant concentration and the distillation fraction of BA-L. He conducted elemental analysis and measured relative average molecular weight and their distribution. Pham (1995) concluded that the most reproducible formulations were those using a 3:2:2 stoichiometry, low fraction of BA-L and reduced prepolymer reactant concentration; and 2:1:2 stoichiometry, low fraction of BA-L and normal prepolymer reactant concentration. The properties of SMMs were characterized using analysis of molecular weight, elemental fluorine, and thermal transition temperature. The reported average molecular weight of SMM raged between 1.2×10^4 and 2.4×10^5 and the molecular weight of SMM is primarily determined by the size of the prepolymer generated in the first step, not the fluorine-containing reactant (Pham, 1995).

The highest fluorine content SMM obtained was 21%, it was synthesized by Ho et al. (2001). There was a general trend of decreasing fluorine content with increasing molecular weight possibly due to the reaction of unreated hydroxyl groups from the polyol with the diisocyanate end-capped prepolymer during the fluoroalcohol capping procedure (Khayet et al., 2003).

Differential scanning calorimetry (DSC) monitoring the change in enthalpy of SMM film was used to determine thermal characterization of SMM. With amorphous polymer, glass-transition temperature (T_g) is a very important parameter determining the polymer state, glassy (below T_g) or rubbery (above T_g). Tang et al., (1996) reported that T_g was highly dependent on the polyol used. They reported that the SMMs containing a PPO soft segment showed higher T_g values than those containing PTMO. Pham (1995) showed

that the reactant mole ratio, the reactant concentration, and the type of flouroalcohol did not show any correlation with the variation in T_g.

When SMMs were blended with PES to make membranes, several characteristics of the membrane were monitored.

The contact angles of both PES-SMM films and membranes were measured. PES-SMMs films were prepared without gelation and were let completely evaporated (usually overnight) as opposed to gelation step in membrane preparation process. Thus, the PES-SMMs films do not contain water and poreless while water forms an integral part of the membranes. When measuring the contact angle of PES-SMM films, a significantly increase in both water advancing and receding surface contact angles was observed, with advancing contact angles approaching those of Teflon, i.e., 116° (Pham et al., 1999). Table 2.5 presents contact angle data for PES films. However, no differences in advancing contact angles were observed on PES-SMM membranes without evaporation time (Mosqueda-Jimenez, 2004b, Suk et al., 2002b). Membrane evaporation time prior to gelation had a great effect on SMM migration and fluxes. Suk et al., (2002a) showed that the contact angle increased when solvent evaporation time increased and at least 3 minutes were necessary to cause a significant increase in contact angle. On the other hand, this was accompanied by greatly decreased fluxes (Mosqueda-Jimenez, 2003). To obtain reasonable fluxes, Mosqueda-Jimenez (2003) prepared membranes with no evaporation time and just three minutes evaporation time at 90°C. While there was a measurable increase in the fluorine content at the surface of the membrane, this was not sufficient to significantly increase the membranes contact angle.

Table 2.5 Air contact angle analysis on PES films

Film	Water Advancing contact angle (°)	Water Receding contact angle (°)	Contact angle hysteresis (°)	Reference
PES	77 ± 2	49 ± 3	28	Pham (1995)
PES+MPB322HN	112 ± 2	60 ± 5	52	Pham (1995)
PES+MPB322HR	102 ± 4	57 ± 2	45	Pham (1995)
PES+MPB212HN	116 ± 2	70 ± 6	46	Pham (1995)
PES+MPB212HR	112 ± 2	74 ± 4	38	Pham (1995)
PES+MPB322LN	93 ± 4	52 ± 1	41	Pham (1995)
PES+MPB322LR	105 ± 2	54 ± 1	51	Pham (1995)
PES+MPB212LN	107 ± 2	57 ± 4	50	Pham (1995)
PES+MPB212LR	107 ± 3	67 ± 4	40	Pham (1995)
PES	67.2 ± 0.4	26.0 ± 3.7	41.2 ± 3.7	Ho el al. (2000)
PES+MDI-PPO-BAL	107.3 ± 1.8	58.2 ± 4.5	49.1 ± 4.8	Ho el al. (2000)
PES+MDI-PPO-FSO1	102.9 ± 2.0	32.9 ± 5.3	70.0 ± 5.7	Ho el al. (2000)
PES+MDI-PPO-FSO2	106.3 ± 2.3	24.2 ± 4.6	82.1 ± 5.1	Ho el al. (2000)
PES+MDI-PPO-FSO3	97.5 ± 1.6	12.4 ± 3.3	85.1 ± 3.7	Ho el al. (2000)
PES+MDI-PCL-BAL	113.2 ±1.1	30.5 ± 3.8	82.7 ± 4.0	Ho el al. (2000)
PES+MDI-PCL-FSO1	119.4 ± 0.8	17.5 ± 1.5	101.9 ± 1.6	Ho el al. (2000)
PES+MDI-PCL-FSO2	112.2 ± 0.7	21.0 ± 1.2	91.2 ± 1.4	Ho el al. (2000)
PES+MDI-PCL-FSO3	99.7 ± 2.8	29.0 ± 6.9	70.7 ± 7.4	Ho el al. (2000)
PES	70.0 ± 1.1	40.4 ± 0.9	29.8 ± 2.0	Mandeep (2001)
PES+MDI-DEG322	105.4 ± 0.7	53.2 ± 0.8	52.2 ± 1.6	Mandeep (2001)
PES+MDI-DPS432	109.8 ± 0.4	89.7 ± 0.3	20.3 ± 0.8	Mandeep (2001)
PES+MDI-PPO322	108.6 ± 0.5	42.8 ± 0.4	65.8 ± 0.9	Mandeep (2001)
PES+THDI-DPS652	98.6 ± 0.7	58.6 ± 0.5	40.0 ± 1.2	Mandeep (2001)

MPB: MDI, PPO, BA-L
322, 212: MDI, PPO, BA-L stoichiometry respectively
H, L: high and low BA-L distillation fraction
R, N: reduced and normal propolymer reactant concentration
PES+MPB322LR, PES+MDI-PPO-BAL, PES+MDI-PPO322 are later referred to as SMM41.

When using X-ray photoelectron spectroscopy (XPS) to determine the chemical and elemental group compositions at the membrane surface, higher fluorine content was observed for SMM-PES modified membranes compared to the unmodified counterparts. Tang et al. (1996), Pham et al. (1999) and Ho et al. (2000) reported ~55%, ~20%, and ~40% surface fluorine content respectively, which indicated the migration of SMM to the membrane surface. The tensile strength and elongation tests showed that SMM modified

membranes have stronger mechanical strength than unmodified membranes (Suk et al., 2002b).

2.5.2 SMMs applications

SMM containing membranes have been used in ultrafiltration, pervaporation and biomedical applications.

Hamza et al. (1997) studied the separation of oily-water emulsions by SMM-PES modified membranes and found that the modified PES membranes had 25% higher fluxes. The addition of SMM reduced the gel formation, which lead to less resistance and thus higher flux. They also found that the oil gel layer resistance of the SMM-modified PES membranes decreased with an increase in the SMM content of the casting solution. However, when the feed was pure water, membranes containing SMM exhibited lower permeation fluxes. They also mentioned that the high degree of receding contact angles suggested that the hydrophobicity character was still maintained after exposing the films to water. Hamza et al. (1997) attributed the lower permeation rate of SMM-modified membranes to the increased hydrophobicity.

Fang et al. (1994) studied the impact of solvent evaporation time on pervaporation of chloroform/water mixture of the unmodified PES and SMM5-modified PES membranes. They found that PES membranes, prepared with an evaporation time of less than 7 minutes were water selective compared with those having longer evaporation time that were chloroform selective. It was also shown in their studies that by adding SMM up to 1 wt % into the casting solution, chloroform enrichment in the permeate could be increased by 50%, and chloroform enrichment increased with increasing SMM concentration up to

an optimal value, after which the enrichment decreased. The increased separation of chloroform from the SMM-modified membranes is hypothesized to be related to the unique fluorinated surface character achieved by the novel modification process (Mahmud et al., 2001).

SMM-modified membranes were tested for blood compatibility with respect to fibrinogen (one of the blood proteins) adsorption and biodegradation mediated by lysosomal enzymes released from inflammatory cells (Tang et al., 1997, Ho et al., 2000). Ho et al., (2000) found that SMM migrated and concentrated at the surface in the form of spherical microdomains dispersed in the top 12 μm of the membranes and thus created a heterogeneous membrane surface.

Tang et al. (1997) attempted to increase the biostability of polyurethanes to lysosomal enzymes by incorporating SMM into PES membranes. Through XPS studies, they found that the SMMs were enriched within the upper 10 nm of the membrane surface surface which helped to inhibit the degradation of a polyester-urea-urethane membrane. They also found that different SMM formulations provided varying degrees of inhibition against the biodegradation of the polyester-urea-urethane. Certain formulations of the SMMs were shown to be physically incompatible with the polyurethane and distorted the surface morphology to the extent that biodegradation was enhanced.

Later, Mosqueda-Jimenez (2003) studied the fouling reduction of SMM-modified ultrafiltration membranes in treating surface water rich in NOM content. The hypothesis of her research was that if the SMM additions helped produce a Teflon-like surface, then the non-stick surface should result in decreased fouling. She observed SMM migration

(in terms of increased surface fluorine concentrations), which decreased the pore size, i.e., lowered MWCO, thus improved TOC removals, decreased NOM deposited on membrane surface and decreased flux reduction. However, she did not observe any change in contact angle without evaporation time prior to gelation and permeate flux, in some cases, the permeate flux was even slightly smaller. As reported by Suk et al. (2002a), at least three minutes evaporation was necessary to cause a significant increase in contact angle. On the other hand, this was accompanied by greatly decreased fluxes (Mosqueda-Jimenez, 2003). Thus, Mosqueda-Jimenez (2003) concluded that the effect of surface modification on membrane performance was positive but marginal.

Through the above review, it is clear that hydrophobic SMMs migrate to the surface of PES membrane and enhance membrane performance in various applications. The work on hydrophilic surface modifying macromolecules (LSMM) has started recently (Rana et al., 2005). The LSMM was endgrouped with polyethelyne glycol (PEG) as opposed fluoroalcohol used in hydrophobic SMM synthesis. When incorporated into PES ultrafiltration membranes, Rana et al. (2005) observed a decrease in static contact angle with increasing LSMM concentrations (up to 11^{o} with the addition of 12 wt % LSMM). LSMM/PES membranes have smaller mean pore size, and more stable flux. However, the fluxes obtained by Rana et al. (2005) were rather low (~12 $l/m^2.h$) compared to the fluxes reported later in this study. It is believed that the flux discrepancies were due to different membrane manufacturing and testing procedures.

A common belief in membrane literature is that hydrophilic membranes can reduce fouling better than hydrophobic membranes. Accordingly, this thesis focuses on the

synthesis and application of hydrophilic SMMs (or LSMMs) to ultrafiltration for drinking water applications.

2.6 Conclusions of the literature review

PES is one of the most widely used polymers in the manufacturing of UF membranes (Hamza et al., 1997) due to its good thermal, chemical and mechanical strength, and it easily generates and regulated pore size membranes (by phase inversion technique). In addition, it is compatible with many other polymers and relatively inexpensive (Zeman and Zedney, 1996). However, they are easily fouled (Wavhal and Fisher, 2002).

Membrane fouling by NOM depends on many factors which determine the interactions of the membrane surface and the solutes. Membrane characteristics affecting fouling include material types, surface properties (roughness/smoothness, hydrophobic/hydrophilic, and charge) and morphology (MWCO, pore size distribution and geometry, membrane thickness), etc. Membranes can be made more fouling resistant via a number of different approaches, among these, the addition of surface modifying additives seem very promising because the membrane manufacturing process only involves a single step. The literature suggests that more hydrophilic membrane surfaces tend to foul less. The development of more hydrophilic membranes through the SMM approach is a fertile area of research with great potential benefits.

Accordingly, this thesis focuses on: 1) NOM fouling reduction by modifying PES membrane surface by the incorporation of LSMMs, and 2) studies the impact of LSMMs concentrations in conjunction with PVP on membrane characteristics and performance.

CHAPTER 3

MATERIALS AND METHODS

This chapter describes the chemicals employed during this research; the LSMM and membrane preparation techniques; the membrane characterization and testing protocols; and the overall experimental plan.

3.1 Chemicals

The base polymer used in the membrane preparation was polyethersulfone (PES, 4100P) with average molecular weight of ~ 17,000 to 19,000 Daltons supplied by ICI Advanced Materials (Billingham, GB). Polyvinylpyrrolidone (PVP) powder with an average molecular weight of 10,000 Daltons supplied by Aldrich Chemical, Inc., (Milwaukee, WI) was added as a pore-forming additive. N-methyl pyrrolidone (NMP) (Aldrich Chemical, Inc., Milwaukee, WI) was used as a solvent. The probe solutes for the solute transport method were either polyethylene glycol (PEG) (Sigma Chemical, St. Louis, MO) of different molecular weights or polyethylene oxide (PEO) (Aldrich Chemical, Inc., Milwaukee, WI). The molecular weight of the different PEG fractions used were 4000, 6000, 10000, 12000, 20000, and 35000 Daltons, while for PEO it was 100000 Daltons. Ethyl alcohol 99% (BDH Inc., Toronto, ON) was used to dry membranes. Sodium hydroxide (NaOH) (97% purity, EMD Chemicals Inc., Toronto, ON) was used to clean the fouled membranes. The three LSMMs used were synthesized by Dipak Rana, a postdoctoral fellow at the Industrial Membrane Institute, Department of Chemical Engineering, University of Ottawa and the author.

The total organic carbon (TOC) standards were prepared with potassium hydrogen phthalate, (A.C.S. grade, 99.98% purity, Fisher Chemicals, Fair Lawn, NJ). Potassium persulfate (A.C.S. grade, 99.98% purity, BDH Inc., Toronto, ON) was used as a reagent during the organic carbon oxidation in the presence of ultraviolet light, and orthophosphoric acid (85%, BDH Inc., Toronto, ON) was used to acidify the samples, in order to convert carbonates to CO_2.

Reagent-grade water was prepared with a Milli-Q Water System by Millipore (Bedford, MA) using mix bed ion exchange resins, synthetic activated carbon, organic scavengers and membranes. This ultrapure water is referred as Milli-Q water. The supplier claims that the organic concentration of this water is less than 10 ppb.

3.2 Methodology

3.2.1 LSMM synthesis

Three different LSMMs were used in the preparation of new membranes to evaluate the effect of their chemical composition. The LSMMs used in this study were synthesized using the methodology developed by Rana et al. (2005). As presented in section 2.5.1, LSMM synthesis is composed of two steps. First, the methylene bis-p-phenyl diisocyanate was allowed to react with a polypropylene diol in N,N-dimethylacetamide (DMAC) solvent to form a urethane prepolymer solution. In the second stage, instead of using the low molecular weight fraction of an oligomeric fluoro-alcohol, as in the previous hydrophobic SMM research, PEG, a hydrophilic polymer, was used to endcap the main chain. This should result in a solution of hydrophilic surface-active polymers. To eliminate the effects of moisture, the polymerization reaction and endcapping steps were

performed in a controlled atmosphere of purified nitrogen inside a glove box. The first reaction was performed at 45-50°C and lasted 3 h, and the second reaction was conducted at 25°C and lasted 24 h. After precipitation, the LSMMs were washed in distilled water and in 30 v/v % acetone-water mixture to leach out unreacted monomer before drying in a 50° C oven until constant weight was achieved. Figure 3.1 presents the LSMM-PEG synthesis process while table 3.1 shows the reagents employed in the synthesis of the various LSMMs. LSMM nomenclature and chemicals involved in LSMMs synthesis can be found in table 3.2.

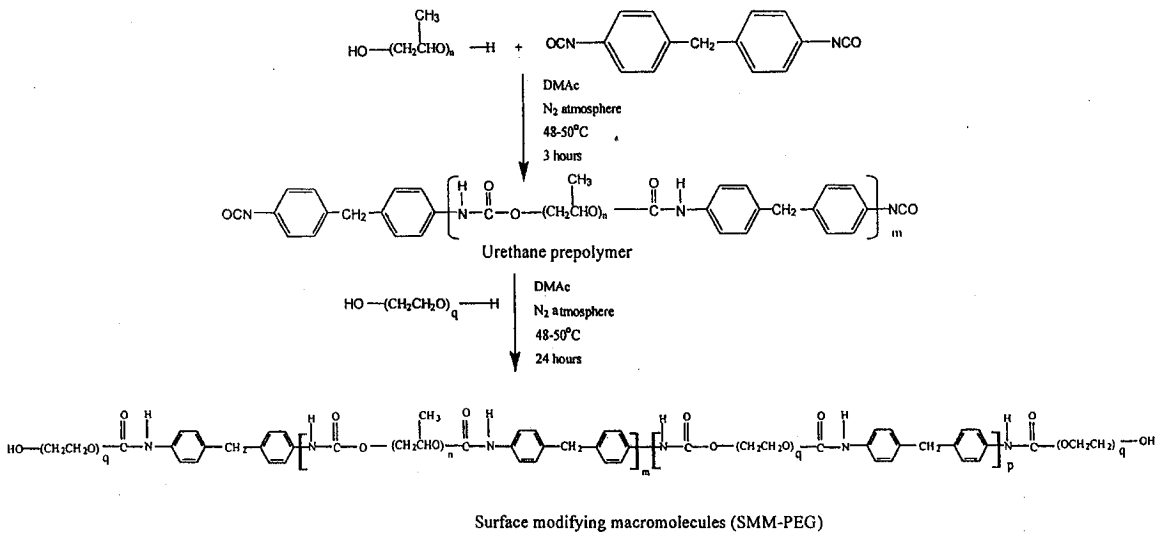


Figure 3.1 LSMM synthesis scheme (after Rana et al., 2005)

The LSMMs were then tested for miscibility with PES. LSMM was first dissolved in NMP at 1.5 wt % in a 150 ml glass bottle. PES was then added at 20 wt % and mixed well in an orbital shaker. LSMM is miscible with PES if the solution is clear or homogenous. With slightly cloudy solutions, membranes were cast to test for homogeneity. The casting solution was still considered well miscible if the membrane

surface was homogenous (i.e., does not have LSMM colonies (dots with diameters of more than 1 mm) on membrane surface). Solution prepared with 1.5% LSMM1000 and 20% PES was very cloudy. When membranes were cast, the membrane surface was not homogenous with intermittent LSMM colonies. Therefore, only LSMM200, 400, and 600 were used for the study.

Table 3.1 Materials for SMM synthesis

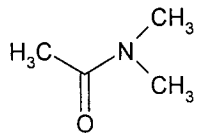
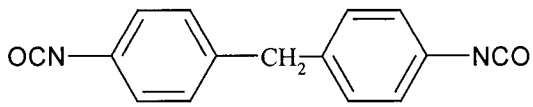
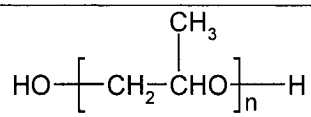
Reagent	Chemical structure	Molecular Weight	Acronym
Solvent: N,N-Dimethylacetamide		87	DMAC
Diisocyanate: Methylene bis-p-phenyl diisocyanate		250	MDI
Polyol: Polypropylene diol		425	PPO
Polyethylene Glycol	$HO-(CH_2CH_2O)_q-H$	200, 400, 600, 1000	PEG

Table 3.2 LSMM Nomenclature and their chemical composition

LSMM	Reagents	MW of PEG (Dalton)
LSMM200	MDI-PPO-PEG	200
LSMM400	MDI-PPO-PEG	400
LSMM600	MDI-PPO-PEG	600
LSMM1000	MDI-PPO-PEG	1000

3.2.2 Membrane preparation

All membranes were prepared using the phase inversion technique described by Matsuura (1994). This technique was particularly chosen because it can be used for a wide variety of polymers and it is easy and fast so it is very suitable for testing new materials. Casting solutions were prepared with different amounts of polyethersulfone (PES), used as the base polymer; polyvinylpyrrolidone (PVP), used as a pore former; hydrophilic surface modifying macromolecules (LSMMs); and N-methyl pyrrolidone (NMP), used as a solvent. PES and the LSMMs were stored in a vacuum dessicator (VWR, Mississauga, ON). NMP, after opened, was kept in the refrigerator at 2°C. NMP was chosen as opposed to the DMAC used in the LSMM preparation because NMP is less toxic. Percentage of all chemicals is calculated as weight percentages. All bottles used to keep casting solutions were 120 ml or 150 ml glass bottle with narrow mouth and Teflon lined cap, sealed with Teflon tape on the threads within the neck of the bottle plus electric tape on the outside of the cap. After weighted, LSMM was the first component to be added, then NMP. After LSMM was completely dissolved, PVP was added and completely dissolved before the base polymer PES was added. After each addition, the bottle was capped, sealed with Teflon and electric tape, and mixed in an environmental incubator orbital shaker (model G24, New Brunswick Scientific Co., Inc., Edison, NJ) operating at 50°C. The time required for complete dissolution increased with the viscosity of the solution. Usually 24 to 96 hours were required for complete dissolution. The homogenous solution would then be filtered using Teflon PTFE 47-mm discs with pore size of 5.0 μm in a stainless steel pressure filter (Millipore, model XX4004700, Bedford, MA) driven by nitrogen gas (98%, Praxair, Mississauga, ON) at pressures ranging from 69 to 345 kPa

(10 to 50 psig) (depending on the viscosity of the solution). After filtering, the filtrate was place in sealed bottles and degassed overnight (or longer) at room temperature inside a vacuum dessicator. Solutions were then ready for casting. With each batch of casting solution it was possible to prepare several sheets of membranes.

The casting was conducted at room temperature via the following steps. First, the polymer solution was poured over a smooth glass plate and evenly spread with a metal rod with side runners to produce a membrane with a thickness of 250 μm (10 mils). The size of the casting area is 28 cm by 22 cm. To make sure that the membrane is defect free, the glass plate must be very clean and with no scratches. Second, the glass plate was immersed into icy distilled water at 4°C for at least 1 h. In this step, gelation, or the exchange of solvent (NMP) and nonsolvent (distilled water) occurred, resulting in the hardening of the membrane. The hardened membranes eventually peel-off by themselves from the glass plate. They were checked for defects using a light box. The defect free part would be chosen for the test. For the first and second stage of the experiments, the membranes were dried using solvent exchange technique (Matsuura, 1994). This consisted of sequentially submerging the membranes in four ethanol/water solutions (25, 50, 75 and 100% w/w ethanol) to remove the water from the membrane. The soaking in each of these solutions lasted at least 6 h. Afterwards, each membrane sheet was placed between filter papers to dry at room temperature. For the filtration and fouling tests, the membranes were cut into 65 mm diameter coupons and were stored at 4°C in Milli-Q water until they were used.

3.2.3 Evaluation of LSMMs migration using contact angle analysis

The hydrophilicity of a membrane can be quantified by measuring the contact angles of water drops deposited on it. Contact angles are not easy to measure because of the porosity of membrane materials. However, contact angle is still considered the most convenient index of membrane hydrophilicity, if measuring methods and times are carefully kept consistent (Amy et al., 2001). Contact angle varies depending on the surface chemistry, roughness and heterogeneity of the material (Johnson and Dettre, 1969). In an idealized smooth, homogeneous, and non-deformable surface, Gibbs (1928) predicted that there would be only one contact angle. The water drop in contact with a solid or liquid substrate would take a spherical shape, which minimizes the free energy of the system. Advancing contact angles, whose name comes from the method employed in measuring the angle, are the largest angles and relatively reproducible. In advancing contact angle measurement, water is continually added at a very slow rate, which makes the water drop grow until it moves (advances). The contact angle measured right after the sudden movement of the water drop is recorded as the advancing contact angle. Advancing contact angle characterizes the ability of a given liquid to spread on a surface caused by the active force exerted by the solid on the liquid. There are many factors affecting the reproducibility of contact angle measurements. Major factors are surface roughness, surface heterogeneity, surface porosity (which lead to absorption of the liquid to the substrate), and thus measuring rate. Johnson and Dettre (1969) found that increasing surface roughness would lead to an increase in advancing contact angle. Drelich et al. (1996) explained that the surface heterogeneity and roughness cause contortions in the shape of the three-phase contact line and the drop, which affect the internal free energy of

the liquid drop and thus cause a variation in contact angles. They observed changes in advancing contact angle while changing the drop volume and attributed surface roughness and heterogeneity to be the cause for contact angle/drop size relationship. They also observed different values for advancing contact angles when using two different measuring techniques (sessile-drop and captive-bubble) and the differences increased with increasing imperfections of the solid surface.

To evaluate the migration of LSMMs to the membrane surface, contact angle were conducted using a goniometer (FTA 200 Dynamic Contact Angle System, Camtel Ltd, Cambridgeshire, UK). This system, with a computer controlled syringe pump, allowed the operator to control the pumping rate and the volume of the water drop. The goniometer also included a digital camera, which recorded and magnified the image of the drop. In addition, it can capture both static and dynamic images to the computer's memory for later analysis. The time scale can vary from 1/60 second (60 images/second) to hours and can be varied nonlinearly to efficiently follow absorption. The manufacturer claimed that the accuracy of this goniometer is better than 1 degree.

For these measurements, the dry membrane was cut into small pieces of 8×36 mm and taped on micro slides (VWR, West Chester, PA), which served as supports. Different pieces from randomly different sheets of membranes were used to measure contact angles so as to account for the heterogeneity of the membrane surface.

Advancing and dynamic contact angles were measured. The technique used follows the sessile drop method, which is an optical contact angle method used to estimate wetting

properties of a localized region on a solid surface. Angle between the baseline of the drop and the tangent at the drop boundary is measured.

With advancing contact angle, the measurement was performed via the following procedure. First, a water drop was deposited on the membrane surface with the needle inside the water drop. Then, the controlled rate pump continued to pump water (usually for 2 second), increasing the water drop until there was a sudden movement of the water drop. The image was immediately captured and analyzed for advancing contact angle. The water drop volume used to measure advancing contact angle ranged from 1.6 to 2.4 μl and an average of 15 to 20 measurements were performed.

In the dynamic contact angle study, images of the water drop were captured for 60 seconds, 10 images per second. By analyzing these images, the changes of contact angle with time were recorded.

3.2.4 Evaluation of the impact of LSMMs and PVP on membrane characteristic and performance

After contact angle analysis, the most hydrophilic membranes were chosen for full characterization and fouling tests. The following subsections describe in detail the experimental set-up for the tests and the testing protocol.

3.2.4.1 Experimental set-up

The experimental setup consisted of six crossflow cells connected within a recirculation system. This apparatus was selected because it permitted the simultaneous evaluation of six coupons with essentially the same results as those of a SEPA® CF membrane cell by

Osmonics®, recommended by the USEPA (Mosqueda-Jimenez et al., 2004a). The recirculation system (Figure 3.2 and 3.3) consists of a feed reservoir, a high pressure diaphragm pump (Hydra-Cell, Wanner Engineering, Inc.; Minneapolis MN), a thermocouple (A-08439-84, LABCOR Technical Sales Inc, Anjou, QC), a prefilter (Integra Environment Inc., 150360, Burlington, ON), a flowmeter (P-32025-20 rotameter, Gilmont Instruments, Barrington, IL), a pressure regulator, the membrane test cells, and the recycling lines that return both the permeate and concentrate streams back to the reservoir to maintain the constant feed concentration. It was essential to have temperature control since the high-pressure pump caused a significant increase in the water temperature. The concentrate stream passed through a concentric-tube heat exchanger (stainless steel) connected to a 13 L heated/refrigerated circulator unit (Model 1150A, VWR, West Chester, PA) helped to cool the concentrate down to room temperature prior to its return to the feed reservoir. To avoid drastic changes in temperature due to the sunlight, the windows of the room were covered with styrofoam insulation with reflective surfaces. All tubing was clear PVC (Nalgene); the test cells, pipes, valves, and flowmeter were made of 316 stainless steel. The photograph below (Figure 3.2) shows the stainless steel UF cells and the experimental set up while the diagram of the recirculation system (Figure 3.3) clearly illustrate the parts of the system and the flow of water within the system.

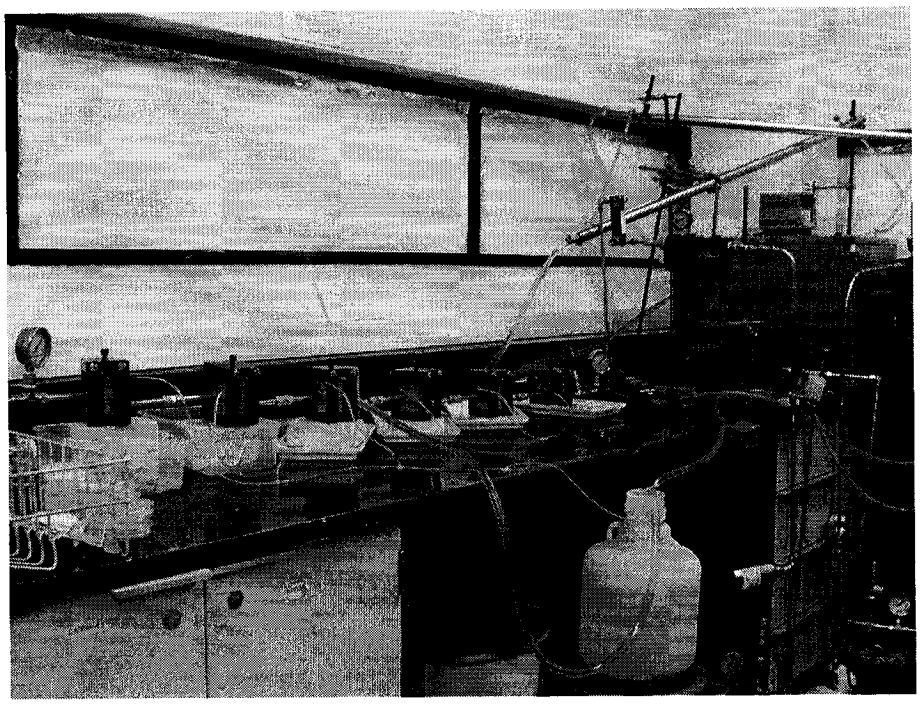


Figure 3.2 Experiment set-up

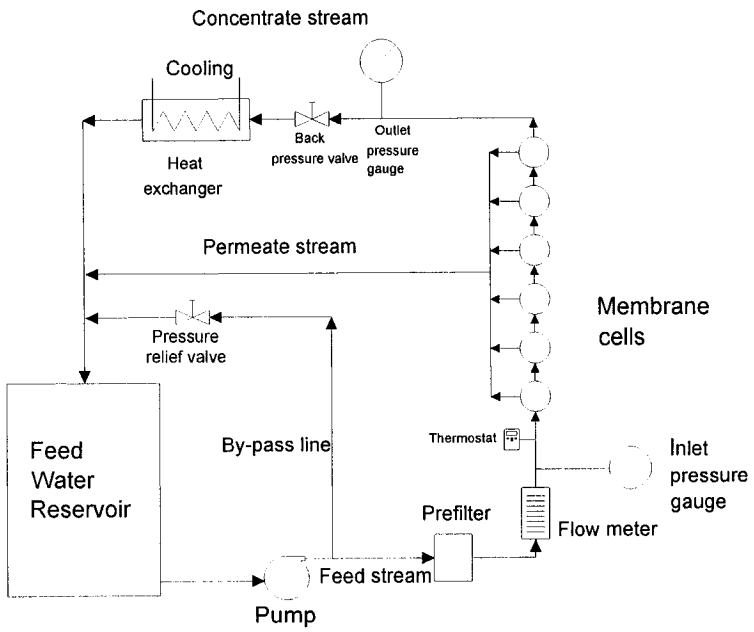


Figure 3.3 The membrane filtration system

3.2.4.2 Testing protocol

The testing protocol consisted of precompaction, pure water permeation rate (PWP) monitoring, solute characterization, and a fouling test with Ottawa River Water (ORW). In the precompaction, Milli-Q water was passed through the membranes for 1 hour at 552 kPa (80 psig). This precompaction time was chosen as a compromise based primarily on the desire to minimize flux reduction due to membrane compaction while avoiding a significant impact on membranes pore structure. This was followed by PWP monitoring for 50 hours at 345 kPa (50 psig). This testing time allowed obtain a constant permeate flux (less than 1% difference in fluxes measured three hours apart). The pure water permeation rate was checked by measuring the volume of the pure water passing through each membrane coupon for a specific time. With higher permeability membranes, fluxes were determined by measuring the volume of the permeate sample by a graduate cylinder. If the flux was very low, weighing was used instead of measuring the volume to obtain greater accuracy.

Afterwards, the UF membranes were characterized based on solute transport data. The molecular weight cut-off (MWCO) of each membrane was calculated from the transport data with solutions of PEG and PEO. PEG solutions of different molecular weights 4000, 6000, 10000, 12000, 20000, and 35000 Daltons and PEO solution with molecular weight of 100,000 Dalton were prepared with approximate concentrations of 100 ppm. Four to six of those solutions were circulated (one at a time) through the system for one hour. The order of the solutions was from low molecular weight to higher molecular weight solution to avoid fouling. The flowrate was 1.1 Lpm. The system was flushed with distilled water after each PEG/PEO solution circulation for 1 hour before the PWP was

measured again to corroborate that it had remained constant throughout the process of MWCO determination. Feed and permeate would then be collected and analyzed for TOC using a Total Carbon Analyzer (Model DC-190, Dohrman, Santa Clara, CA) with the combustion-inflared method as described in the standard method 5310 B, (Standard Methods, 1995). Using the results of the solute transport tests and the proper equations, the pore distribution, pore density, and surface porosity of each membrane were computed.

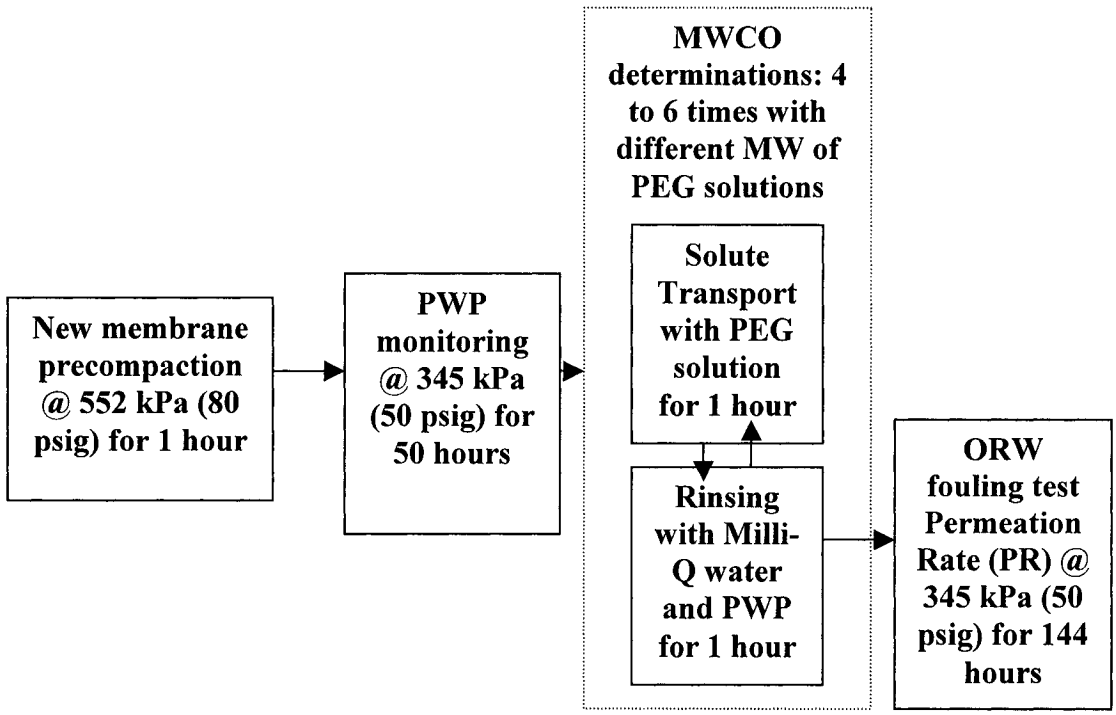


Figure 3.4 Membrane test protocol

The fouling tests with ORW that followed lasted for 144 hours (6 days). This duration allowed the permeate flux to reach a pseudo-steady state. The transmembrane pressure was set at 345 kPa (50 psig), which is within the UF operating ranges, to obtain reasonable permeate fluxes. The permeation rate was measured by weighing the mass of the permeate collected during predetermined times or measuring the volume of permeate

with higher permeability membranes (as in the PWP determination). The temperature of the feed was kept constant at 23° C by adjusting the temperature of the heat exchanger (i.e., water bath solution). The flow was set at 1.1 Lpm to allow the operation of six cells in series with a pressure drop of less than 14 kPa (2 psig) while creating turbulent flow conditions so as to avoid concentration polarization (Mosqueda-Jimenez et al., 2004c).

At the end of every experiment, the permeation area was checked, using a Manostat caliper (IQ Instruments, Switzerland). The NOM concentration was assessed by measuring the dissolved organic carbon (DOC) concentration using the Model DC-180 Dohrman Total Carbon Analyzer (Santa Clara, CA), which was based on the persulfate-ultraviolet wet oxidation method and an infrared detector.

The amount of NOM accumulated on top of the individual membranes at the end of the six-day fouling test (referred to as NOM deposition) was measured using the technique described by Hong and Elimelech (1997). Beakers were preconditioned in the oven at 105°C overnight. After they reached room temperature inside of a desiccator, they were weighed. Each membrane coupon was removed very carefully from the test cells and deposited in each beaker. Then, the NOM was dissolved using 25 mL of 0.1 M NaOH solution within the preconditioned beakers. After the NOM was completely removed from the membrane coupons, all the membrane coupons were taken out. The beakers containing the dissolved NOM would then be put in an air-circulated oven at 105°C for 24 h, together with at least two of blanks (with just 25 mL of NaOH solution). Afterwards, the beakers were allowed to reach room temperature inside of a desiccator and then were reweighed. The mass of NOM was calculated by the difference between

the dry weight of the NOM-NaOH solution and the average dry weight of the blanks (just containing NaOH solution).

3.2.5 Characterization of the feed water:

The water tested was Ottawa River Water (ORW) collected at the intake of Britania Water Treatment Plant on May, 2004. The water was stored in a freezer room at 2^{o} C to eliminate the potential for further biodegradation. One day prior to its use, the water was moved to the testing room so that it can reach room temperature (20^{o} C) before the test.

The chemical and physical characteristics of ORW were measured. The TOC concentration was measured using a total carbon analyzer (Model DC-180, Dohrman, Santa Clara, CA) based on the persulfate-ultraviolet oxidation method and infrared spectrometry. UV absorbance was measured at 254 nm using a spectrophotometer (DU-40, Beckman Instruments Inc., Irvine, CA) with a 1-cm quartz cell. Colour was determined using a colour comparator Aqua Tester by Orbeco Analytical Systems Inc (Farmingdale, NY). An Accumet pH meter by Fisher (Pittsburgh, PA) was used to read pH (Method 4500-H^{+} B, Standard Methods, 1995). Turbidity was determined using a turbidimeter Hach 2100AN (Loveland, CO) (Method 2130 B, Standard Methods, 1995). Alkalinity was determined by titration with H_2SO_4 (Method 2320 B, Standard Methods, 1995). Hardness was determined by titrating with EDTA (Method 2340 C, Standard Methods, 1995).

The molecular weight of the NOM in ORW was determined by UF fractionation using a 50 ml Amicon batch stirred UF cell (model 8050, Amicon Corp., Danvers, MA) and regenerated cellulose membranes (Millipore, Bedford, MA) with four MWCOs: 1, 3, 10,

and 30 kDaltons. UF fractionation technique followed in this study is described in detail by Nilson and DiGiano (1996) and Mosqueda-Jimenez (2003). Prior to their usage, the membranes were rinsed in Milli-Q water and kept in cold water. The applied pressure ranged from 241 kPa to 483 kPa to attain the flow recommended by the manufacturer. The applied pressures for 1, 3, 10, 30 kDaltons were 483 kPa (70 psig), 414 kPa (60 psig), 345 kPa (50 psig), and 241 kPa (25 psig), respectively. The first 3 ml of filtrate were wasted. Filtrates were collected until 70% of the water was filtered. The filtrates and retentates TOC concentrations were measured by a TOC analyzer (Tekmar/Dohrmann Phoenix 8000, Mason, Ohio) using UV-Persulfate oxidation followed by Infra-Red detection. The TOC concentration of a particular molecular weight fraction was calculated by substracting the TOC concentration of the filtrate from one membrane from the TOC concentration of the filtrate from the membrane of the next larger nominal MWCO (Nilson and DiGiano, 1996).

3.3 Experimental Design

The research in this thesis was divided into one preliminary study and three different stages. Figure 3.1 shows a flow diagram of the general methodology followed in this thesis. Depending on the results of each stage, an experimental plan was identified for the next stage.

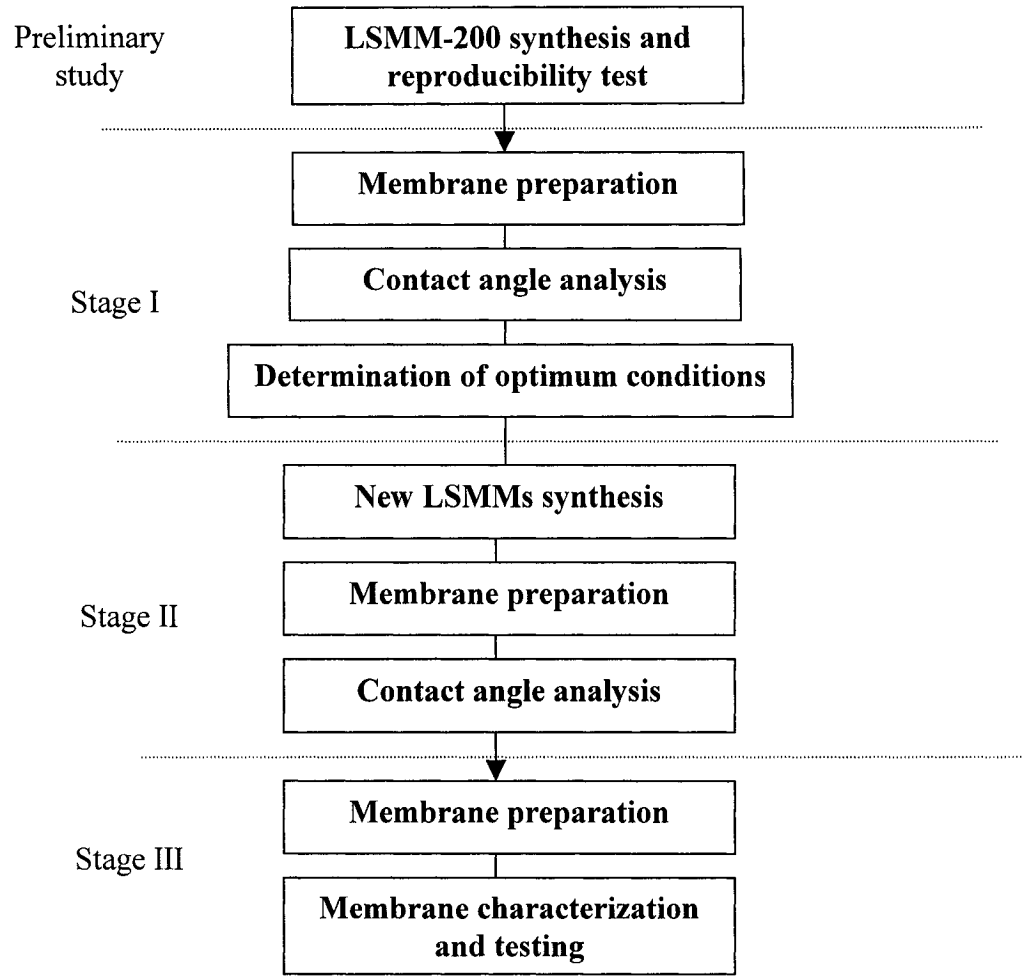


Figure 3.5 Methodology overview

In preliminary stage of the experiment, LSMM reproducibility was studied based on monitoring PWP and solute separation efficiency. To simplify the studies, membranes at only one concentration (20%) of the base polymer, PES, was used. LSMM200 from two batches A and B (referred to as LSMM200A and LSMM200B) was added at 1.5%. The study showed that membranes prepared with LSMMs from different batches showed statistically the same (with 95% confidence interval of three different coupons) PWP and solute separation. Results of the preliminary stage are presented in appendix A.

Stage 1 studied the impacts of different variables on membrane hydrophilicity using LSMM200. There were three variables suspected to affect the contact angle: PES concentration, the presence of PVP, and the concentration of LSMM 200. A 3×4×2 multi factor design was used to evaluate the effect of PES concentration, LSMM-200 concentration, and the absence and presence of PVP in the casting solution. The design generated 24 types of membranes that needed to be analyzed for contact angle. The PES concentrations were chosen at 15, 18, and 21%. The concentrations were not lower to avoid making very fragile and difficult to manufacture membranes, but not higher to produce very tight (low flow) membranes. LSMM200 was added as an additive at 1.5, 3, and 4.5% based on the study of hydrophobic SMMs (Mosqueda-Jimenez, 2003). PVP was absent or added at a ratio PVP:PES of 1 to 3. This is a ratio recommended in the membrane literature to produce a high flux and make the membrane manufacturing easier by increasing the casting solution viscosity (Mosqueda-Jimenez, 2003). Table 3.3 presents the 24 types of membranes tested in stage 1 of this study. Contact angle measurements were conducted on at least three different coupons of each type and at various locations within each coupon. The impact of PES concentrations on LSMM200 migration is presented in chapter 5, while the dynamic contact angle results are presented in appendix C.

Table 3.3 Membranes tested in the first stage

Membrane code	Composition			
	% PES	% PVP	% LSMM200	% NMP
PES15	15	0	0	85
PES18 (Control)	18	0	0	82
PES21	21	0	0	79
PES15P	15	5	0	80
PES18P (ControlP)	18	6	0	76
PES21P	21	7	0	72
PES15-200-1.5	15	0	1.5	83.5
PES18-200-1.5 (LSMM200-1.5)	18	0	1.5	80.5
PES21-200-1.5	21	0	1.5	77.5
PES15-200-1.5P	15	5	1.5	77.5
PES18-200-1.5P (LSMM200-1.5P)	18	6	1.5	74.5
PES21-200-1.5P	21	7	1.5	70.5
PES15-200-3	15	0	3	82
PES18-200-3 (LSMM200-3)	18	0	3	79
PES21-200-3	21	0	3	76
PES15-200-3P	15	5	3	77
PES18-200-3P (LSMM200-3P)	18	6	3	73
PES21-200-3P	21	7	3	69
PES15-200-4.5	15	0	4.5	80.5
PES18-200-4.5 (LSMM200-4.5)	18	0	4.5	77.5
PES21-200-4.5	21	0	4.5	75.5
PES15-200-4.5P	15	5	4.5	75.5
PES18-200-4.5P (LSMM200-4.5P)	18	6	4.5	71.5
PES21-200-4.5P	21	7	4.5	67.5

Stage 2 of the experiments studied the impact of LSMMs concentration of two other LSMMs as well as the impact of the presence and absence of PVP on membrane hydrophilicity. The base polymer, PES, was fixed at 18 wt % as PES concentrations did not have any impact on membrane hydrophilicity according to the result of stage 1. Three different concentrations of LSMMs were still studied because it was suspected that changing LSMM concentration would have a greater impact on membrane hydrophilicity than changing the PES concentration. The absence and presence of PVP was still

considered since it likely had a significant impact on membrane performance. A multifactor 2×3×2 factorial was chosen to study the impact of two types of LSMMs: LSMM-400, LSMM-600; three LSMM concentrations: 1.5, 3, 4.5%; and the absence and presence of PVP. That generated 12 types of membranes that needed to be analyzed for contact angle which are presented in table 3.4. Results presented in chapter 4 and 5 were the average of three different coupons.

Table 3.4. List of membranes tested in stage 2

Membrane code	Composition				
	% PES	% PVP	% LSMM added		% NMP
			400	600	
LSMM400-1.5	18	0	1.5	-	80.5
LSMM400-1.5P	18	6	1.5	-	74.5
LSMM400-3	18	0	3	-	79
LSMM400-3P	18	6	3	-	73
LSMM400-4.5	18	0	4.5	-	77.5
LSMM400-4.5P	18	6	4.5	-	71.5
LSMM600-1.5	18	0	-	1.5	80.5
LSMM600-1.5P	18	6	-	1.5	74.5
LSMM600-3	18	0	-	3	79
LSMM600-3P	18	6	-	3	73
LSMM600-4.5	18	0	-	4.5	77.5
LSMM600-4.5P	18	6	-	4.5	71.5

LSMM200, 400, 600: with the addition of LSMM200, 400, and 600
1.5, 3, 4.5: LSMM concentration added
P: With PVP

In the last stage of the experiments, the most hydrophilic membranes from the results of stage 1 and stage 2 were chosen for a full characterization and fouling evaluations. Table 3.5 listed the 12 types of membranes tested in stage 3. At least three different coupons of each membrane type were tested. Membranes number 1 and 2 are the two controls. Number 3 was the only membrane chosen from stage 1. It consisted of 18 wt % PES, and 4.5 wt% LSMM-200). Membranes number 5, 6, 7, 9, 10, 11 were chosen from the results

of stage 2. From stage 2 results, the impacts of two types of LSMMs (LSMM-400, LSMM-600), LSMM concentrations (1.5, 3, 4.5%), were considered which led to a 2×3 multifactor design. Membranes number 4, 8, 12 were chosen to study the impact of the presence of PVP on membrane performance, the PVP: PES ratio chosen was 1:3 was chosen. This design allowed evaluating the impacts of each LSMM type, LSMM concentrations, as well as the presence of PVP on membrane characteristics and performance.

The experimental design was presented in chronological order. The phase listed in chapter 4 and 5 do not follow exactly the same order presented in this chapter, but are based on types of experiment and experimental results.

Table 3.5. List of membranes tested in stage 3

No	Membrane code	Composition					
		% PES	% PVP	% LSMM added			% NMP
				200	400	600	
1	Control	18	0	-	-	-	82
2	ControlP	18	6	-	-	-	76
3	LSMM200-4.5	18	0	4.5	-	-	77.5
4	LSMM200-4.5P	18	6	4.5	-	-	71.5
5	LSMM400-1.5	18	0	-	1.5	-	80.5
6	LSMM400-3	18	0	-	3	-	79
7	LSMM400-4.5	18	0	-	4.5	-	77.5
8	LSMM400-4.5P	18	6	-	4.5	-	71.5
9	LSMM600-1.5	18	0	-	-	1.5	80.5
10	LSMM600-3	18	0	-	-	3	79
11	LSMM600-4.5	18	0	-	-	4.5	77.5
12	LSMM600-4.5P	18	6	-	-	4.5	71.5

LSMM200, 400, 600: with the addition of LSMM200, 400, and 600
1.5, 3, 4.5: LSMM concentration added
P: With PVP

CHAPTER 4

THE IMPACTS OF HYDROPHILIC SURFACE ADDITIVES ON POLYETHERSULFONE ULTRAFILTRATION MEMBRANES

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4.1 Abstract

One of the most serious disadvantages of membrane applications in water treatment is the decreasing water permeation rate with time, which is often called fouling. This study investigates surface modification of polyethersulfone (PES) ultrafiltration membranes as a fouling reduction strategy for drinking water treatment applications. Surface modification was achieved through the addition of three different tailor-made hydrophilic surface modifying macromolecules (LSMMs). Flat sheet membranes were prepared via a single-step casting procedure; their surface hydrophilicity was quantified via contact angle measurements. The surface modification produced slightly more hydrophilic membranes (contact angle reduction of up to 8°) and improved membrane performance compared with the PES membrane without blending. The molecular weight cut-off (MWCO) of LSMM200 modified membrane was reduced by a factor of 2. LSMM400 and LSMM600 modified membranes achieved up to 32% higher fluxes. Surface modification resulted in significantly decreased flux reductions and NOM deposition.

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Dissolved organic carbon (DOC) removals were approximately 70% for all the studied membranes. There was a clear trend of increasing long-term flux with decreasing contact angle.

Key words

Ultrafiltration, surface water, surface modification, fouling, NOM, DOC removal.

4.2 Introduction

Membranes have been increasingly used in drinking water treatment as they provide more reliable in bacterial and protozoal removal while avoiding the formation of toxic disinfection by-products (DBPs) by eliminating the need for chemical disinfection. Nanofiltration (NF) and ultrafiltration (UF) membranes have been reported to increasingly used to treat waters with high color and natural organic matter (NOM) concentrations, especially in northern countries where these organics are the main reason for their brownish color of the water (Thorsen, 1999). However, NOM has also been identified as an important foulant of microfiltration (MF), UF, and NF membranes (Amy et al., 2001) and fouling is an important concern in the operation of membrane systems.

Fouling reduction can be achieved through a number of different approaches including modification of membrane modules, operational procedures and membrane materials (Mulder, 1996). Polyethersulfone (PES) membranes have been modified by plasma treatment (Wavhal and Fisher, 2002), by physical coating with hydrophilic surfactants and by graft-polymerisation of hydrophilic monomers (Caroll et al., 2002). These surface modification approaches are complicated, require one or more additional manufacturing

steps, and are not always more effective. The incorporation of tailor-made surface active polymers in membrane casting solution to manufacture surface modified membranes via a single step casting is an attractive approach for membrane surface modification (Mosqueda-Jimenez et al., 2004c). The use of hydrophobic surface modifying macromolecules (SMMs) has proven to have positive impacts in membrane performances in pervaporation (Fang et al., 1994; Mahmud et al., 2001), and biomedical applications (Ho et al., 2000). Mosqueda-Jimenez et al. (2004c) found that these additives led to marginal improvements in the filtration of river water and suggested that hydrophilic additives may be more promising.

The aim of this work is to incorporate newly-developed hydrophilic surface modifying macromolecules (LSMMs) in PES ultrafiltration membranes and to evaluate their impacts on membrane hydrophilicity and performance. The LSMMs were specially designed and synthesized in our lab to be compatible with PES and capable of migrating to the surface of the membrane during the membrane manufacturing process, resulting in more hydrophilic membranes. The membrane performance will be evaluated in terms of pure water permeation rate (PWP), molecular weight cut-off (MWCO) and long term fouling tests. The fouling tests used Ottawa River Water (ORW), which has a high color content, and evaluated dissolve organic carbon (DOC) removal, long term fluxes, flux reduction and NOM accumulation on the membrane surface.

4.3 Experimental methods and analysis

4.3.1 Materials

PES (Victrex 4100P, ICI Advanced Materials, Billingham, UK, molecular weight ~ 17,000 to 19,000 Daltons) was the base polymer used in the preparation of the membrane casting solution. The solvent was reagent grade N-methyl-2-pyrrolidone (NMP) (Aldrich Chemical Company, Inc., Milwaukee, WI). The three LSMMs employed in the surface modification were referred to as LSMM200, LSMM400, and LSMM600. These LSMMs differ from each other only in the molecular weight of polyethylene glycol (PEG) used in their synthesis. The LSMM synthesis was performed according to the method outlined by Rana et al. (2005). The main chain is a urethane prepolymer formed from methylene bis-p-phenyl diisocyanate and polypropylene glycol in N,N-dimethylacetamide (DMAC) solvent. PEG (Sigma Chemical, St. Louis, MO) was used to endcap the main chain. The LSMM number, i.e., 200, 400, and 600, corresponds to the molecular weight of the PEG used in the end-capping.

PEG and polyethylene oxide (PEO) (Aldrich Chemical, Milwaukee, WI) were used as probe solutes for the solute transport tests in the molecular weight cut-off (MWCO) determinations. The molecular weight of PEG used were 6000, 8000, 12000, 20000, and 35000 Daltons, while for PEO the molecular weight was 100,000 Daltons. Ethyl alcohol 99% (BDH Inc., Toronto, ON) was used to dry the membranes for the contact angle measurements. Ultra pure water was prepared with a Milli-Q Water System (Millipore, Bedford, MA).

The test water used was Ottawa River water (ORW), the source water for the city of Ottawa, Canada. It was collected at the intake of the Britannia Water Treatment Plant on May 8th, 2004.

4.3.2 Membrane preparation

Flat-sheet membranes were prepared by the immersion precipitation technique described by Matsuura (1994). PES, NMP, with and without LSMM were the ingredients of the casting solutions. LSMM, then PES were completely dissolved in NMP before the solution was filtered and degassed inside a vacuum dessicator (VWR, Mississauga, ON). The homogeneous solution was then poured onto a clean glass support and spread by a casting rod to form a 250 μm thick layer. Right after casting, the cast film together with the glass plate was immersed into ice-water at 4°C for at least 1 h resulting in the hardening (i.e., gelation) of the membranes which peeled from the glass plate spontaneously. The membranes were stored in ultra pure water until they were tested. Each 22 × 28 cm membrane sheet produced one or two defect-free 51-mm diameter coupons. The casting solution consisted of 18 wt % PES, LSMM (0, 1.5, 3.0, or 4.5 wt %) and NMP, the solvent, making up the rest. Table 4.1 presents the 10 types of membranes tested in this study. The results for each membrane type were calculated based on the average of three different coupons. For contact angle measurements, membranes were dried by sequentially submerged for at least six hours in four ethanol/water solutions (25, 50, 75 and 100% w/w ethanol) to remove the water from the membrane before being placed between filter papers to dry at room temperature.

Table 4.1 Composition of membranes tested.

No	Membrane code	Composition				
		% PES	% LSMM added			% NMP
			200	400	600	
1	Control	18	-	-	-	82
2	LSMM200-1.5	18	1.5	-	-	80.5
3	LSMM200-3	18	3	-	-	79
4	LSMM200-4.5	18	4.5	-	-	77.5
5	LSMM400-1.5	18	-	1.5	-	80.5
6	LSMM400-3	18	-	3	-	79
7	LSMM400-4.5	18	-	4.5	-	77.5
8	LSMM600-1.5	18	-	-	1.5	80.5
9	LSMM600-3	18	-	-	3	79
10	LSMM600-4.5	18	-	-	4.5	77.5

L200, L400, L600: With LSMM 200, 400, and 600 respectively
1.5, 3, 4.5: concentration of LSMMs added (wt %)

4.3.3 Analysis

4.3.3.1 Water sources

Physicochemical characteristics of the test water were determined using standard methods (Standard Methods, 1995). DOC concentrations (feed and permeate) were measured using a total carbon analyzer (Model DC-180, Dohrman, Santa Clara, CA) based on the persulfate-ultraviolet oxidation method and infrared spectrometry. UV absorbance was measured at 254 nm using a spectrophotometer (DU-40, Beckman Instruments Inc., Irvine, CA) with a 1-cm quartz cell. In this analysis, Milli-Q water was used as a blank. UV absorbance was used as TOC surrogate for approximately one third of the samples since they were linearly related.

The molecular weight distribution of the organic matter in the ORW was determined by UF fractionation using the 50 ml stirred UF cell (model 8050, Amicon Corp., Danvers, MA) and regenerated cellulose membranes from Millipore (Bedford, MA) with MWCO

values of 1, 3, 10, and 30 kDaltons. The procedure was conducted according to the method outlined by Nilson and DiGiano (1996).

4.3.3.2 Contact angle analysis

The hydrophilicity of the membranes was quantified via contact angle measurement using a goniometer (FTA 200 Dynamic Contact Angle System, Camtel Ltd, Cambridgeshire, UK). This system has a computer controlled digital camera and a syringe pump that allowed the operator to control the water pumping rate and the volume of the water drop. The manufacturer claims that the accuracy of this goniometer is better than 1 degree.

The dry membrane samples were cut into 8×36 mm pieces and taped on micro slides (VWR, West Chester, PA). Different pieces from randomly chosen sections of membrane sheets were used to measure contact angles so as to account for the heterogeneity of the membrane surface.

The sessile drop method is a quick and simple method for measuring advancing contact angles (Zhang et al., 1989). To minimize the impact of gravity, water drop volumes were kept as constant as possible, ranging from 1.4 to 2 μl. The advancing contact angle measurements were performed via the following procedure. First, a water drop was deposited on the membrane surface with the needle inside the water drop. Then, the pump continued to pump water at a constant rate (usually for two seconds), increasing the water drop size until there was a sudden movement of the water drop. The image was immediately captured and analyzed for the advancing contact angle. The results presented are average values of 15 to 20 measurements.

4.3.4 Experimental set-up and membrane testing protocol

Membrane coupons were placed randomly in the six continuous crossflow cells connected in series within a recirculation system (Figure 4.1). This apparatus was selected because it permitted the simultaneous evaluation of six coupons with essentially the same results as those of a SEPA® CF membrane cell by Osmonics®, recommended by the USEPA (Mosqueda-Jimenez et al., 2004a). The experimental set-up consists of a feed reservoir, a high pressure diaphragm pump (Hydra-Cell, Wanner Engineering, Inc., Minneapolis, MN), a Digi-sense type T thermocouple thermometer (A-08439-84, LABCOR, Anjou, QC), a prefilter (150360, Integra Environment Inc., Burlington, ON), a flowmeter (P-32025-20 rotameter, Gilmont Instruments, Barrington, IL), a pressure regulator gauge, the membrane test cells, and the recycling lines that return both the permeate and concentrate streams back to the reservoir to maintain the constant feed concentration.

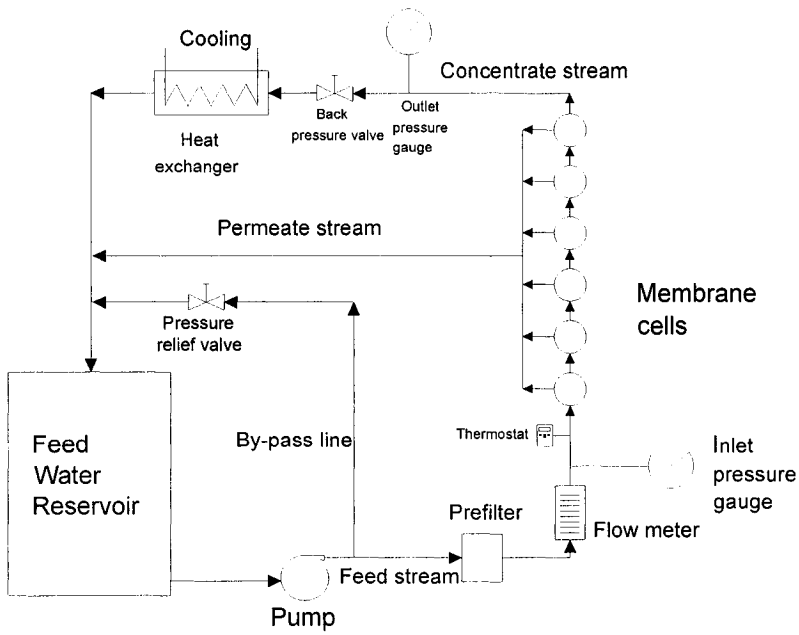

Figure 4.1 The membrane filtration system

The testing protocol consisted of precompaction, PWP monitoring, MWCO determinations and a fouling test with ORW. Figure 4.2 presents the testing protocol. A 552 kPa (80 psig) one-hour precompaction step was chosen based on preliminary studies to minimize flux reduction by membrane compaction while avoiding significant changes in the membrane pore structure. The PWP monitoring, which lasted 50 hours, yielded a constant permeate flux (less than 1% difference in fluxes measured three hours apart). In the MWCO determinations, 100 mgC/L PEG (molecular weight 6000, 8000, 12000, 20000, 35000 Daltons) and PEO (molecular weight 100,000) solutions were filtered through the membranes. The feed and permeate samples were collected and analyzed for TOC using a Total Carbon Analyzer (Model DC-190, Dohrman, Santa Clara, CA) based on high temperature catalytic oxidation. The membrane system was flushed for one hour with distilled water after each PEG/PEO solution circulation before the PWP was remeasured to corroborate that the membrane had remained the same. Based on the results of solute separation test, the MWCO was determined as the molecular weight that would yield 90% solute separation. Other membrane characteristics including the pore distribution, pore density, and surface porosity of each membrane could also be determined. The fouling test with ORW that followed, lasted for 144 hours (6 days), which allowed the permeate flux to reach a pseudo-steady state. The transmembrane pressure was set at 345 kPa (50 psig), which is within the UF operating range. Permeation rate was measured by weighing the mass of the permeate over predetermined time intervals. With higher permeability membranes, fluxes were determined by measuring the volume of the permeate sample by a graduated cylinder. The feed flow was set at 1.1 Lpm to allow the operation of six cells in series with a pressure drop of less

than 14 kPa (2 psig) while creating turbulent flow conditions so as to avoid concentration polarization (Mosqueda-Jimenez et al., 2004c). The temperature of the feed was kept constant at 23°C with the help of a heat exchanger.

At the end of every experiment, the permeation area was checked, using a Manostat caliper (IQ Instruments, Jona, Switzerland). Within the fouling tests, the NOM concentrations of the feed and the permeate were quantified by measuring dissolved organic carbon (DOC) removal using a persulfate-ultraviolet wet oxidation based analyzer with an infrared detector (Model DC-180 Dohrman Total Carbon Analyzer, Santa Clara, CA). DOC removal was calculated by equation 4.1:

$$DOC \text{ removal} = 100 \times \left(1 - \frac{C_{p(t)}}{C_f}\right) \tag{4.1}$$

where $C_{p(t)}$ is the permeate concentration at time t and C_f is the feed concentration (mass/volume). The long-term DOC and long-term fluxes refer to those measured at the end of the 144-hour ORW filtration/fouling test.

The amount of NOM accumulated on top of the individual membranes at the end of the six-day fouling test (referred as NOM deposition) was measured using the technique described by Hong and Elimelech (1997).

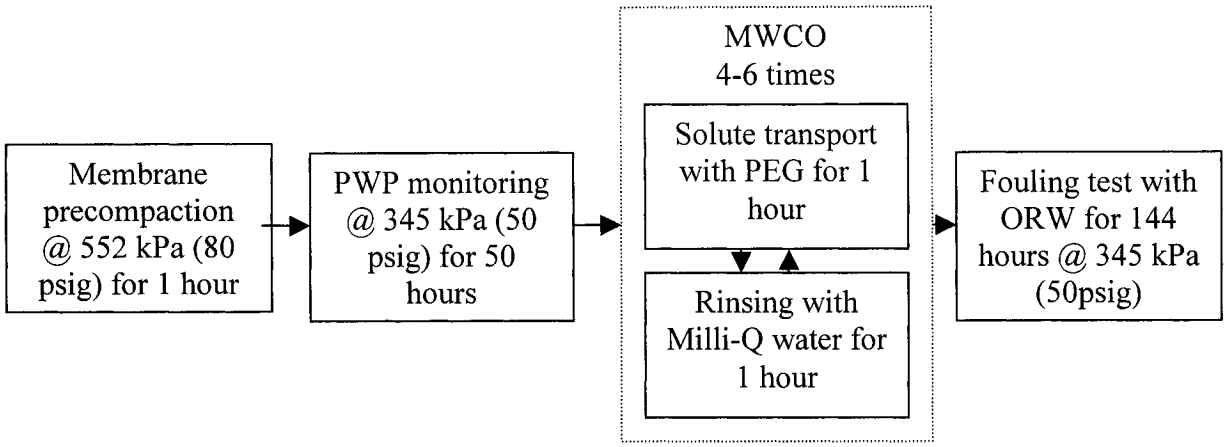

Figure 4.2 Membrane testing protocol

4.4 Results and discussion

The characteristics of the test water (ORW) are presented in Table 4.2. ORW is a clear but colored water with low hardness and alkalinity. The color arises from the organics (NOM= 7mg/l) and the SUVA (SUVA= UVA_{254}/TOC is an indicator of the humic content of the NOM) is in the middle range. The NOM fractionation of the organics in ORW (Figure 4.3) showed that approximately 18% of the NOM was smaller than 1,000 Daltons; 5% was in the range of 1,000 to 3,000 Daltons, 55% of the TOC of the NOM was between 3,000 to 10,000 Daltons; 22% was in the range of 10,000 and 30,000 Daltons; and only 1% of the NOM was bigger than 30,000 Daltons. This was somewhat similar to the results reported by Mosqueda-Jimenez et al. (2004a) (95% of the NOM had molecular weight smaller than 30 kDaltons) and Jacangelo et al. (1994) (92% were smaller than 30 kDaltons). The sample fractionated by Mosqueda-Jimenez et al. (2004a), which was collected at the same location at almost the same time of the year (June 6 as opposed to May 8 for the current sample) four years earlier, differed somewhat in that the

10-30 kDaltons fraction accounted for almost 60% of the DOC while for the current sample, the 3-10 kDaltons fraction was similarly dominant.

Table 4.2 Ottawa River water quality characteristics

Parameter	*ORW*
TOC concentration (mg/L)	7
SUVA ($m^{-1}mg^{-1}L$)	3.7
Colour (cu)	30
pH	7.2
Alkalinity (mg/L as $CaCO_3$)	26
Turbidity (NTU)	0.7
Total hardness (mg/L as $CaCO_3$)	22
Calcium hardness (mg/L as $CaCO_3$)	17

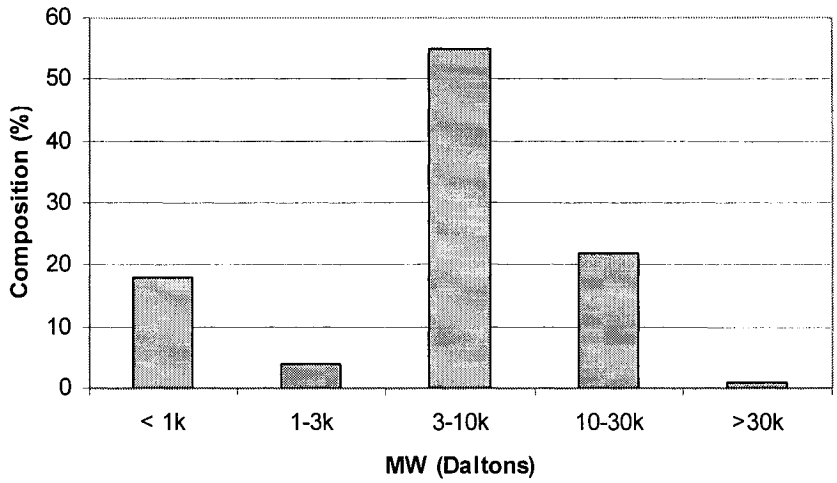

Figure 4.3 Molecular weight distribution of ORW

4.4.1 Impacts of LSMMs on membrane hydrophilicity

The advancing contact angle of the LSMM modified membranes decreased up to 8° demonstrating the migration of LSMM to the membrane surface (Figure 4.4). The contact angle decrease of LSMM200 modified membranes was lower than that of the membranes prepared with other two LSMMs indicating that LSMM migration is related to the molecular weight of PEG used in the LSMM synthesis. Increasing the LSMM concentration was expected to increase the chance of LSMM migration to the membrane

surface and thus reduce the contact angle. With LSMM200 and LSMM400 membranes, increasing LSMM concentration resulted in statistically the same advancing contact angle values. The insignificant impact of increasing LSMM200 and LSMM400 concentration may be the result of the opposing impacts of increasing migration driving force and the greater resistance to migration due to the increased viscosity. For PES/LSMM600 membranes, increasing the LSMM concentration increased the advancing contact angles (increasing 2^{o} with 1.5% LSMM concentration increase). This may be due to a possible increase in solution viscosity (as experienced by the greater difficulty in filtering the casting solutions), which may interfere with the movement of LSMMs and thus hindering their migration to the membrane surface.

It is well known that contact angle measurements are impacted by a number of factors, including porosity (Chan, 1994). The MWCO and the surface porosity results, presented in the next section, showed that the increase of LSMMs concentration produced membranes with lower MWCOs, and smaller pore sizes and lower porosity. The lower porosity also might reduce the adsorption of water drops into the membrane, thus resulting in higher advancing contact angle values. In addition, increasing LSMM concentration might increase surface roughness, which has been reported to cause an increase in advancing contact angle (Chan, 1994; Andrade, 1985; Drelich et al., 1996). These observed results somewhat contradict those of Rana et al. (2005). When increasing the LSMM200 concentration from 0 to 6 wt %, they observed a decrease of 8^{o} in static contact angle. It is believed that these differences were due to different gelation bath temperatures ($4^{o}C$ in this study as opposed to $25^{o}C$ in Rana et al., 2005). The higher temperature might accelerate LSMM migration because increases in temperature reduce

the frictional resistance, enhancing the mobility of each component (Akthakul et al., 2002). This observation agrees well with Hester and Mayes (2002). However, lower temperature gelation bath has been shown to produce more favorable membrane characteristics (smaller MWCO, smaller pore size, but higher pore density and higher surface porosity, which led to better membrane performances (Alsari et al., 2001)). That partly explains why the PWP and the ORW fluxes observed in this study were 6 to 10 and 3 to 5 times higher, respectively, than those observed in Rana et al. (2005) studies.

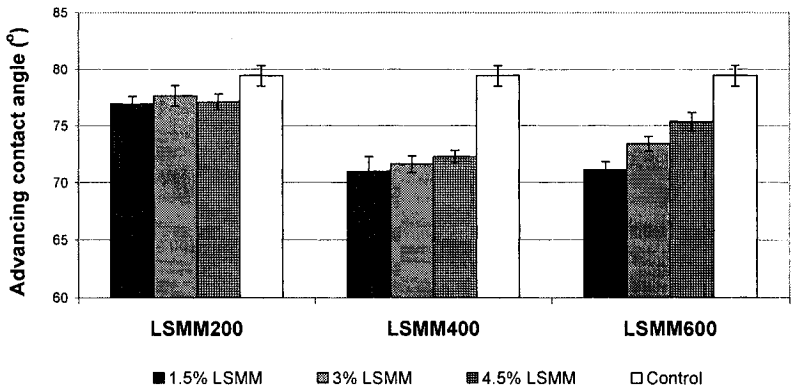

Figure 4.4 Advancing contact angle of PES/LSMM membranes as a function of LSMM type and dose

4.4.2 Effects of LSMMs on membrane performance and fouling reduction

To investigate the impact of hydrophilicity on membrane performance, only the membranes with the highest hydrophilicity were tested, i.e., membranes with 4.5 wt % of LSMM200 and membranes with all three concentrations of LSMM400 and 600.

4.4.2.1 MWCO and PWP

Figure 4.5 presents the MWCO of unmodified and modified membranes. In general, adding LSMM increased MWCO except for the LSMM200-4.5 and LSMM600-4.5

membranes. This is considered to be due to the increase in surface hydrophilicity as Mosqueda-Jimenez et al. (2004b) reported the opposite effect on MWCO with hydrophobic SMM surface modification. It is unclear why this is the case. Increasing the LSMM concentration, i.e., increasing the polymer concentration in the casting solution, was expected to result in tighter membranes, or a decrease in MWCO. The expectation was met when the LSMM400 and 600 concentrations were increased from 1.5 wt % to 4.5 wt %.

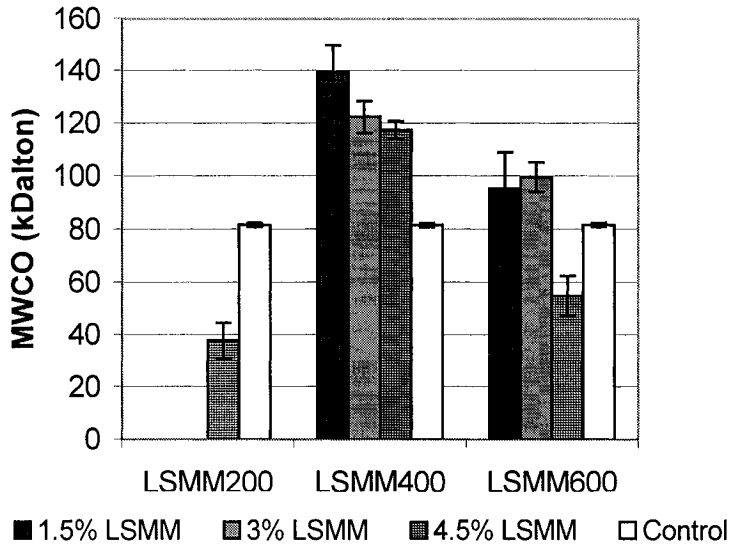

Figure 4.5 MWCO values of unmodified and LSMM modified PES membranes.

For the first six hours testing (with Milli-Q water) during the PWP monitoring stage, the flux declined drastically indicating a high degree of mechanical compaction. After that, the flux decreased at much lower rate and reached a pseudo-steady state after 50 hours of PWP. In spite of the increase in MWCO and hydrophilicity, the PWP of LSMM modified membranes were lower than that of the unmodified counterpart (Figure 4.6). This observation is consistent with Amy et al. (2001) who observed lower PWP for several

membranes with increasing hydrophilicity and MWCOs. The higher PWP in spite of higher MWCOs and hydrophilicity could be explained by the increases in surface porosity of the modified membranes. In fact, for this study, there was a clear trend of increasing PWP with increasing surface porosity. The addition of LSMMs increased the volume fraction of polymer, leading to a lower surface porosity membranes and consequently, lower permeability (Mulder, 1996).

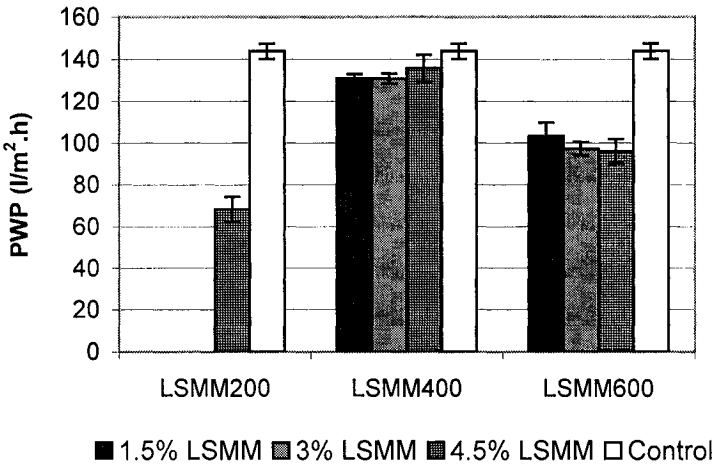

Figure 4.6 Pure water permeation (PWP) rate

4.4.2.2 ORW fouling test

4.4.2.2.1 ORW normalized permeate flux monitoring with time

The permeate fluxes of the membranes were monitored during the test with ORW. There was a drastic reduction of flux with time. There are several reasons for the flux decrease including mechanical compaction, and fouling. In general, the flux decline rates of the unmodified membrane and of high MWCO membranes were higher than those of the modified membranes and of lower MWCO membranes, respectively. Figure 4.7 presents the normalized flux decline (J/J_0) with time of three typical membranes: the control (MWCO 82 kDaltons), LSMM400-4.5 (MWCO 117 kDaltons), and the LSMM200-4.5

(MWCO 38k Daltons). For membranes with bigger MWCOs (82 and 117 kDaltons), there was a rapid normalized flux decline in the first six hours, as opposed to much lower flux decline in the membrane with lower MWCO (37 kDaltons). That might due to the fact that the first two membranes had bigger pore size, which might allowed large amount of NOMs to pass through the membrane and thus were more vulnerable to pore blocking. This was indirectly confirmed by the lower initial DOC removals of the control and the LSMM400-4.5 membranes compared to those with lower MWCOs including the LSMM200-4.5. Among the two membranes with high MWCO values, the modified membrane (LSMM400-4.5) retained a higher normalized flux compared to the control despite its higher MWCO. After the first six hours with ORW, the fluxes were much more stable.

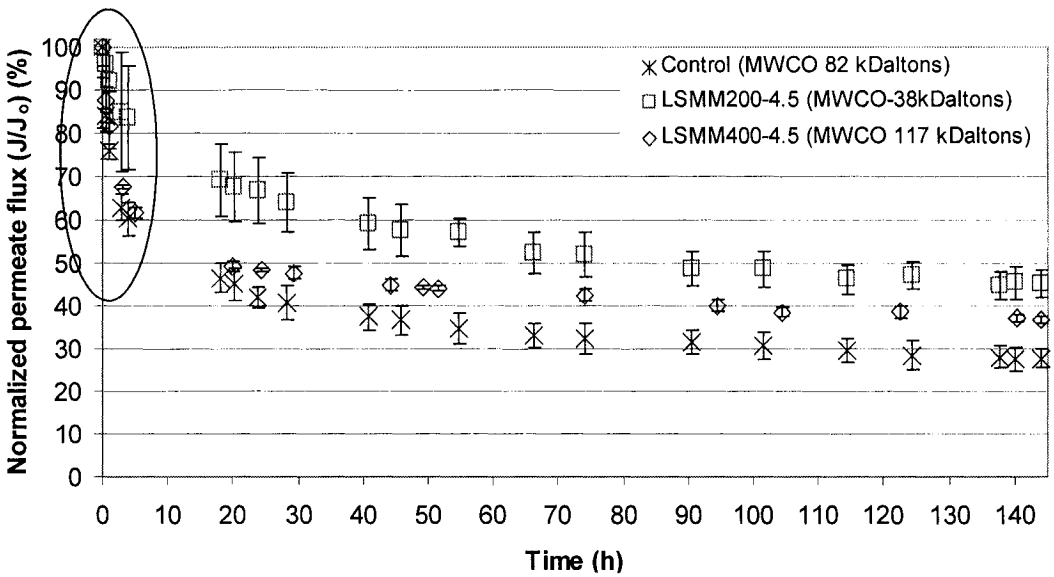

Figure 4.7 Normalized flux with time within the ORW filtration test

4.4.2.3 Long term flux

At the end of the test, the modified membranes (except for LSMM200-4.5 which had much lower MWCO) achieved higher fluxes than the control (Figure 4.8). Increasing the concentration of LSMMs resulted in membranes with statistically similar final fluxes except for the LSMM400-4.5 membrane. Regardless of its smaller MWCO compared to other LSMM400 membranes (with 1.5 and 3%), the LSMM400-4.5 membrane had 32% higher flux than the control. Among the LSMM600 membranes, the highest flux was 28% larger than the control.

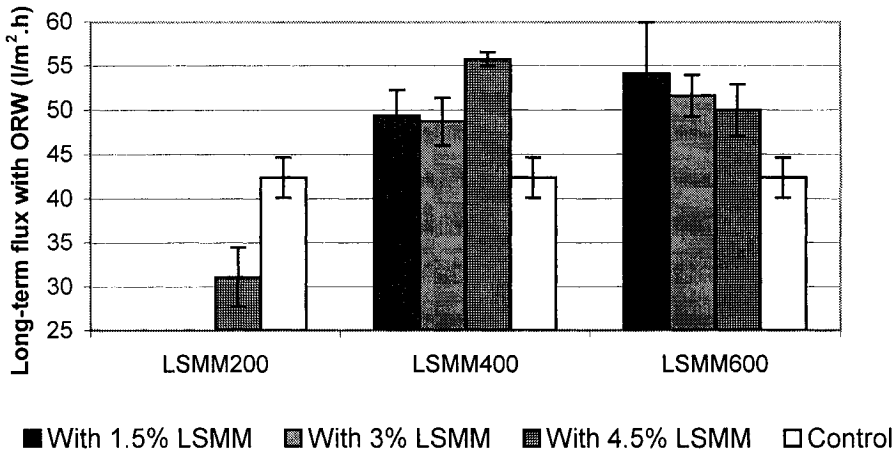

Figure 4.8 Long term permeate flux with ORW

4.4.2.4 Long term flux-hydrophilicity correlation

The higher final fluxes of the modified membranes in spite of their lower initial PWPs were presumably due to the increase in surface hydrophilicity. Therefore, long-term flux versus advancing contact angle was plotted. A general trend of slightly increasing long-term flux with increasing hydrophilicity was observed for the PES-LSMM400 and 600 membranes (Figure 4.9). Again, the LSMM200-4.5 deviated from the correlation because it had a totally different impact on the membrane (much lower MWCO). This is

consistent with the observations of Wavhal and Fisher (2002) and Kull et al. (2005). Amy et al. (2001) reported the opposite effect however their membranes not only differed in their contact angle but also in the base polymer, preparation procedure and other key characteristics. This suggests that the comparison of the impact of membrane hydrophilicity on membrane performances should be based on membranes of similar characteristics in which the base polymer play the essential role.

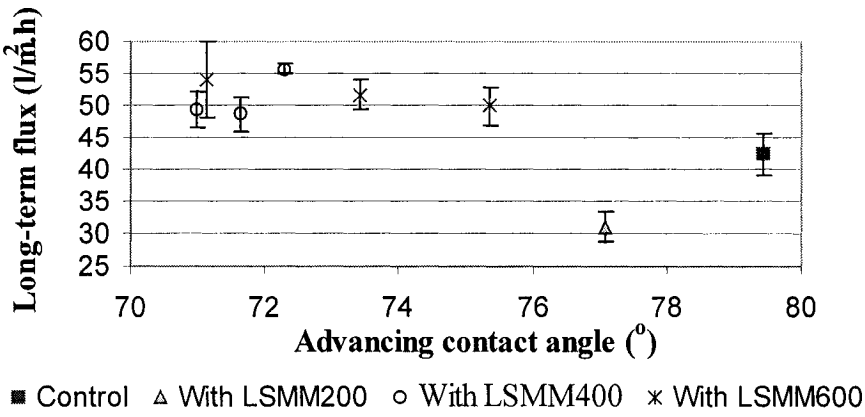

Figure 4.9 Long term permeate flux versus advancing contact angle

4.4.2.5 MWCO-final flux correlation

MWCO was plotted against final flux from the ORW filtration tests to see if all membranes followed a similar trend (Figure 4.10). Most of the data followed the expected increasing MWCO with increasing flux pattern. There was one exceptional good case (LSMM600-4.5) that produced both higher flux and lower MWCO compared to the control. This higher flux in spite of its lower MWCO might be due to its smaller mean pore size, greater hydrophilicity (which according to Jucker and Clark (1994) should result in a decrease in NOM fouling/adsorption), or its lower mechanical compaction), or the combination of the three.

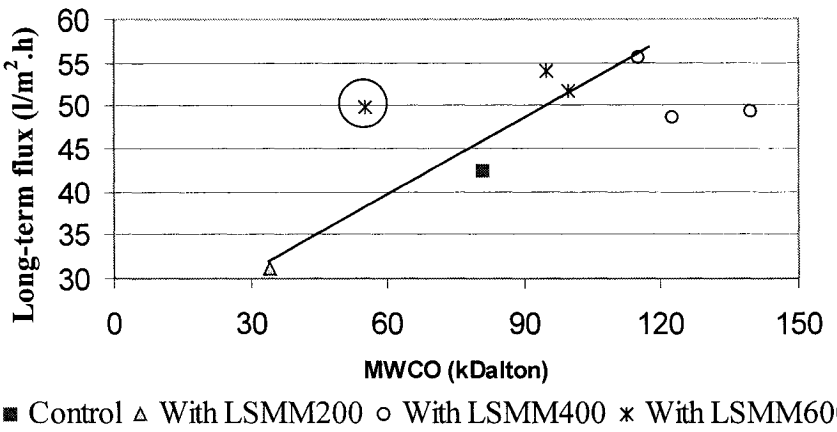

Figure 4.10 Long term permeate flux – MWCO trade-off boundary

4.4.2.6 Flux reduction

Membrane fouling was experimentally measured through the determination of the normalized flux reduction, which is calculated according to equation 4.2.

$$\text{Normalized flux reduction}_{(t)}\ (\%) = 100\left(1 - \frac{PR_{(t)}}{PWP}\right)_{ORW} \tag{4.2}$$

where $PR_{(t)}$ is the permeate flux (product rate) of ORW at time t (t=144 hours), and PWP was the stable pure water permeation rate. Both have dimensions of volume/time/area. A higher flux reduction, which leads to a lower final flux, indicates more fouling. Flux reduction was significantly reduced by the addition of LSMMs, especially LSMM600 (around 25% of the control) as shown in Figure 4.11, which indicated less fouling in the unmodified membranes. The impact of three different LSMMs resulted in different impacts. LSMM600 membranes achieved the lowest flux reduction, i.e., these membranes fouled the least. Among the modified membranes, LSMM400 membranes had the highest flux reductions. The concentration of LSMM400 and 600 did not have

any statistically significant impacts of flux reduction except for one case (LSMM400-4.5).

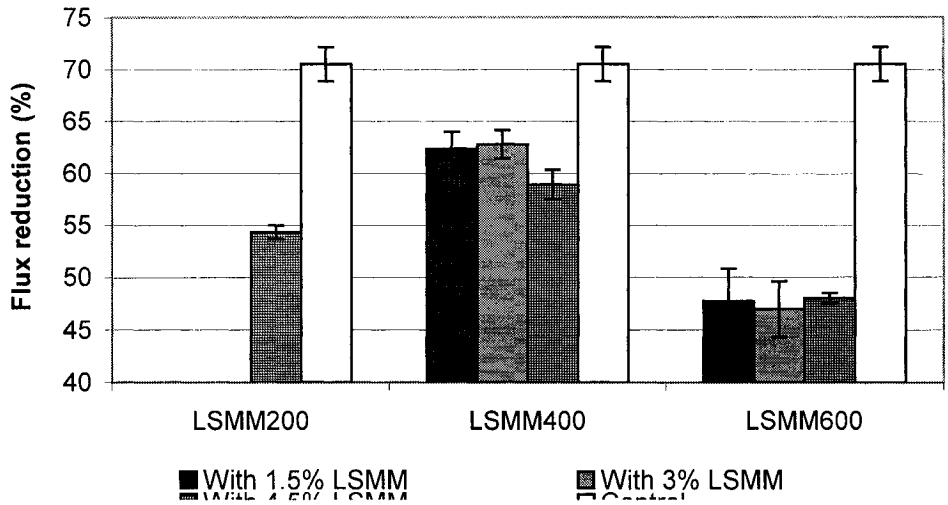

Figure 4.11 Flux reduction of unmodified and LSMM modified membranes

4.4.2.7 DOC removal

During the 144-hour test with ORW, DOC removal increased drastically for the first 40 hours and then reached a plateau. At the end of the test, the DOC removals for all membrane types were in the range of 67 to 73% with the control having the highest DOC removal (73%). When a non-fouling feed (PEG solution) was used in the MWCO determinations, the solute rejection efficiency decreased with increasing membrane MWCO, as expected. However, with ORW, only the initial DOC removal (measured after 30 min of the fouling test) followed the expected MWCO trend, after that point, that trend was not observed.

The DOC removal levels were high despite of the high MWCO values. The fact that the membranes show a higher NOM rejection than expected based on their large MWCOs, is

likely due to charge repulsion (electrostatic exclusion) between the membrane surface charge and the charge of NOM components (Amy et al., 2001). In addition, given the molecular weight of the NOM in ORW (99% of the NOM has MW less than 30 kDalton) and the MWCO of the membranes (all membranes have MWCO more than 35 kDalton), and the slightly different final DOC removal values of different membrane types, it is highly likely that pore adsorption was more dominant. The NOM adsorption can happen in multilayers, which might eventually resulted in pore blocking. This adsorption would reduce the membrane pore size, thus increase the DOC rejection. It is also likely that fouling was most severe in the unmodified membrane since it had the highest DOC removal regardless of its bigger MWCO compared to some other membrane types. Therefore, although fouling decreased flux, at the same time increased DOC rejection.

Other than NOM size, other water source characteristics might also contribute to the impact of MWCO on DOC removal. Amy et al. (2001) found DOC removal to be independent of MWCO of a water with SUVA=5.7 $m^{-1}mg^{-1}L$, while a water with SUVA=2.9 $m^{-1}mg^{-1}L$ showed a dependence. As ORW falls in between these values, it is evident that the impact of SUVA, an indicator of the humic content of the NOM, on DOC removal/MWCO needs further study. DOC removal levels in this study were much higher than reported for commercial UF membranes, however generally they are consistent with those reported by Mosqueda-Jimenez et al. (2004c) in laboratory-scale tests of PES UF membranes using ORW.

Figure 4.12 presents DOC rejection rate versus final flux. Mosqueda-Jimenez (2003) observed a compromise between final flux and DOC removal, i.e., higher DOC removal was achieved by membranes with smaller permeation rate. In this study, the overall DOC

removal and final flux appeared to be independent. Although there was a significant difference in the final fluxes, DOC removal rate was statistically (with 95% confidence level) similar. However, the PES-LSMM400 and PES-LSMM600 did show a slight trend of decreasing average DOC removal with increasing long term flux as expected.

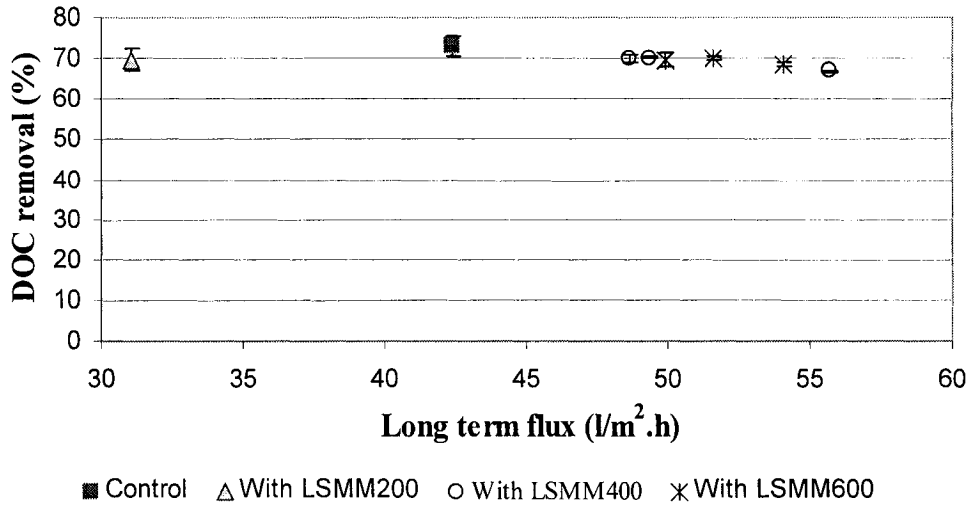

Figure 4.12 Long-term DOC removal versus long-term flux for ORW

4.4.2.8 NOM deposition

NOM deposition on top of the membrane at the end of the test was measured because it was likely related to membrane fouling. Figure 4.13 presents how the NOM accumulation on top of the membrane surface was significantly reduced by surface modification. However, since very small amounts of NOM accumulate, the results are subject to large errors. Considering the 95% confidence intervals, only the three types of membranes (with 4.5% LSMMs) had significantly lower NOM deposition. No clear correlation of the amount of NOM deposition and contact angle was observed due to high degree of variability of the measurement. The control had highest amount of NOM accumulation

which is reasonable given it has the highest DOC removal, highest flux reduction and second lowest final flux. Presumably this occurred because it allowed large amounts of NOM to pass through, thus was more vulnerable to fouling and more flux decline. Figure 4.14 presents the mass of NOM deposited versus final flux. With LSMM400 and 600 membranes, higher fluxes were obtained with less NOM deposition. Interestingly, most of least fouled membranes were those with highest LSMMs concentration (4.5%). This suggests the positive impacts of increasing LSMM400 and LSMM600 concentration in fouling reduction. Once again, the LSMM200-4.5 deviated from the rest data.

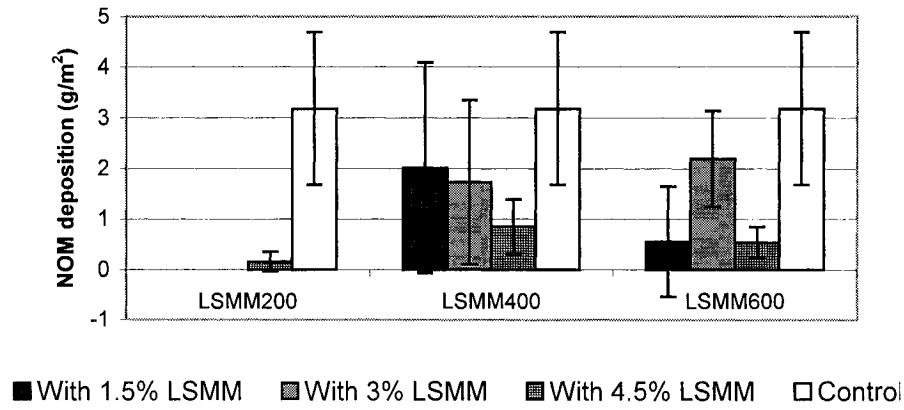

Figure 4.13 NOM accumulation on membrane surface

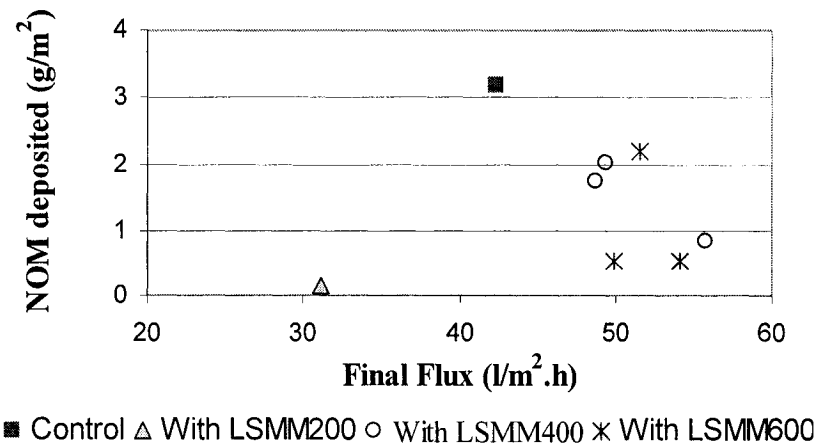

Figure 4.14 NOM accumulation versus long-term flux for ORW filtration

4.5 Conclusions

There was a clear evidence of the LSMM migration to the membrane surface. Increasing LSMMs concentration did not decrease advancing contact angle as expected. The impact of LSMM400 and 600 on membrane hydrophilicity was greater than that of LSMM200. The incorporation of LSMMs decreased advancing contact angle only up to 8^{o}, which makes the modified membranes more hydrophobic compared to commercial hydrophilic membranes. However, the membrane performance improved significantly. The impacts of three different LSMMs were quite different. The incorporation of LSMM200 at 4.5% resulted in a tighter membrane; MWCO was reduced by a factor of 2. With LSMMs addition, flux reduction decreased which indicates less fouling. In general, the addition of LSMM400 and LSMM600 increased the final flux (up to 32%), decreased NOM deposition (up to 83%), and decreased flux reduction (up to 25%) while it maintained high DOC removal levels (67-73%). Compared to the membranes with similar MWCO values reported by commercial membrane manufacturers, the long-term fluxes of the membranes in this study (31 to 56 $l/m^2.h$) are in the average range. However, while reported values of DOC removals of UF membranes are mostly lower than 50%, these modified membranes obtained much higher DOC removals (67 to 73%). Compared to commercial membranes with similar high level of DOC removals, the fluxes of the membranes developed in this study are relatively high. These differences may be in part due to the differences in testing conditions or MWCO determinations. In this study, the lack of impact of MWCO on DOC removal was presumably due to the enhancement of NOM internal pore adsorption.

Except for LSMM200, there was a clear trend of increasing final flux with increasing membrane hydrophilicity. A trend of decreasing flux reduction with increasing membrane hydrophilicity was also observed, but it was different for the LSMM400 and LSMM600 membranes.

4.6 Acknowledgements

This project was conducted thanks to the financial support of Materials and Manufacturing Ontario (MMO). Thanks to Dr. Raluca Voicu of Institute for Microstructural Sciences at the National Research Council of Canada for providing access to the contact angle analysis equipment and help operating it.

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rate but these membranes had lower long-term fluxes and were more susceptible to mechanical compaction and fouling.

Key words

Ultrafiltration, surface modification, PVP, fouling

5.2 Introduction

Membrane fouling is a key feature that has been hindering the more widespread use of membranes. Natural organic matter (NOM) has been identified as an important foulant in microfiltration (MF), ultrafiltation (UF), and nanofiltration (NF) membranes in drinking water applications [1]. Membrane modification is a fairly popular strategy in reducing the impact of membrane fouling [2]. Polyethersulfone (PES) membranes have been modified by plasma treatment [3], by physical coating with hydrophilic surfactants and by graft-polymerization of hydrophilic monomers [4]. These surface modification approaches require two or more manufacturing steps, and are not always particularly effective. For the past twelve years, Dr. Matsuura, Santerre, Narbaitz and coworkers have been studying the blending of tailor-made surface active polymers in PES membrane casting solutions to manufacture surface modified membranes via a single step casting [5]. During membrane manufacturing process, these additives migrate to the membrane surface and render it more hydrophobic or hydrophilic. So far, there have been two types of surface modifying polymers developed: hydrophobic and hydrophilic additives. The use of hydrophobic **s**urface **m**odifying **m**acromolecules (SMMs) has proven to have positive impacts in membrane performances of ultrafiltration [6, 7, 8, 9]; in pervaporation [10]; and biomedical applications [11]. Recently, Rana et al. [12] developed hydrophilic

surface modifying macromolecules (LSMMs) for the modification of PES ultrafiltration membranes. In addition to such additives, other factors, such as the base polymer concentration and the addition of other polymers, also can significantly affect membrane performance [13]. The objective of this study is to evaluate the impact of PES concentration and the addition of polyvinylpyrrolidone (PVP), a pore former, on the characteristics and performance of PES membranes prepared with three types of LSMMs (LSMM200, 400 and 600).

5.3 Experimental methods and analysis

5.3.1 Materials

PES (Victrex 4100P, ICI Advanced Materials, Billingham, UK, average molecular weight ~ 17,000 to 19,000 Daltons) was the base polymer used in the preparation of the membrane casting solution. The solvent was reagent grade N-methyl-2-pyrrolidone (NMP). PVP powder with average molecular weight of 10,000 Daltons was used as a pore former. Both NMP and PVP were supplied by Aldrich Chemical Company, Inc., Milwaukee, WI. The three LSMMs employed in the surface modification were referred to as LSMM200, LSMM400, and LSMM600. The LSMM synthesis was performed according to the method outlined by Rana et al. [12]. The main chain is a urethane prepolymer formed from methylene bis-p-phenyl diisocyanate and polypropylene glycol in N,N-dimethylacetamide (DMAC) solvent. Polyethylene glycol (PEG) (Sigma Chemical, St. Louis, MO) was used to endcap the main chain. The three LSMMs only differ from each other in the molecular weight of PEG in their synthesis. PEG and polyethylene oxide (PEO) (Aldrich Chemical, Milwaukee, WI) were used as probe

solutes for the solute transport method used to determine the molecular weight cut-off (MWCO). The molecular weight of the different PEG fractions used were 6000, 8000, 12000, 20000, and 35000 Daltons, while for PEO it was 100,000 Daltons. Ethyl alcohol 99% (BDH Inc., Toronto, ON) was used to dry the membranes. Ultra pure water was prepared with a Milli-Q Water System (Millipore, Bedford, MA).

The test water used was ORW, the source water for the city of Ottawa, Canada. It was collected at the intake of the Britannia Water Treatment Plant on May 8th, 2004.

5.3.2 Membrane preparation

Flat-sheet membranes were manufactured by the immersion precipitation technique described by Matsuura [13]. PES, NMP, PVP, and LSMM were the ingredients of the casting solutions. LSMM, PVP, and then PES were completely dissolved in NMP before the solution was filtered and degassed inside a vacuum dessicator (VWR, Mississauga, ON). A uniform layer of 250 μm thickness was formed by pouring the homogenous casting solution onto a clean glass support plate and spread by a casting rod. Right after casting, the glass plate was immersed into icy distilled water at 4°C for at least 1 h. Solvent (NMP) diffused out of the cast layer, and nonsolvent (water) diffused in resulting in their hardening into membranes (i.e., gelation); the membranes rapidly peeled from the glass plate once placed in the water bath. The membranes were stored in cold ultra pure water until they were used. Each 22 × 28 cm membrane sheet produced one or two defect-free 51-mm diameter coupons. For contact angle measurements, the membranes were dried by sequentially submerging them for at least six hours in four ethanol/water

solutions (25, 50, 75 and 100% w/w ethanol) to remove the water from the membranes before being placed between filter papers to dry at room temperature.

5.3.3 Analysis

5.3.3.1 Water sources

Physicochemical characteristics of the test water were determined using standard methods [14]. Dissolved organic carbon (DOC) concentrations (feed and permeate) were measured using a total carbon analyzer (Model DC-180, Dohrman, Santa Clara, CA) with the persulfate-ultraviolet oxidation method and infrared spectrometry. UV absorbance was measured at 254 nm using a spectrophotometer (DU-40, Beckman Instruments Inc., Irvine, CA) with a 1-cm quartz cell. In this analysis, Milli-Q water was used as a blank. UV absorbance was used as a DOC surrogate for about one third of the samples since DOC and UV_{254} were linearly related.

The molecular weight distribution of the organic matter in the OWR was determined by UF fractionation using the 50 ml stirred UF cell (model 8050, Amicon Corp., Danvers, MA) and regenerated cellulose membranes from Millipore (Bedford, MA) with MWCO values of 1, 3, 10, and 30 kDaltons. The fractionation was conducted according to the method outlined by Nilson and DiGiano [14].

5.3.3.2 Contact angle analysis

Contact angle measurements were used as an indirect measure of LSMM migration and membrane hydrophilicity. The measurements were conducted using a goniometer (FTA 200 Dynamic Contact Angle System, Camtel Ltd, Cambridgeshire, UK). This system has

a computer controlled digital camera and syringe pump that allows the operator to control the pumping rate and the volume of the water droplets. The dry membrane were cut into 8×36 mm pieces and taped on micro slides (VWR, West Chester, PA). To account for the heterogeneity of the membrane surface, contact angle measurements were conducted on several pieces of the membrane from different locations within one sheet and from different membrane sheets. The advancing contact angle was measured using the sessile drop method. Advancing contact angle measurements were chosen (as opposed to static contact angle measurements) since it is more reproducible. The measurement of advancing contact angle was performed via the following procedure. First, a water droplet was deposited on the membrane surface with the needle inside the water drop. Then, the controlled-rate pump continued to pump water (usually for two seconds), increasing the water droplet volume until there was a sudden movement of the water drop. The image was instantly captured by the digital camera and analyzed by the computer to determine the advancing contact angle. The water droplet volume in these measurements ranged from 1.6 to 2.4 μl and the reported values were averages of 15 to 20 measurements.

5.3.4 Experimental set-up and testing protocol

The membrane coupons were placed randomly in the six continuous crossflow cells connected within a recirculation system (Figure 5.1). This apparatus was selected because it permitted the simultaneous evaluation of six coupons with essentially the same results as those of a SEPA® CF membrane cell by Osmonics®, recommended by the USEPA [15]. The experimental set-up consists of a feed reservoir (1) connected to a high pressure diaphragm pump (Hydra-Cell, Wanner Engineering, Inc., Minneapolis, MN) (2), a prefilter (Integra Environment Inc., 150360, Burlington, ON) (3), a flowmeter (P-32025-

20 rotameter, Gilmont Instruments, Barrington, IL) (4), pressure valves (5, 8, 9, 10), a thermocouple (A-08439-84, LABCOR Technical Sales Inc, Anjou, QC) (6), the membrane test cells (7), and the recycling lines that return both the permeate (12) and concentrate (13) streams back to the reservoir to maintain a constant feed concentration. The temperature of the feed water was kept constant by a heat exchanger (11) cooling the concentrate stream before returning it to the feed water reservoir. The membrane test cells (7) consist of six stainless steel crossflow cells in series.

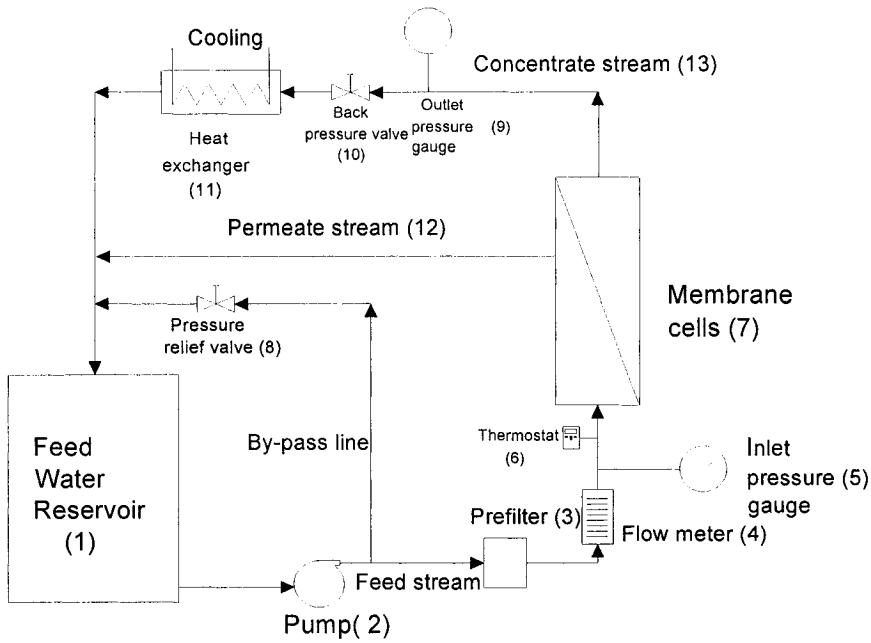

Figure 5.1 The membrane filtration system

The testing protocol consisted of precompaction, pure water permeation (PWP) monitoring, MWCO determinations and a fouling test with ORW. Precompaction was accomplished by operating the system at 552 kPa (80 psig) for one hour. This duration was chosen (based on the result of preliminary studies) to minimize flux reduction caused

by membrane compaction yet avoiding any significant impact on the membrane pore structure. The PWP evaluation consisted of filtering Milli-Q water at 345 kPa (50 psig) and monitoring the flux for 50 hours. The permeate flux initially decreased with time but it stabilized (less than 1% difference in fluxes measured three hours apart) and this flux is referred to as PWP.

The MWCO determinations consisted a series of one-hour filtration cycles with 100 ppmC solutions of PEG (or PEO) of known molecular weights followed by an one-hour Milli-Q water rinsing cycle prior to testing with a different molecular weight PEG (or PEO) solution. The feed and permeate were collected and analyzed for total organic carbon (TOC) removal using a high-temperature catalytic total carbon analyzer (Model DC-190, Dohrman, Santa Clara, CA). Based on the results of solute separation test, the MWCO was determined as the molecular weight that would yield 90% solute separation. Other membrane characteristics including the pore distribution, pore density and surface porosity of each membrane were also calculated based on these results [16, 6]. The fouling test with ORW lasted for 144 hours (6 days), which allowed the permeate flux to reach a pseudo-steady state. The transmembrane pressure was set at 345 kPa (50 psig), which is within the UF operating range and yields reasonable permeate fluxes. Permeation rate was measured by weighing the mass of the permeate over predetermined time intervals. With higher permeability membranes, fluxes were determined by measuring the volume of the permeate sample by a graduated cylinder. The flow was set at 1.1 Lpm to create turbulent flow conditions so as to minimize concentration polarization. The temperature of the feed was kept constant at 23° C. The total pressure drop across six cells in series system was less than 14 kPa (2 psig)

At the end of every experiment, the permeation area was checked, using a caliper (Manostat, IQ Instruments, Jona, Switzerland). The NOM concentrations were quantified by the measurement of dissolved organic carbon (DOC) using a total organic carbon analyzer (Model DC-180 Dohrman, Santa Clara, CA), based on the persulfate-ultraviolet wet oxidation method and an infrared detector. DOC removal was calculated by equation 5.1:

$$DOC \text{ removal} = 100 \times \left(1 - \frac{C_{p(t)}}{C_f}\right) \tag{5.1}$$

where $C_{p(t)}$ is the permeate DOC concentration at time t and C_f is the feed DOC concentration (mass/volume).

The amount of NOM accumulated on top of the individual membranes at the end of the six-day fouling test (referred as NOM deposition) was measured using the technique described by Hong and Elimelech [18].

5.3.5 Membrane characterization by solute transport

The Stokes radius is the radius of a hypothetical sphere that would diffuse at the same rate as the particle under study [6]. Solute diameters were calculated from the following expressions for the Stokes radius (a) of PEG and PEO as a function of their molecular weights (M):

$$a_{PEG} = 16.73 \times 10^{-10} M^{0.557} \tag{5.2a}$$

$$a_{PEO} = 10.44 \times 10^{-10} M^{0.587} \tag{5.2b}$$

Equations 5.2a and 5.2b were derived by Singh et al. [19] from empirical expressions of PEG and PEO's intrinsic viscosities and the Stokes-Einstein equation for diffusivity.

Based on the solute (PEG, PEO) separation data, the pore size distribution of the membranes was computed. According to Micheals [17], the log-normal probability function is an accurate way to describe UF membranes sieving curves, i.e., the solute separation, f(%), versus the solute diameter (d_s) follow the log-normal relationship [19].

If the dependence of solute separation on the steric and hydrodynamic interaction between solute and pores are not significant, the pore size equals the solute size. [18]. Therefore, the pore size distribution of an UF membrane is expressed by the log-normal distribution:

$$\frac{df(d_p)}{dd_p} = \frac{1}{d_p \ln\sigma_p \sqrt{2\pi}} \exp\left[-\frac{1}{2}\left(\frac{\ln(d_p/\mu_p)}{\ln\sigma_p}\right)^2\right] \tag{5.3}$$

where d_p is the pore diameter, μ_p is the geometric mean of the pore diameter and, σ_p is the geometric standard deviation (GSD) of the pore diameter. These parameters are denominated geometric, because they correspond to a *log-normal* distribution. $\mu_p = d_s @ f = 50\%$ (solute diameter that conrespond to 50% separation of PEG obtained from the PEG separation data), and σ_p, is calculated by:

$$\sigma_p = \frac{d_s @ f = 84.13\%}{d_s @ f = 50\%} \tag{5.4}$$

where d_s is the solute diameter ($d_p = d_s$). Their geometric means ($\mu_p = \mu_s$) and their geometric standard deviations (GSD) ($\sigma_p = \sigma_s$) were considered to be the same. μ_s is the

geometric mean, and σ_s is the GSD of the solute diameter. Library functions from Microsoft Excel for the standard normal distribution and base-10 logarithm (i.e., NORMSINV and LOG10, respectively) were used to compute solute separation f(%) at a predetermined pore size base on PEG separation data. These f values were then used together with the value of μ_p and σ_p obtained from equation 5.4 to compute the pore size distribution of the membrane based on equation 5.3.

5.3.6 Experimental Design

The study was divided into three stages. Table 5.1 presents membranes tested in three stages. In stage one, the impact of PES concentration (added at three different concentrations: 15, 18, and 21 wt %) on LSMM200 migration was evaluated based on advancing contact angle measurements. LSMM200 was added at 3 wt %. Based on the results of stage one, a PES concentration was selected for all the remaining studies. Stage two studied the contact angle of membranes containing PVP and three types of LSMMs (LSMM200, 400, and 600). LSMMs were added at 1.5, 3, and 4.5 wt % and PVP was added at 6 wt %.

Stage three investigated the impact of PVP on LSMM modified membrane characteristics and performance for a group of membranes selected from the stage two results. LSMM concentration was set at 4.5 wt % to investigate the greatest impact LSMMs might have on the membrane characteristics and performances. The values reported are averages of three different coupons.

Table 5.1 List of membranes studied

Stage	No	Membrane code	Composition					
			% PES	% PVP	% LSMM added			% NMP
					200	400	600	
I	1	PES15-200-3	15	0	3	-	-	82
	2	PES18-200-3	18	0	3	-	-	79
	3	PES21-200-3	21	0	3	-	-	76
II & III	4	Control	18	0	-	-	-	82
	5	ControlP	18	6	-	-	-	76
	6	LSMM200-1.5	18	0	1.5	-	-	80.5
	7	LSMM200-3	18	0	3	-	-	79
	8	LSMM200-4.5	18	0	4.5	-	-	77.5
	9	LSMM200-1.5P	18	6	1.5	-	-	74.5
	10	LSMM200-3P	18	6	3	-	-	73
	11	LSMM200-4.5P	18	6	4.5	-	-	71.5
	12	LSMM400-1.5	18	0	-	1.5	-	80.5
	13	LSMM400-3	18	0	-	3	-	79
	14	LSMM400-4.5	18	0	-	4.5	-	77.5
	15	LSMM400-1.5P	18	6	-	1.5	-	74.5
	16	LSMM400-3P	18	6	-	3	-	73
	17	LSMM400-4.5P	18	6	-	4.5	-	71.5
	18	LSMM600-1.5	18	0	-	-	1.5	80.5
	19	LSMM600-3	18	0	-	-	3	79
	20	LSMM600-4.5	18	0	-	-	4.5	77.5
	21	LSMM600-1.5P	18	6	-	-	1.5	74.5
	22	LSMM600-3P	18	6	-	-	3	73
	23	LSMM600-4.5P	18	6	-	-	4.5	71.5

LSMM200, LSMM400, LSMM600: types of LSMM added
1.5, 3, 4.5: percentage of LSMM concentration added
P: With PVP
Membranes in shaded lines were used for stage three study (No 4, 5, 8, 11, 14, 17, 20, 23).

5.4 Results and discussion

The measured TOC of ORW was 7 mgL^{-1}. UF fractionation of ORW showed that the majority of the NOM (approximately 55%) had molecular weight (MW) ranging from 3 to 10 kDaltons, and 99% of the NOM has MW smaller than 30 kDaltons (Figure 5.2). This ORW sample had fairly similar NOM fraction distributions to those reported in the literature [15, 19].

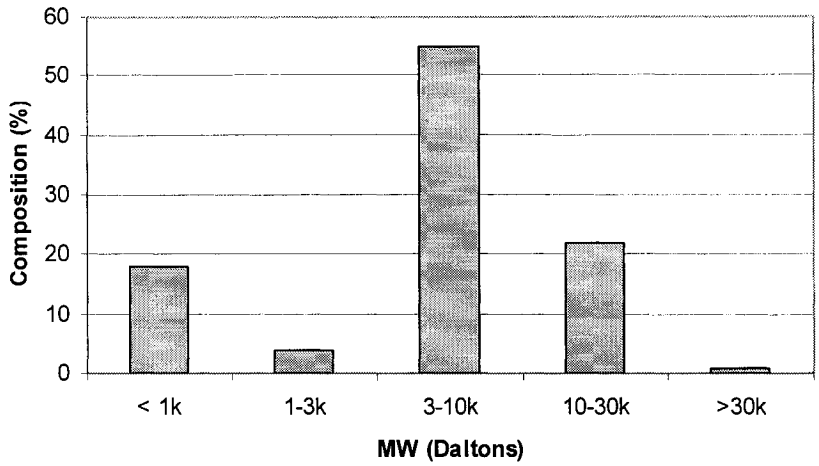

Figure 5.2 Molecular weight distribution of organic matter in the ORW

5.4.1 Impact of PES concentrations on LSMM200 migration

Figure 5.3 presents the advancing contact angles of membranes prepared with 3% LSMM200. Increasing the PES concentration was expected to increase the contact angle since PES is more hydrophobic than the additive. Surprisingly, the average advancing contact angle decreased with increasing PES concentration. However, the variability in the contact angle was large, resulting in statistically the same advancing contact angles at the 95% confidence level. Therefore, the impact of PES concentration on the LSMM migration was insignificant.

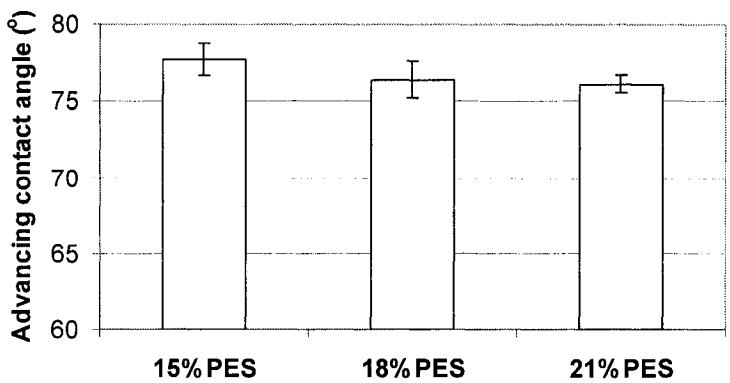

Figure 5.3 Advancing contact angle results for membranes with 3% LSMM200.

5.4.2 Impacts of PVP and LSMMs on PES membranes hydrophilicity

Figure 5.4 presents the results of advancing contact angle measurements for membranes prepared with three different concentrations of LSMM200, 400, and 600, both with and without PVP.

Adding PVP did not change advancing contact angle values compared to their counterparts without PVP for eight out of nine cases. Only for one membrane (with 3 wt % LSMM400), adding PVP statistically increased the advancing contact angle by statistically significant amount. The addition of LSMMs resulted in a decrease in advancing contact angle up to 8^{o}. Increasing LSMMs concentration (i.e., increasing the concentration of the hydrophilic polymer) was expected to decrease the advancing contact angle. However, with 95% confidence interval, the advancing contact angle did not decrease with increasing LSMM concentration. It is believed that the presence of PVP and increasing LSMMs concentration increased the solution viscosity (as experienced by the greater difficulty of filtering the casting solution), which interfered with the movement of LSMMs and thus hindered their migration to the membrane-water interface during gelation. Moreover, the addition of PVP (which is a hydrophilic polymer) may also weaken the migration driving force between the more hydrophobic polymer (PES) and the hydrophilic LSMM, which somewhat reduce LSMM migration. PVP itself may also occupy some of the same pathways as the LSMM, which again retard the LSMM migration to the membrane-water interface. Therefore, the addition of PVP did not have significant impact on LSMMs migration.

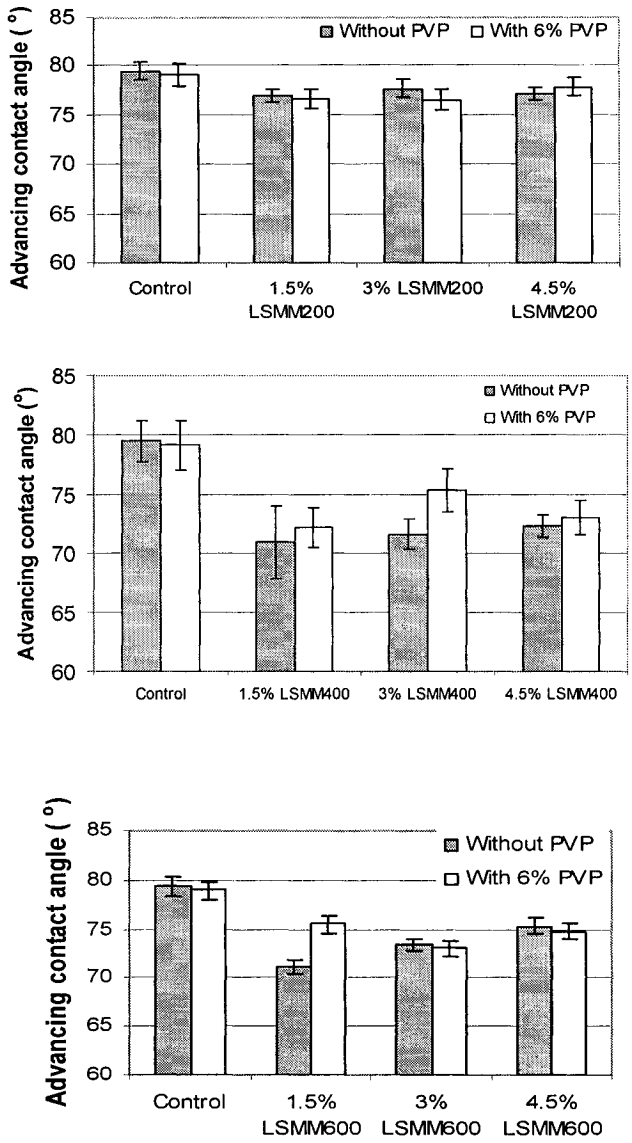

Figure 5.4 Advancing contact angle of membranes with and without PVP

5.4.3 Impacts of PVP on membrane characteristics

This section discusses the impact of the presence of PVP on the unmodified and modified membrane characteristics. Membranes studied are at 18 wt % PES, with 4.5 wt % LSMMs, and 6 wt % PVP. Parameters monitored are pore size distribution, MWCO, and PWP.

5.4.3.1 Pore size distribution

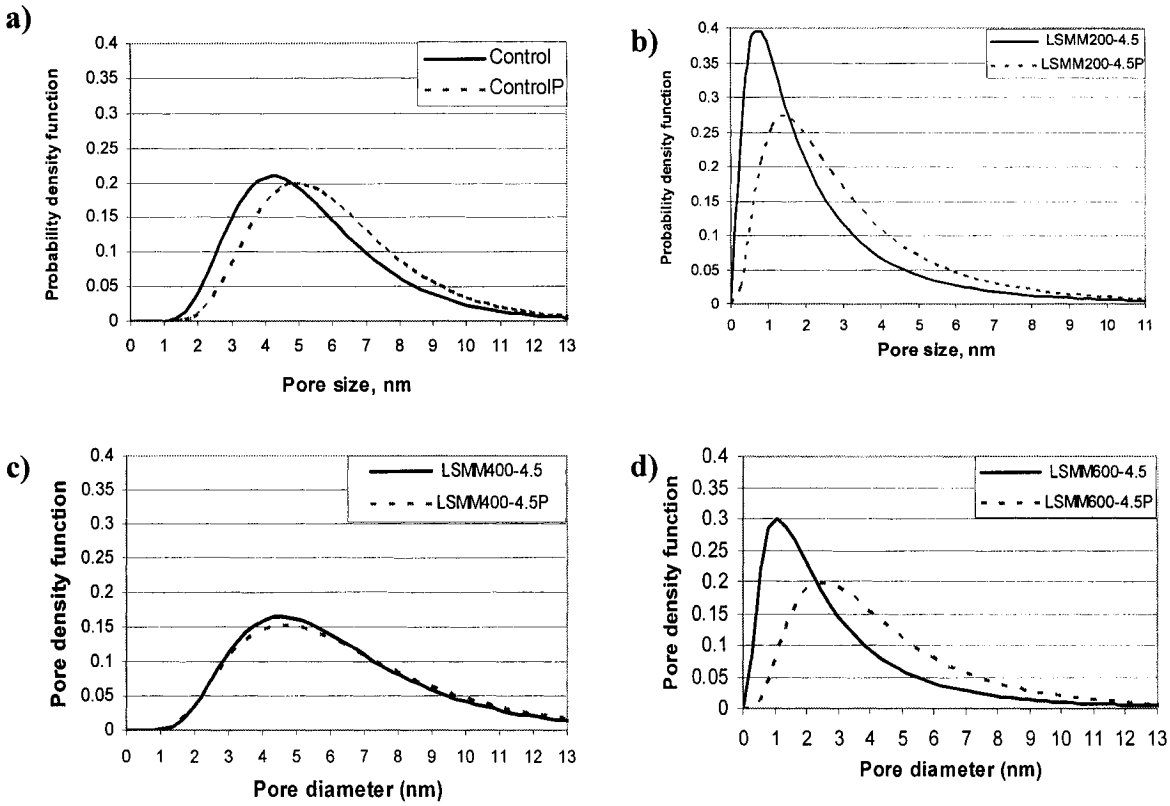

Figure 5.5 Pore size distribution of unmodified and modified membranes: a) Without LSMM; b) With LSMM200; c) With LSMM400; d) With LSMM600

Figure 5.5 presents the pore size distribution of unmodified and modified membranes (calculated from equation 5.3). In general, adding PVP (with LSMM200 and 600) reduced the most probable pore density (mode or the maximum in the probability density function curve) and increased the most probable pore sizes. Membranes without PVP had narrower pore size distribution. For the membranes without PVP, the most probable size of the pores (pore size at which the probability density function curve is maximum) was higher for the control than for the membranes with 4.5 wt % LSMM200 and 600. However, adding LSMM400 at 4.5% resulted in almost the same pore size distribution as the unmodified membrane. The modified membranes with PVP followed the same trend.

5.4.3.2 MWCO and PWP

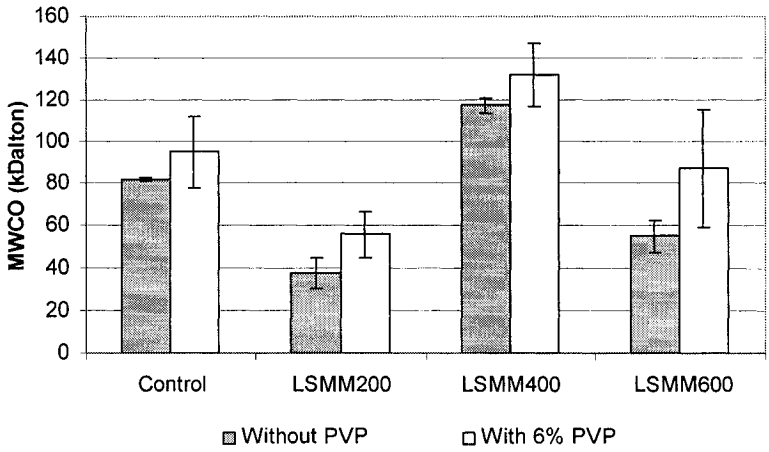

Figure 5.6 MWCO of membranes with and without PVP

The average MWCO values of membranes with PVP were higher than those of their counterparts without PVP (Figure 5.6). However, the membranes with PVP had a high degree of variability which caused membranes with and without PVP to have statistically (at the 95% confidence level) the same MWCOs for three out of four cases and a small difference for the remaining (LSMM200-4.5 and LSMM200-4.5P). The difference for the low end and high end of the 95% confidence level for the membranes with and without PVP was only 180 daltons.

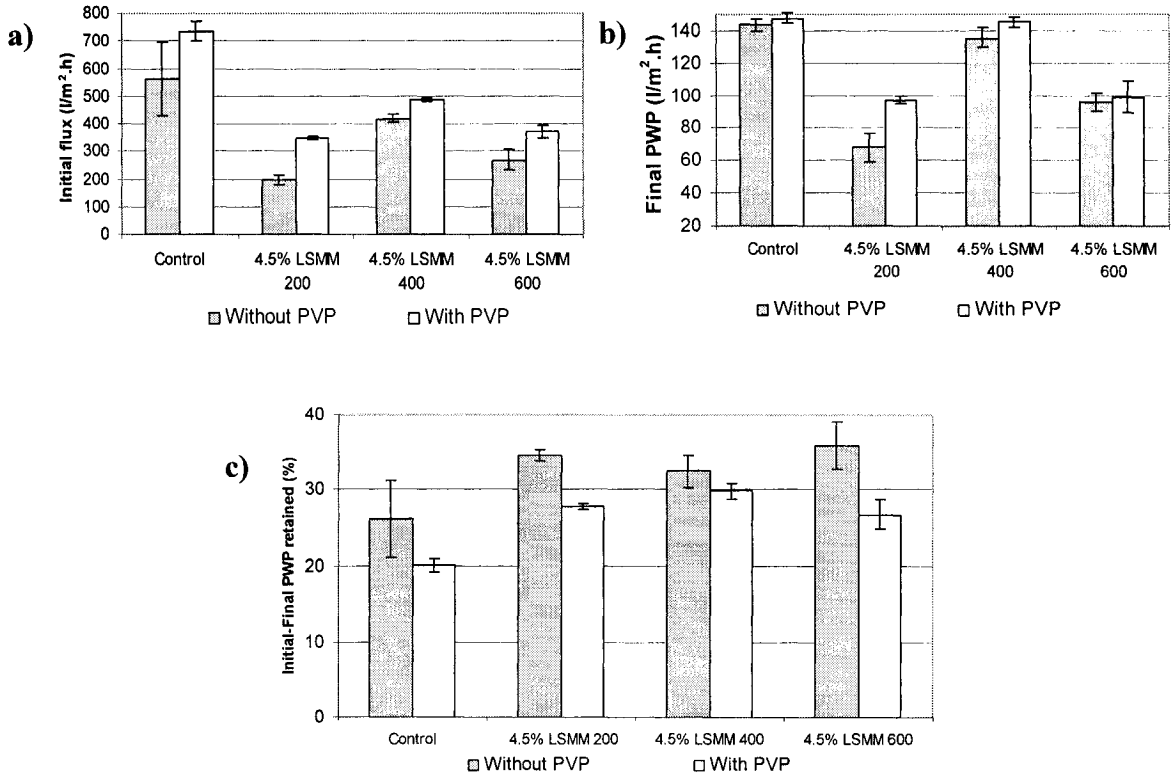

Figure 5.7 PWP of membranes with and without PVP: a) Initial; b) Final; c) Percentage of initial-final PWP retained

In this study, the initial fluxes of membranes with PVP were much higher that those without PVP (Figure 5.7a). However, after one hour of precompaction and 50 hours of PWP monitoring, the difference in fluxes between membranes with and without PVP decreased tremendously and reached statistically the same level for three out of four cases (Figure 5.7b). In addition, the percentages of the initial flux retained (Figure 5.7c) were higher for the membranes without PVP than those with PVP, and the differences were statistically significant for three out of four cases. As fouling was excluded since the feed was with Milli-Q water, the flux decline can be attributed to mechanical compaction, and thus, it is clear that adding PVP might increase membrane porosity initially, but it also makes them more susceptible to mechanical compaction, which

decreased the membrane porosity and thus subsequent PWP measurements. The initial PWP of the membrane with PVP (LSMM200-4.5P) was much higher than its counterpart without PVP (LSMM200-4.5) (77% as opposed to less than 40% in the other three cases) so that even with mechanical compaction, the LSMM200-4.5P still had higher PWP at the end. However, this higher PWP was accompanied by a higher MWCO. Other researchers [8, 20, 21] also observed the same trend, statistically higher PWP for membranes with PVP and at different polymer concentrations.

The percentages of the initial PWP retained were higher for LSMM modified membranes than for their unmodified counterparts (for both cases with and without PVP) indicating that LSMMs helped increase the membrane mechanical strength.

5.4.4 Impacts of PVP and LSMMs on membrane performance and fouling reduction

The impact of PVP and LSMMs on membrane performance and fouling reduction was quantified via long-term fouling tests in which the permeate flux, DOC removal, flux reduction, and NOM deposition were measured.

5.4.4.1 Permeate flux

The permeate fluxes presented in Figure 5.8 were the stable values at the end of the 144 hours ORW filtration test. The fluxes of membranes containing PVP continued to decrease with time even at the end of the 144 fouling tests. Three out of four membrane types with PVP had lower average fluxes than those without PVP. However, due to the large variability, only one membrane type (LSMM400-4.5P) had significantly lower flux; the other two types had statistically the same values. In the case of the membranes with 4.5 wt % LSMM200, the difference in the fluxes of the membranes with and without

PVP decreased from 30 % for the PWP to 18 % for the final flux. Thus, membranes with PVP tend to foul more than membranes without PVP. Among membranes without PVP, except for the 4.5 wt %LSMM200 membranes, adding 4.5 wt % LSMMs increased the final permeate flux

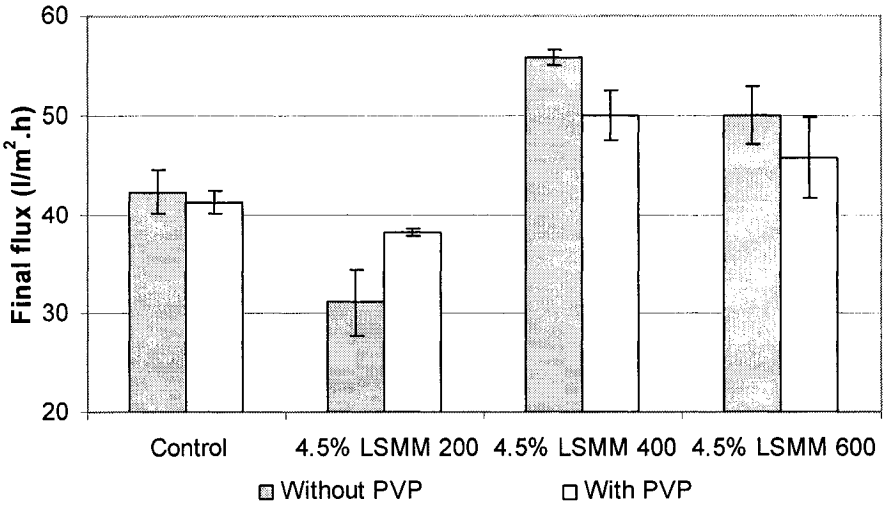

Figure 5.8 Final fluxes of membranes with and without PVP

5.4.4.2 Flux reduction

Normalized flux reduction was calculated following equation 5.5:

$$\text{Normalized flux reduction}_{(t)}\ (\%) = 100\left(1 - \frac{PR_{(t)}}{PWP}\right)_{ORW} \tag{5.5}$$

where $PR_{(t)}$ is the permeate flux (product rate) of ORW at time t = 144 hour, and PWP was the stable pure water permeation rate. Both have dimensions of volume/time/area. Flux reduction (i.e., fouling) was significantly reduced by the addition of the LSMMs at 4.5%, especially with LSMM600 (Figure 5.9). Adding PVP resulted in higher flux reduction, however in two out of four cases (the control and LSMM400-4.5) the

differences were not statistically significant. Thus, membranes with PVP were subjected to more fouling which led to higher flux reduction.

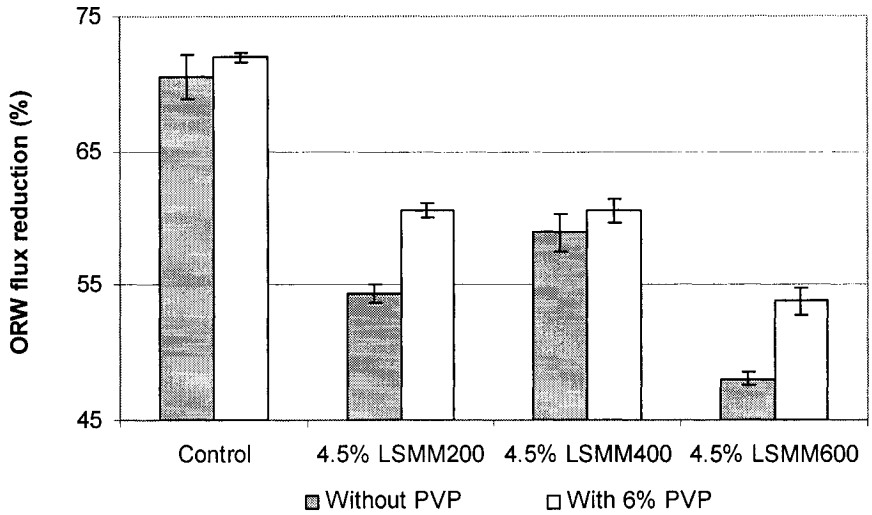

Figure 5.9 Flux reduction of membranes with and without PVP

5.4.4.3 DOC removal

The DOC removal was evaluated daily during the fouling test with ORW and the reported values were averages of the last values (after DOC removal has reached a stable level) of three replicate coupons (Figure 5.10).

During the 144-hour test, DOC removal increased drastically for the first 40 hours then reached a plateau. At the end of the test, the DOC removals of all membrane types were very similar, in the range of 66 to 74%. Similar DOC removal values (59 to 77%) were obtained by Mosqueda-Jimenez et al. [7] when they tested hydrophobic SMM modified PES membranes using a different sample of ORW.

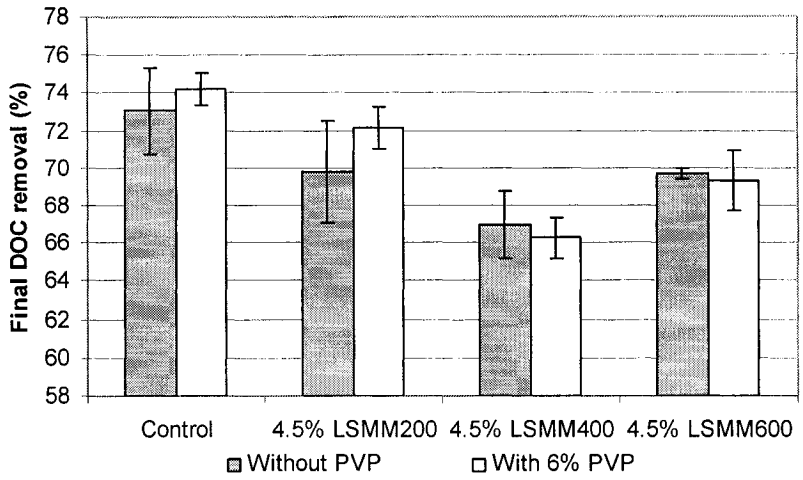

Figure 5.10 Final DOC removal of membranes with and without PVP

This is a high DOC removal level given the small molecular weight of the NOM (99% of the NOM are smaller than 30 kDaltons) and their big MWCO values (all membrane had MWCOs bigger than 35 kDaltons). That the membranes show a higher NOM rejection than expected based on their MWCOs is likely due to charge repulsion between the membrane surface charge and the charge of NOM components [1].

In addition, considering the NOM molecular weight of ORW (99% were smaller than 30 kDaltons) and the MWCOs of the membranes (all membranes had MWCO larger than 35 kDaltons) and the slightly different final DOC removal values, it is reasonable to say that fouling via pore adsorption seems to be the dominant fouling mechanism in these membranes. The pore adsorption reduced the membrane pore size and thus enhanced DOC rejection. The controls attained the highest DOC removal in spite of their high MWCO values (73% and 74% for membranes with and without PVP, respectively), which might indicate more severe fouling via pore adsorption in the control membranes. However, among the membranes with 4.5% LSMMs, there was a clear trend of

increasing initial and final DOC removal with decreasing MWCO. A similar trend was observed when comparing membranes with PVP. The increase in DOC removal from the beginning to the end of the fouling test was much higher for the membranes with PVP and with high MWCO than for those without PVP and lower MWCO. This indicates that fouling was more severe in membranes without modification, in membranes with PVP, and in those modified membranes with high MWCO values.

5.4.4.4 NOM deposition

NOM deposition on top of the membrane at the end of the test was measured because it was likely related to membrane fouling (Figure 5.11).

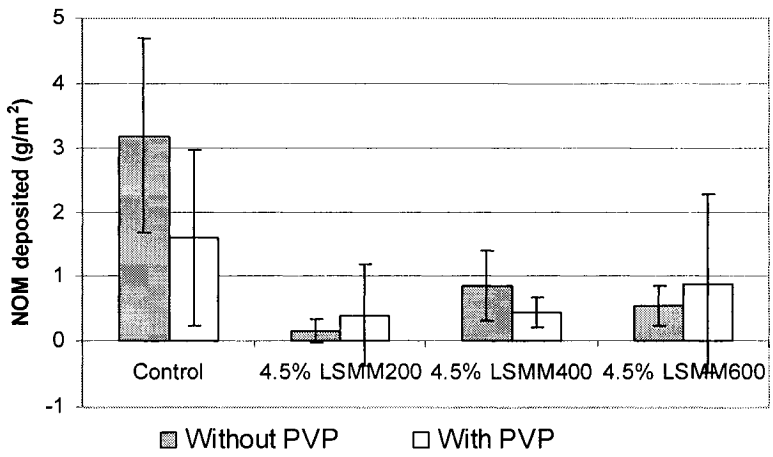

Figure 5.11 NOM deposition of membranes with and without PVP

There is a clear reduction of the NOM accumulated on the membrane surface with surface modification. It was expected that membranes with PVP would have more NOM accumulated since they had more throughput, and become more fouled [7]. However, no

clear trend was observed for membranes with and without PVP probably because of the high variability of the test results.

5.5 Conclusions

1. Based on advancing contact angle results, PES concentration did not have an impact on the hydrophilicity of LSMM200 modified membranes. Decreasing advancing contact angles provided a clear sign of LSMM migration to the membrane surface. The LSMMs concentration and the presence of PVP did not have a clear impact on the membrane hydrophilicity.

2. 4.5% LSMM400 and 600 membranes achieved higher final fluxes. In general, the addition of LMMs at 4.5% reduced the amount of NOM deposition and flux reduction, and resulted in membranes with more mechanical strength.

3. The addition of PVP to unmodified and modified membranes resulted in more widespread pore size distribution (with LSMM200 and 600) and increases the most probable pore sizes. Membranes with PVP had higher initial PWPs, but were more sensitive to mechanical compaction and thus had statistically the same MWCOs and final PWPs. The addition of PVP which helps increase the casting solution viscosity and facilitate membrane manufacturing, did not have any other favorable impacts to membrane characteristics and performance.

4. Fouling by pore adsorption appeared to be dominant and more severe in membranes without surface modification. Fouling also helped increase DOC removal. Fouling (measured by long term flux, DOC removal, and flux reduction)

was more severe in unmodified membranes, modified membranes with higher MWCOs, and membranes with PVP.

5.6 Acknowledgements

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5.7 Nomenclature

a_{PEG}	Stokes radius of PEG (nm)
a_{PEO}	Stokes radius of PEO (nm)
C_f	Feed concentration (mass/volume)
$C_{p(t)}$	Permeate concentration at time t (mass/volume)
d_p	Pore diameter (nm)
f_i	Fraction of pores with diameter d_i (dimensionless)
J	Total flux (m^3/m^2-s)
J_i	Solvent flux for pores with diameter d_i (m^3/m^2-s)
N	Number of pores per unit area
N_i	Density of pores with diameter d_i (dimensionless)
$PR_{(t)}$	Permeate flux (product rate) of ORW at time t ($l/m^2.h$)
ΔP	Pressure difference across the pores (Pa)
δ	Length of the pores, considered equivalent to the thickness of the skin layer

(no tortuosity) (m)

μ_p Geometric mean of the pore diameter (dimensionless)

σ_p Geometric standard deviation (dimensionless)

5.8 References

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CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

Based on the results of the study, some general conclusions can be made:

1. The incorporation of LSMMs in the preparation of PES membranes resulted in surface modification: contact angle of surface modified membranes was reduced up to 8^{o}. Increasing LSMMs concentration did not help to decrease advancing contact angle.

2. Based on advancing contact angle results, PES concentration and the presence of PVP did not have any major impact on the migration of LSMMs to the membrane surface.

3. Membranes prepared with the three different LSMMs performed quite differently. LSMM200 reduced the membrane MWCO by a factor of two. LSMM400 additions increased final flux by 33% and the incorporation of LSMM-600 resulted in both higher flux and lower MWCO.

4. Although the LSMMs addition only achieved a maximum 8^{o} contact angle reduction, it had significant impacts on the membranes performance: higher long-term fluxes, lower flux reduction, mechanically stronger membranes, and less NOM deposition.

5. The DOC removal was high for the membranes tested given their high MWCO values and the molecular weight of the NOM. These high removals were probably linked to the fouling, in which pore adsorption seems to be more dominant. Fouling decreased fluxes, but also enhanced DOC removal.

6. Other than making membrane manufacturing easier due to increasing casting solution viscosity, the addition of PVP did not have any positive impact on LSMMs modified membranes' characteristics and performances.

6.1.1 Minor conclusions

1. Membranes with PVP had higher initial PWP but they compacted to a greater extend than those without PVP. This reduced the PWP and the final fluxes to the same levels as those of the membranes without PVP.

2. In general, there was a clear trend of increasing permeate flux with decreasing membrane surface hydrophobicity.

3. Fouling (measured by long term flux, DOC removal, and flux reduction) was more severe in PVP containing membranes and those with higher MWCOs.

6.2 Recommendations

The following recommendations might help to improve the understanding of the phenomena involved in the membrane studies:

1. Characterize the feed water and the permeate (hydrophilic/hydrophobic) to have a better understanding of the NOM characteristics and functional groups that may cause fouling.

2. Study the membrane characteristics by AFM, SEM, zeta potential, to account for the impact of LSMMs on membrane structure, roughness, and charge to have a better understanding of the actual causes of fouling reduction of these additives.

3. Test alternative water sources (different NOM functional groups, different SUVA values) to assess for which types of water that these membranes work best.

4. Clean fouled membranes to see if the modified membranes have greater flux recoveries.

5. Test lower concentrations of LSMM200.

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APPENDIX A

PREMILINARY STUDY OF THE LSMM SYNTHESIS REPRODUCIBILITY

LSMM200 synthesized from two batches (A, B) was studied for reproducibility based on PWP and PEG (4 kDaltons) solution separation. The PES concentration was kept constant at 20 wt %, and LSMM200 was added at 1.5 wt %. Initially, membranes were precompacted for one hour at 552 kPa (80 psig). This was followed by pure water filtration (PWP) 345 kPa (50 psig) for 50 hours. Then PEG solution was passed through the membranes for one hour before samples were collected and analyzed for TOC removal. At the end, the system was flushed with Milli-Q water for one hour and PWP was measured to corroborate that the membranes stayed the same. The values reported (Figure A.1) are averages of at least 3 different membrane coupons. PWP values reported were measured at the end of 50-hour PWP monitoring period after the PWP has reached stable level (i.e., difference between fluxes measured three hours apart is smaller than 1%). The results showed a high degree of variability within membranes from one batch and membranes from different batches. Although LSMM200A and B had different physical appearance, they gave statistically the same PWP and PEG separation efficiency.

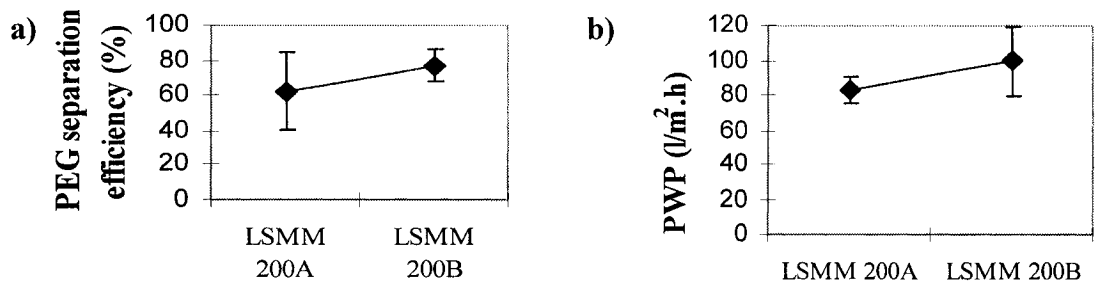


Fig. A.1 LSMM200 synthesis reproducibility: a) PWP; b) Solute separation efficiency

APPENDIX B

ADVANCING CONTACT ANGLE MEASURED WITH DIFFERENT WATER DROPLET SIZES

To study the impact of different droplet volumes on advancing contact angle readings, advancing contact angle measurements were conducted on membranes with 18 wt % PES, 1.5 wt % LSMM400 with different droplet sizes. The volume of the water droplets changed from 0.6 μl to 46 μl. Figure B.1 shows that with increasing water droplet volumes, the advancing contact angle decreased. It is believed that increasing water droplet volumes increased the gravity of the water droplet which resulted in smaller advancing contact angle.

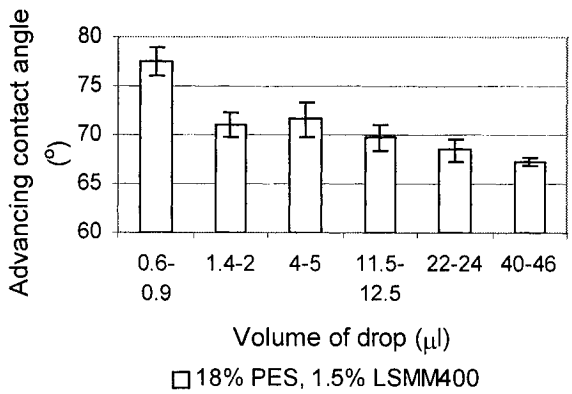


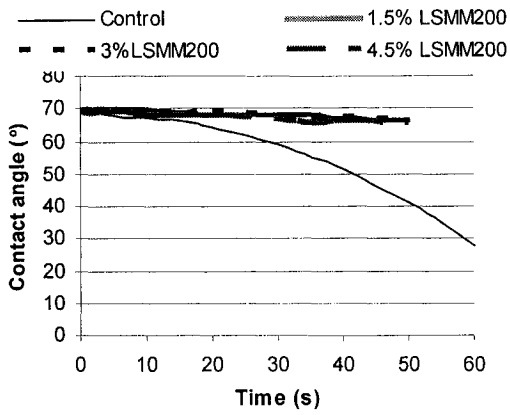
Figure B.1. Advancing contact angles with different water droplet sizes

APPENDIX C
DYNAMIC CONTACT ANGLE GRAPHS AND IMAGES

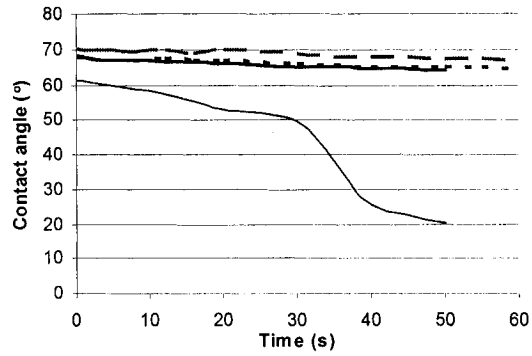
Dynamic contact angles were measured to record the adsorption of water from a droplet into the membrane. Significant differences in dynamic contact angles were observed between modified and unmodified membranes without PVP and with PES15P membranes (Figure C1). In all these cases without LSMM, the water drop penetrated quickly into the membrane, decreasing the contact angle significantly within 50 seconds. With the addition of the surface-active polymer, the water droplets were much more stable. When just PVP was added to 18 and 21% PES membranes, the water absorption rate was reduced significantly, reaching almost the same contact angles as the ones with LSMM200. Membrane porosity is believed to play a very important role in this phenomenon. Results presented in appendix D showed that the addition of LSMM200 reduced surface porosity (both in pore size and pore density) to such an extent that the water drop did not readily absorb into the membrane. This however does not explain for the case when PVP was added (PES18P and PES21P) since PVP is believed to increase membrane porosity. Roughness might be another reason for these different water adsorption rates. However, to confirm this, further studies with surface roughness measurements need to be done.

Without PVP **With PVP**

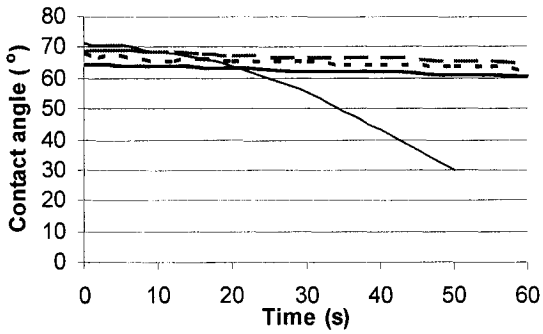
a) With 15% PES



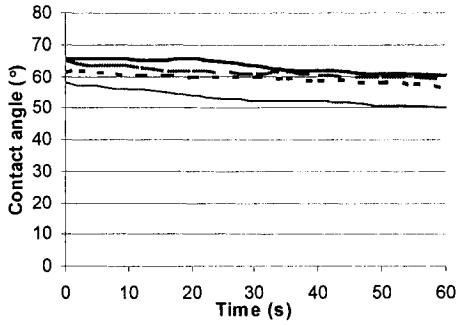
d) With 15% PES



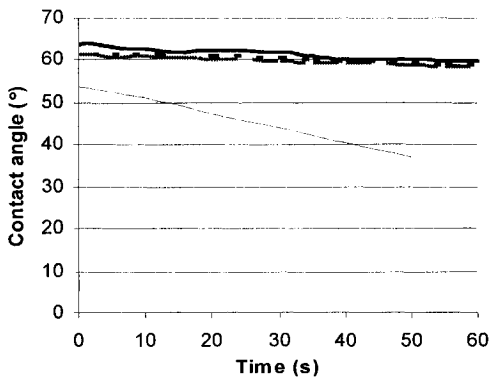
b) With 18% PES



e) With 18% PES



c) With 21% PES



f) With 21% PES

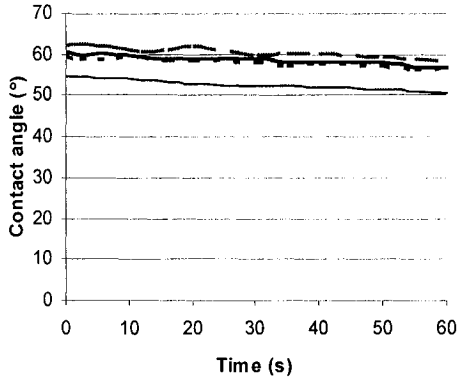


Figure C1. Dynamic contact angle results

Images of dynamic contact angle of the control (18 wt % PES) are presented in Figure C.2 and of the PES18-200-1.5 (LSMM200-1.5) in Figure C.3.

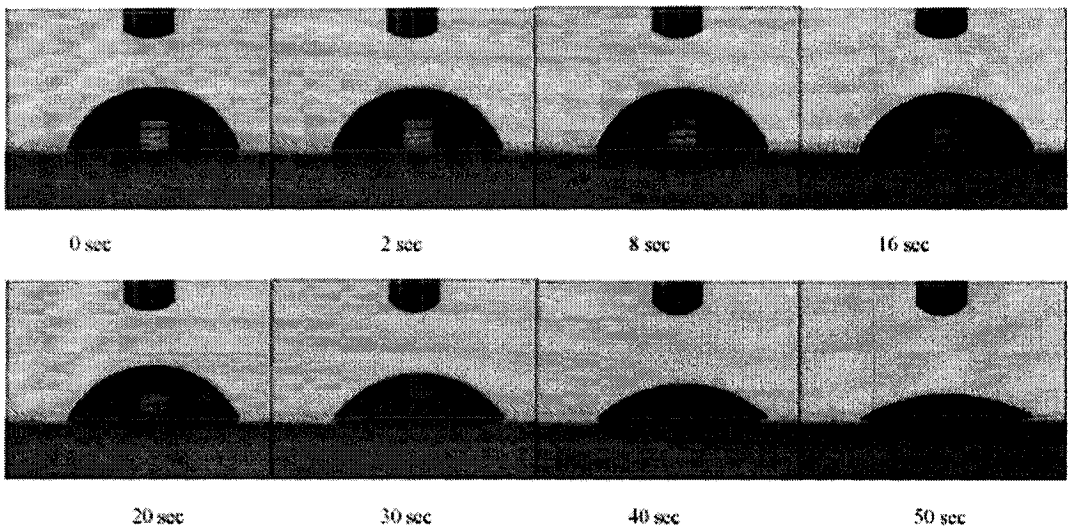


Figure C.1 Dynamic contact angle of PES18 (control) membrane

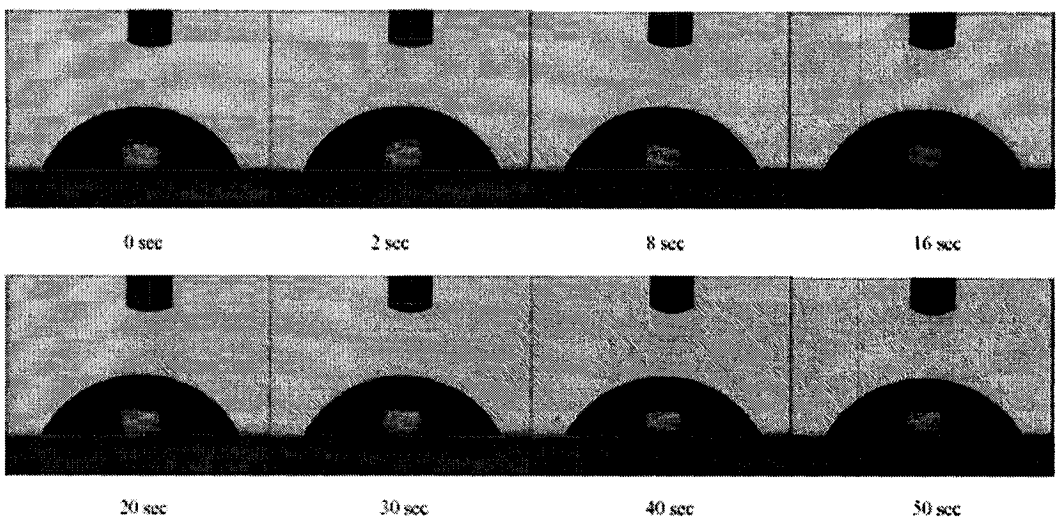


Figure C.2 Dynamic contact angle of PES18-200-1.5 (LSMM200-1.5) membrane

APPENDIX D

PORE SIZE DISTRIBUTION, PORE DENSITY, AND SURFACE POROSITY OF TESTED MEMBRANES

The pore size distribution calculations have been shown in chapter 5 (equation 5.3). Calculations of pore density (number of pores per unit area, N) and surface porosity (ratio of the area of pores to the total membrane surface area, S_p) were based on the Hagen-Poiseuille equation (Singh et al., 1998) modified for a porous membrane, assuming laminar flow (Porter, 1990):

$$J_i = \frac{N_i \pi d_i^4 \Delta P}{128 \eta \delta} \tag{C.1}$$

where

J_i = solvent flux for pores with diameter d_i (m^3/m^2-s)

N_i = density of pores with diameter d_i (dimensionless)

ΔP = pressure difference across the pores (Pa) (345 kPa in this study)

η = solvent viscosity (N-s/m^2) ($\eta = 9.34 \times 10^{-4}$ at water temperature of 23°C)

δ = length of the pores, considered equivalent to the thickness of the skin layer (no tortuosity) (m) (approximately $\delta = 2 \times 10^{-7}$ m)

Thus, total flux (J, i.e., the final PWP) through the membrane was the summation of all fluxes through the pores with different sizes:

$$J = \Sigma J_i = \frac{\pi \Delta P}{128 \eta \delta} \Sigma N_i d_i^4 = \frac{\pi \Delta P N}{128 \eta \delta} \sum_{d_{min}}^{d_{max}} f_i d_i^4 \tag{C.2}$$

where

f_i = fraction of pores with diameter d_i

Therefore,

$$N = \frac{128\eta\delta J}{\pi\Delta P \sum_{d_{\min}}^{d_{\max}} f_i d_i^4} \tag{C.3}$$

The surface porosity was the same as the void volume of the membrane skin (Porter, 1990):

$$S_p(\%) = \left(\frac{\pi}{4}\sum_{d_{\min}}^{d_{\max}} N d_i^2\right) \times 100 = \left(\frac{N\pi}{4}\sum_{d_{\min}}^{d_{\max}} f_i d_i^2\right) \times 100 \tag{C.4}$$

Figure D.1 and D.2 present the sieving curves of membranes with LSMM400 and 600, respectively.

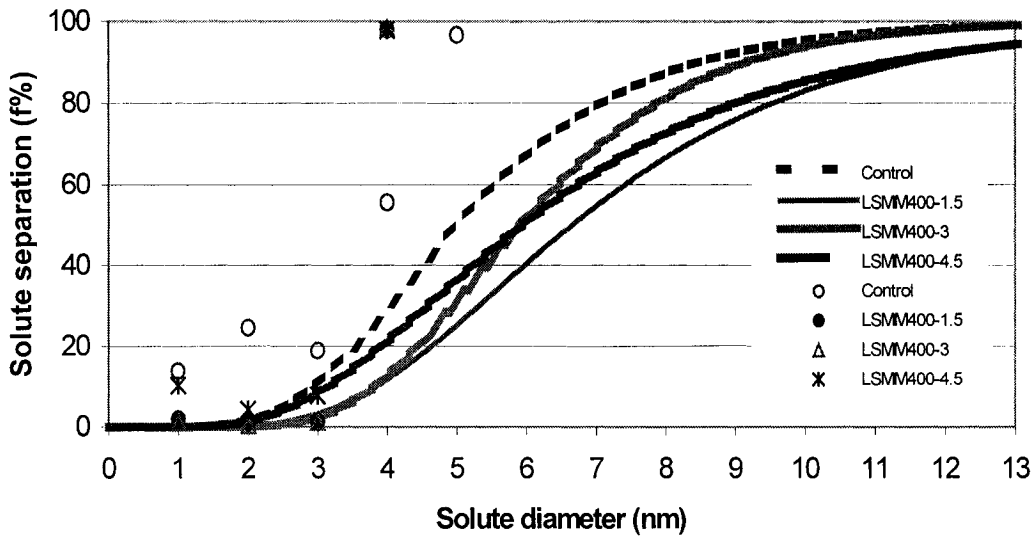


Figure D.1 Sieving curve of LSMM400 modified membranes

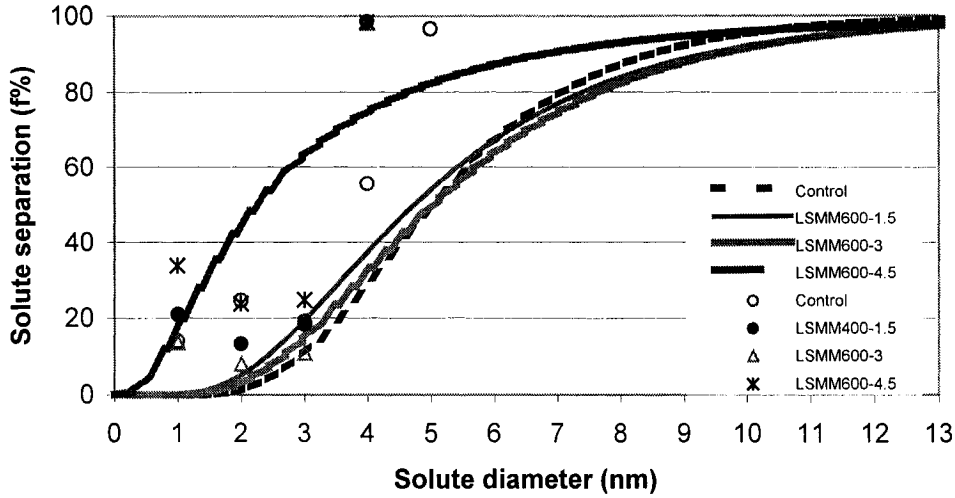


Figure D.1 Sieving curve of LSMM600 modified membrane

The pore size distributions of membranes prepared with 18 wt % PES and different concentrations of LSMM400 and 600 are presented in Figures D.3 and D.4, respectively.

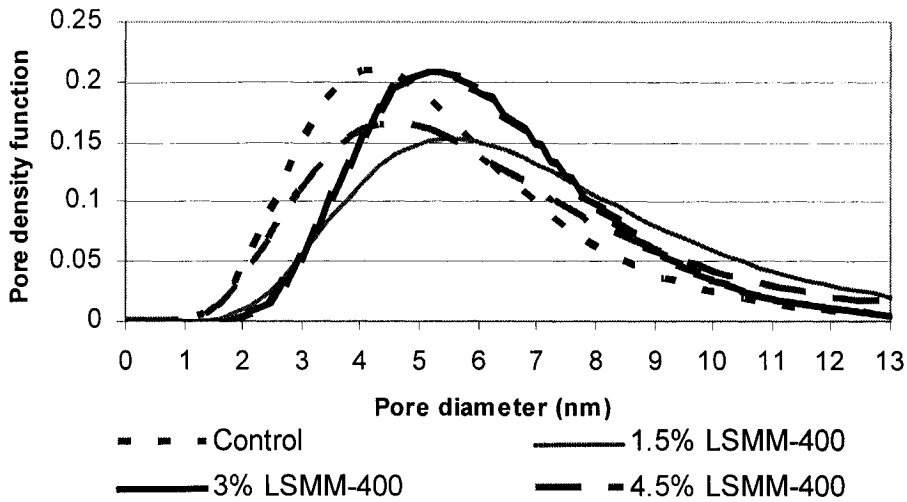


Figure D.3 Pore size distribution of LSMM400 modified membranes

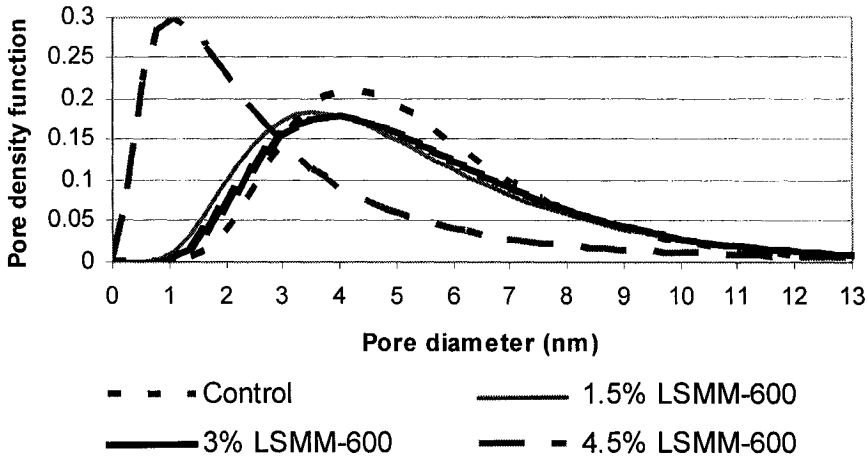


Figure D.4 Pore size distribution of LSMM600 modified membranes

Figures D.5, D.6 present the pore density of surface porosity of LSMM400, 600 modified membranes, while Figure D.7 presents those of membranes with 4.5 wt % LSMMs with and without PVP.

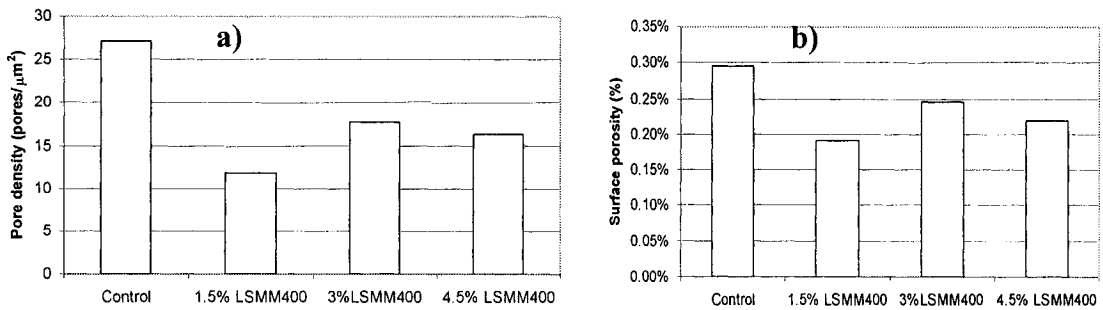


Figure D.5 LSMM400 modified membranes: a) Pore density; b)Surface porosity

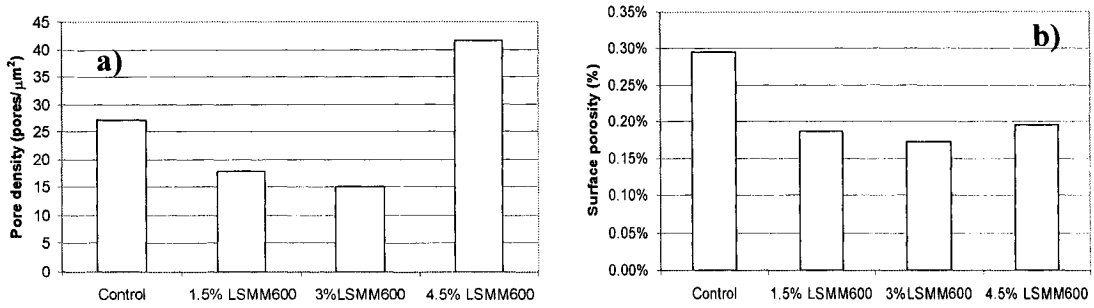


Figure D.6 LSMM600 modified membranes: a) Pore density; b) Surface porosity

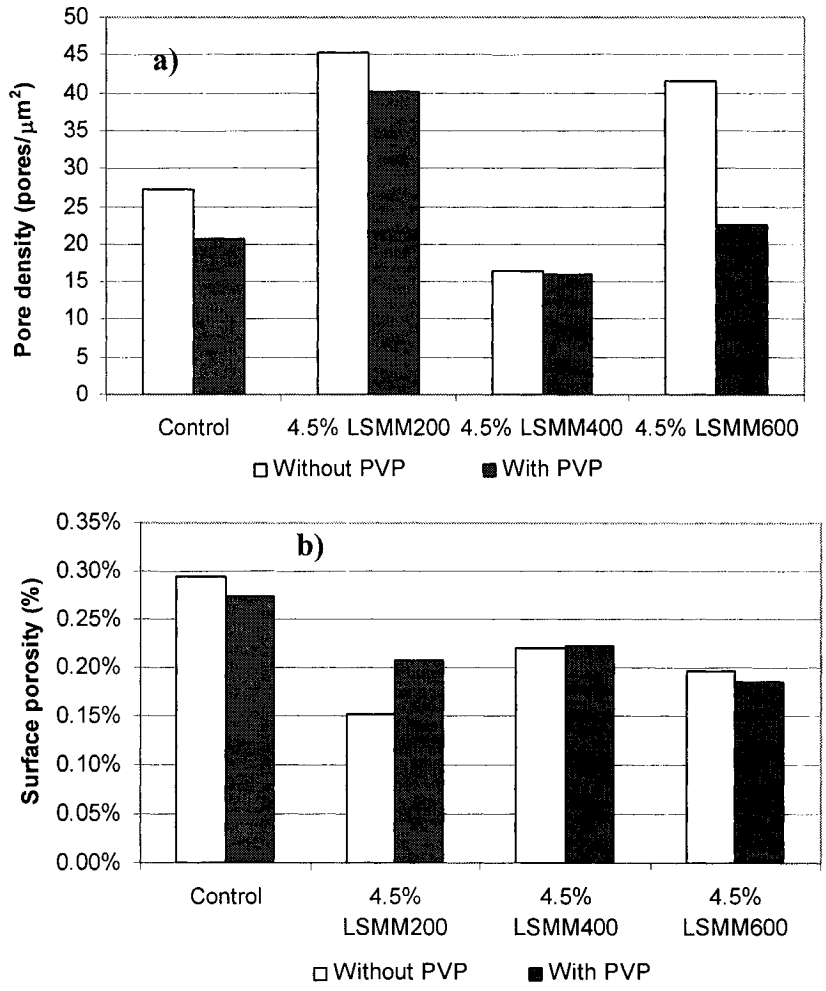


Figure D.7 Membranes with 4.5% LSMMs with and without PVP: a) Pore density; b)Surface porosity

APPENDIX E
FLUX MONITORING WITH TIME

This appendix presents the flux monitoring over the whole test including precompaction, PWP monitoring, and the filtration test with ORW. Values plotted in the graphs are averages of three different repeats (i.e., runs with three different membrane coupons). Figures E.1, E.2, E.3, E.4 present flux reduction with time of membranes with LSMM400, 600, and with 4.5 wt % LSMMs with and without PVP, respectively.

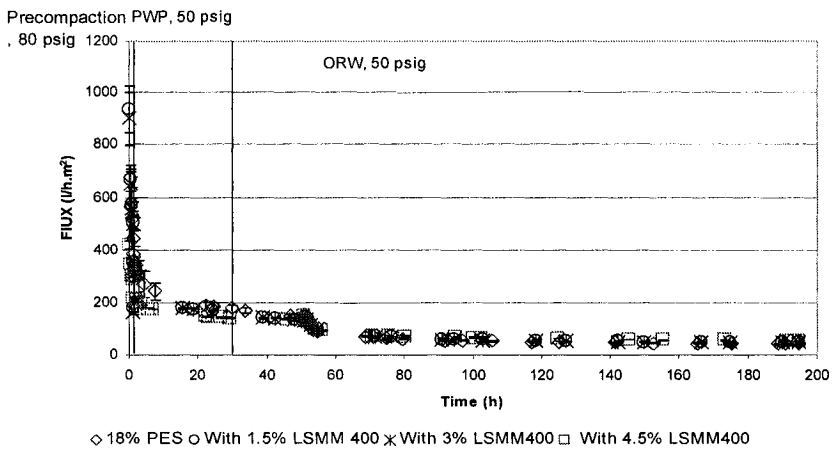


Figure E.1 Flux reduction of LSMM400 modified membranes

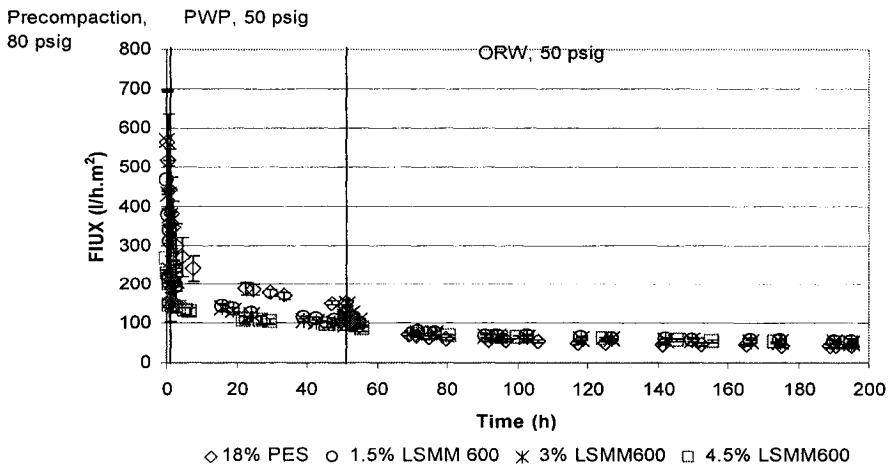


Figure E.2 Flux reduction of LSMM600 modified membranes

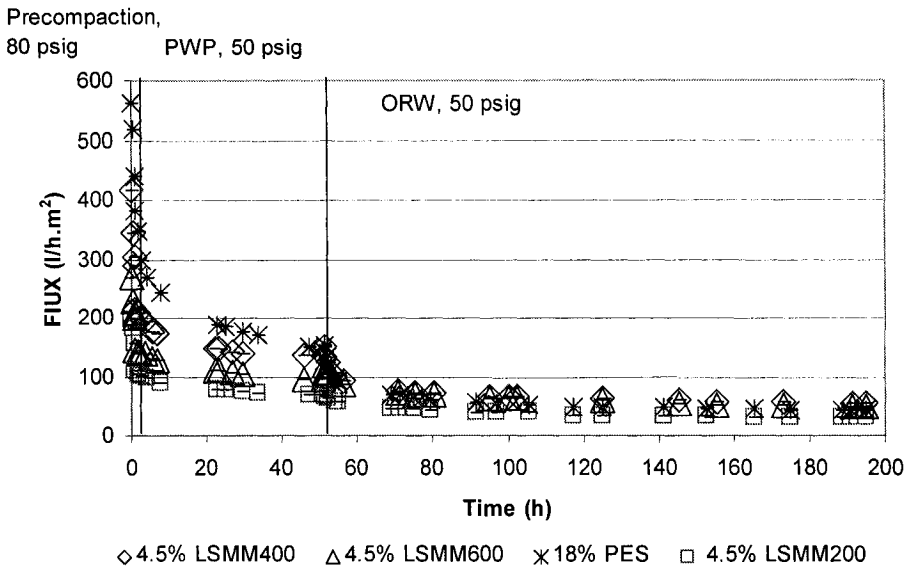


Figure E.3 Flux reduction of 4.5% LSMMs modified membranes

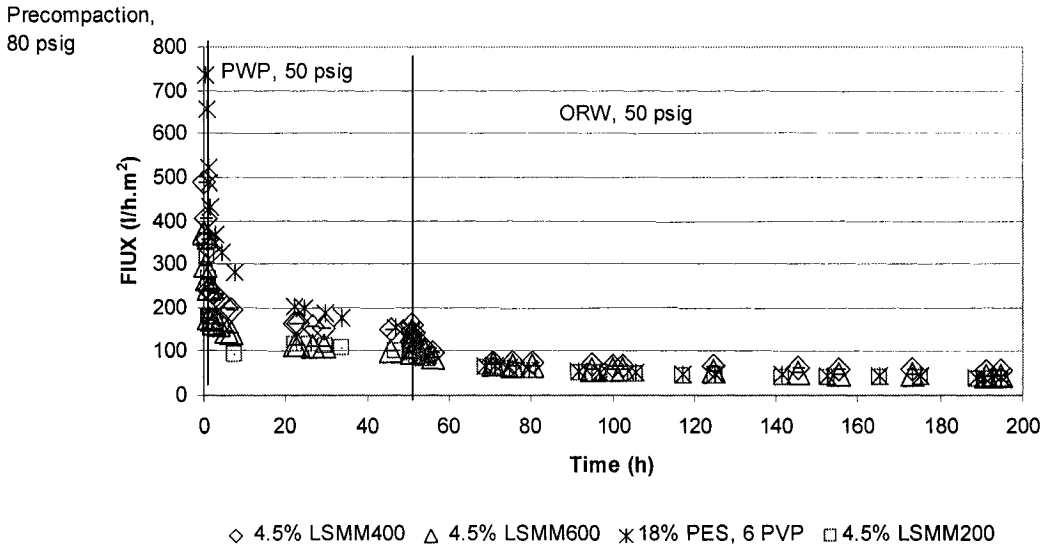


Figure E.4 Flux reduction of 4.5% LSMM, 6% PVP membranes

APPENDIX F

UV AND DOC REMOVAL MONITORED DURING ORW FILTRATION TESTS

Appendix F presents the UV and DOC removals of membranes with time. The UV and DOC removals were monitored during the filtration test with ORW. UV and DOC removals increased for the first 40 hours and then reached a pseudo-steady state. Figures F.1, F.2, F.3, and F.4 present DOC and UV removal of membranes modified with LSMM400, 600, with 4.5% LSMMs, and with 4.5% LSMMs and 6% PVP, respectively.

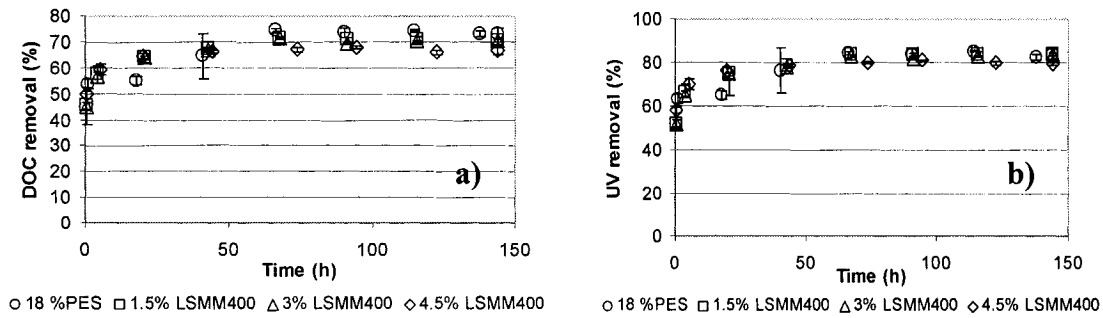


Figure F.1 NOM removal of LSMM400 modified membranes with time: a) DOC removal; b) UV removal

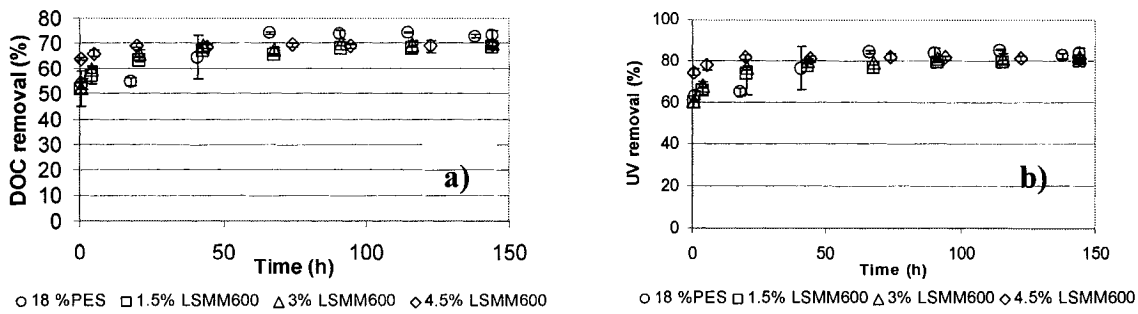


Figure F.2 NOM removal of LSMM600 modified membranes with time: a) DOC removal; b) UV removal

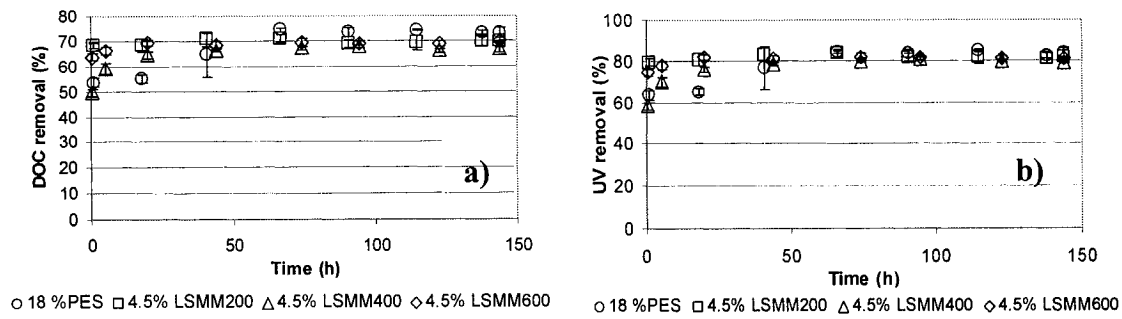


Figure F.3 NOM removal of 4.5% LSMM modified membranes with time: a) DOC removal; b) UV removal

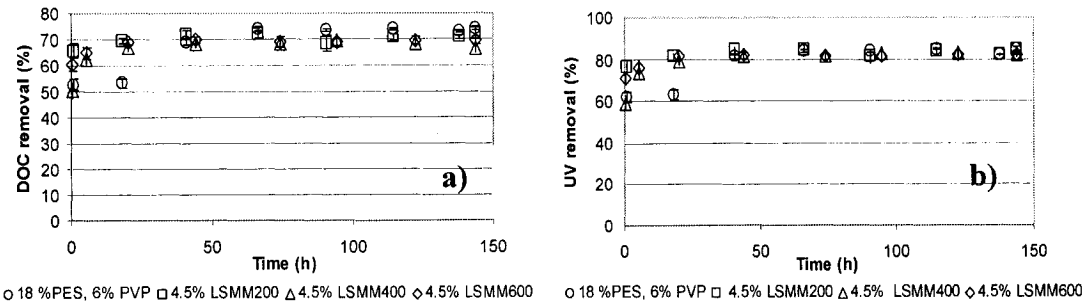


Figure F.4 NOM removal of 4.5% LSMMs, 6% PVP membranes with time: a) DOC removal; b) UV removal

APPENDIX G

SURFACE POROSITY VERSUS PWP CORRELATION

The PWP was found to relate to the surface porosity, presented in Figure G.1.

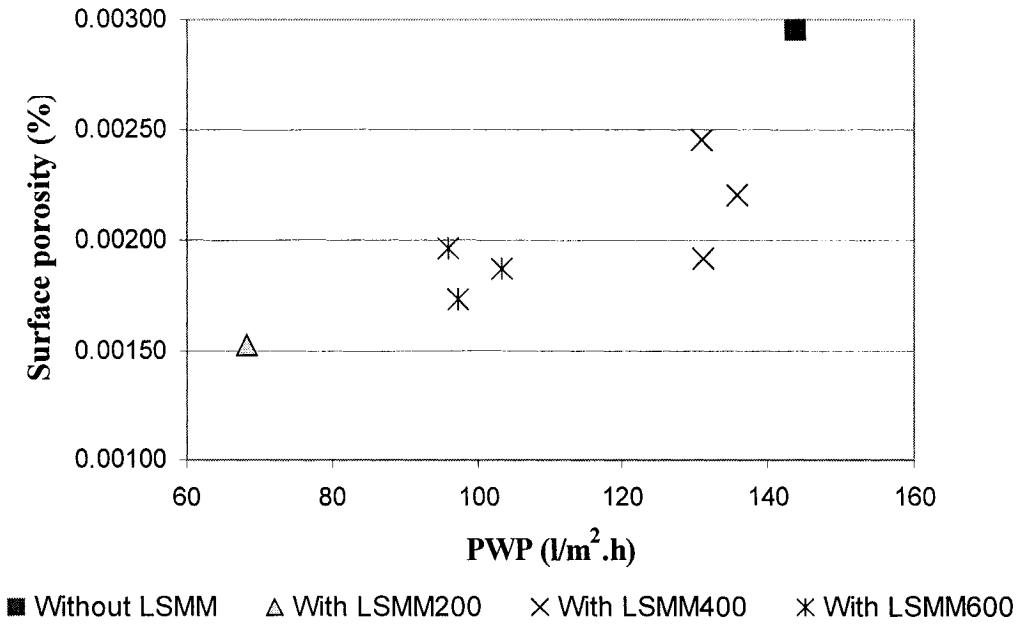


Figure G.1 PWP and surface porosity correlation

APPENDIX H
EXPERIMENTAL DATA

The raw experimental data is quite voluminous so it is presented as a set of files with a CD.

File H.1: Experimental data for contact angle analysis (CD attached)

File H.2: Experimental data for run 1 (precompaction, PWP monitoring, filtration test with ORW) for four types of membranes: Control, ControlP, LSMM200-4.5, and LSMM200-4.5P (CD attached).

File H.3: Experimental data for membrane characterization (MWCO, pore size distribution, pore density, porosity) for four types of membranes: Control, ControlP, LSMM200-4.5, and LSMM200-4.5P (CD attached).

File H.4: Experimental data for run 2 (precompaction, PWP monitoring, filtration test with ORW) for four types of membranes: LSMM400-1.5, LSMM400-3, LSMM600-1.5, and LSMM600-3 (CD attached).

File H.5: Experimental data for membrane characterization (MWCO, pore size distribution, pore density, porosity) for four types of membranes: LSMM400-1.5, LSMM400-3, LSMM600-1.5, and LSMM600-3 (CD attached).

File H.6: Experimental data for run 3 (precompaction, PWP monitoring, filtration test with ORW) for four types of membranes: LSMM400-4.5, LSMM400-4.5P, LSMM600-4.5, and LSMM600-4.5P (CD attached).

File H.7: Experimental data for membrane characterization (MWCO, pore size distribution, pore density, porosity) for four types of membranes: LSMM400-4.5, LSMM400-4.5P, LSMM600-4.5, and LSMM600-4.5P (CD attached).