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GRADE / DEGREE:	ANNÉE D'OBTENTION / YEAR GRANTED
Ph.D - Civil Engineering	2003
TITRE DE LA THÈSE / TITLE OF THESIS: Membrane Fouling Reduction Through the Addition of Surface Modifying Macromolecules	

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**IMPACT OF MANUFACTURING CONDITIONS OF
POLYETHERSULFONE MEMBRANES ON FINAL
CHARACTERISTICS AND FOULING REDUCTION**

by

Daniella Berenisse Mosqueda-Jimenez

Ph. D. 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

Ph. D. in Environmental Engineering

Department of Civil Engineering

University of Ottawa

Ottawa, Ontario

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0-612-85380-2

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Abstract

The use of membrane processes in drinking water treatment has increased exponentially in the last few years. However, one of the shortcomings that hinders their wider application is the propensity of membranes to become fouled, causing the permeate flux to decrease with time. One of the main membrane foulants is the natural organic matter (NOM) present in water sources. Membrane characteristics and performance are affected by membrane preparation conditions. The objective of this thesis was to investigate the impact of hydrophobic surface modifying macromolecule (SMM) addition and other manufacturing conditions on the membrane characteristics and performance of polyethersulfone (PES) membranes.

As it was necessary to test numerous membrane coupons prepared under many different conditions, during the first stage of this study a membrane test protocol was established. Small test cells gave very similar results to those produced by a larger test cell, which is recommended by USEPA for membrane testing. The test protocol was relatively short in duration and required a small amount of test solution. Moreover, as membrane compaction rate depends on the material, it was important to incorporate a precompaction step into the test protocol in order to quantify the contribution of membrane compaction when fouling was studied.

The second stage of the study evaluated the impact of different membrane preparation conditions (i.e., solvent evaporation time and PES concentration) and the impact of three different SMM formulations. The three SMMs differed only in the polyol used in their synthesis. SMM41, the most miscible SMM, proved to be the most promising SMM. In general, the increase of PES concentration and/or evaporation time, together with the surface modification, produced tighter membranes with improved TOC removals, decreased NOM deposition on top of the membranes and decreased flux reduction, but also resulted in a reduced permeation rate. The best SMM41-modified membranes performed as well as their unmodified counterparts in terms of pure water permeation rate, TOC removal, and final flux. SMM41 modification significantly reduced the amount of NOM deposited on the membrane surface, and in general reduced the percentage of

flux reduction. Thus, the effect of surface modification on the membrane performance was positive but marginal.

Membranes prepared with PVP had higher porosities and consequently, larger permeation rates than the membranes prepared without PVP, and similar TOC removals. In this case the effect of the SMM41-modification was statistically insignificant.

When different fractions of NOM were used as feed solutions a significant effect was observed for all the response variables. Low-molecular-weight NOM, as that present in most groundwaters and coagulated surface waters, caused less fouling, having a higher permeate flux at the end of the experiment; however, smaller TOC removals were observed. In general, there is a compromise between the TOC removal that the membrane can achieve and the permeation rate. Higher TOC removal is achieved by membranes with smaller permeation rate.

Résumé

L'utilisation de procédés membranaires dans la transformation d'eau de sources naturelles en eaux potables a augmenté exponentiellement dans les dernières années. Cependant, un des problèmes majeurs qui limitent l'utilisation de ces membranes est leur tendance à se colmater, ce qui se traduit par une diminution du flux d'eau à travers la membrane en fonction du temps. Les principaux produits colmatants contenus dans les sources d'eau naturelle ont été identifiés comme les substances naturelles organiques (NOM). Les caractéristiques et les performances des membranes sont affectées par les conditions de préparation. L'objectif de la thèse a été d'étudier l'effet de l'addition de macromolécules modifiants de surface (MMS) hydrophobiques et d'autres conditions de production sur les caractéristiques et la performance des membranes polyethersulfone (PES).

Le test d'un nombre important de membranes dans différentes conditions expérimentales a nécessité dans un premier étape la mise au point d'un protocole de test des membranes. Les petites cellules tests utilisées ont données des résultats identiques aux cellules tests plus volumineuses recommandées par l'U.S.E.P.A. pour le test de membranes. Le protocole de test mis en place est relativement court et ne nécessite qu'un petit volume de solution de test. De plus, comme la vitesse de compactage dépend du matériau, une étape de pré-compactage a été ajoutée dans le protocole de test pour quantifier la contribution du compactage de la membrane quand le colmatage a été étudié.

Dans un deuxième étape, les effets des conditions de préparation des membranes (le temps d'évaporation du solvant, la concentration du PES) et de trois formulations différentes de MMS ont été étudiés. Les trois MMS diffèrent seulement par les polyalcools utilisés pour leurs synthèses. MMS41, le plus miscible des MMS s'est aussi montré comme le plus prometteur. En général, l'augmentation de la concentration en PES et/ou le temps d'évaporation, ajouté aux modifications de surface, induisent la formation de membranes plus denses permettant une plus grande séparation des TOC, diminuant la formation de dépôt de NOM à la surface membranaire et ayant moins de diminution de flux, mais aussi induisent une diminution de la vitesse de perméation. Les meilleures

membranes MMS41 modifiées ainsi que les non modifiées ont données les mêmes résultats en terme de vitesse de perméation, de séparation des TOC et de flux final. La modification des MMS41 a réduit significativement la quantité de NOM déposée sur la surface des membranes et en général a réduit le pourcentage de réduction du flux. Donc l'effet induit par la modification de la surface fut seulement marginal.

Les membranes préparées avec le PVP ont une porosité plus grande et, du fait, une plus grande vitesse de perméation et des séparations de TOC similaires que les membranes préparées sans PVP. Dans ce dernier cas, l'effet de la modification des MMS41 est statistiquement insignifiant. Lorsque des fractions différentes de NOM sont utilisées, un effet important sur toutes les paramètres de comparaisons a été observé. Les NOMs de faibles poids moléculaires, qui sont les principaux constituants de la majeure partie des eaux du sol et des eaux de surfaces coagulées, induisent moins de colmatage et gardent un flux de perméat plus grand en fin d'expérience. Cependant, une plus faible séparation de TOC a été observée. En général, un compromis existe entre la séparation des TOC que la membrane peut faire et la vitesse de perméation. Les plus grandes séparations de TOC sont obtenues pour des petites vitesses de perméation.

A mis padres, Bertha y Ramón, por su amor, su apoyo incondicional, y la confianza en su hija, que han hecho de mí la persona que soy.

A mi hermana, Lu, por todo tu cariño, tu aliento y ayuda constante.

A Jaime, por tu amor y comprensión, gracias por dejarlo todo para seguirme.

A toda mi familia en México.

ACKNOWLEDGMENTS

I would like to express all my gratitude to Dr. Roberto M. Narbaitz, for giving me the opportunity to work in this project, for believing in me, for his continued encouragement, for his support and guidance. I am very grateful to Dr. Takeshi Matsuura, for his invaluable guidance, comments and suggestions throughout this research.

A todos mis profesores en la Universidad Autónoma de San Luis Potosí, por inspirarme a tomar este camino.

I am indebted to my professors at the Environmental Engineering Program, Dr. A. Tremblay, Dr. L. Fernandes, Dr. K. Kennedy, Dr. R. Droste, Dr. W. Parker. Special thanks to Dr. D. McLean for all his help with statistics.

My sincere thanks to Frank at the Civil Engineering Department, for all his help and patience in the laboratory. Thanks to the technicians at the Chemical Engineering Department, Louis, Gérard, and Franco.

A mis amigos, Francisc, Martha, Javier y Adriana, por su invaluable compañía y amistad a mi llegada a Canadá.

A very special thanks to Louise Duguay and Daniel Melanson, for the time that we shared, for always being there when I needed you.

I am very grateful to my friends Anh, Jeff, Véro, Frasier, Ayoub, Elisabeth, Rendra, and Stacie, for creating a friendly and helpful environment every day.

Special thanks to Laurent Simon, for his help in translating the abstract.

Thanks to all students, classmates and staff at the Civil and Chemical Engineering Departments.

Special gratitude to all the people at the Industrial Membrane Research Institute, specially, Geeta, Chaoyang, and Mehrdad, for their guidance in the laboratory. Thanks to Dr. Santerre, Jeannette, and Mandeep at the University of Toronto, for providing and helping in the SMM synthesis.

Special thanks to Dr. K. C. Khulbe (Department of Chemical Engineering), for the AFM images; to Mr. Lewis Ling (Department of Earth Sciences, Carleton University), for his tutoring with the SEM; to Dr. Tiow-Gan Ong (Department of Chemistry), for helping in the synthesis of the SMM41; to Dr. David Lean, (Department of Biology), for allowing the use of the NOM concentrator system; to Mr. John Van den Oever (Britannia Water Treatment Plant), for his help in the collection of the Ottawa River water.

This project was possible thanks to the funding of: Materials and Manufacturing Ontario (MMO), Consejo Nacional de Ciencia y Tecnología, México (CONACYT), Natural Sciences and Engineering Research Council of Canada (NSERC), and the Ministry of Training, Colleges and Universities of Ontario (OGS).

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CHAPTER 1

INTRODUCTION

Natural organic matter (NOM) removal from surface waters is critical to drinking water treatment because both hydrophobic and hydrophilic NOM fractions react with chemical disinfectants to form toxic disinfection by-products (DBPs). This is a particular problem for northern Canadian waters because they tend to have large concentrations of NOM, giving these waters their characteristic brownish colour. Membranes are starting to be used in drinking water treatment, not just for desalination, but also in the removal of microorganisms, hardness and NOM (Hamann et al., 1990). Membranes are used to comply with the more stringent regulations and to exploit water resources of lower quality. Their key advantages are: limited use of chemicals, disinfection without DBPs, better performance than conventional treatment, lower operations requirement (i.e., manpower, costs), smaller space requirement, and potential for fully automated operation (Madaeni, 1999). However, an important characteristic of membranes is that their flux (i.e., the amount of water produced per unit area) decreases with time; this phenomenon is called membrane fouling. One of the main foulants in the drinking water treatment is NOM. To minimize membrane fouling, researchers have used many different approaches (Cheryan, 1986), such as modifying the flow configuration within membrane systems, optimizing existing membrane manufacturing methods, developing of new materials and modifying existing materials so they are less susceptible to fouling.

Membrane characteristics are determined by the conditions employed during its manufacturing. For the phase inversion technique some of the variables involved in membrane fabrication include, the composition of the casting solution, the solvent evaporation temperature and time, the nature and the temperature of the gelation media, and the nature of the different solvents used during the solvent exchange technique (Matsuura, 1994). Moreover, the use of certain additives also influences the final membrane characteristics.

During the past 10 years, a group at the University of Ottawa and the University of Toronto have been developing Surface Modifying Macromolecules (SMMs), a special kind of additives, in an attempt to improve polyethersulfone (PES) membranes for environmental applications. The characteristics of the membrane surface are altered by the addition of these tailor-made SMMs. The membrane modification has been achieved using a practical and simple method, which consists of blending the SMM additives, which were specially developed to be compatible with PES, into the polymer casting solution. The SMMs migrate to the membrane's surface during the casting process and the surface of the membrane becomes more hydrophobic while keeping its bulk properties essentially the same as those of an unmodified membrane. Thus, the membranes prepared with these SMMs through this single-step casting method are surface-modified membranes. The surface modified membranes have demonstrated to have a somewhat better performance in the separation of volatile organic compounds (VOCs) from aqueous solutions via pervaporation (Pham, 1995; Mahmud, 1996; Fang, 1997), for chloroform and water separation, (Minnery, 2000); ultrafiltration of oil/water emulsions (Hamza et al., 1997); as well as, biomedical ultrafiltration and microfiltration applications (Ho, 1997). 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., 2002a).

1.1 Scope of the research

This thesis focuses on the development of new membranes to address two different problems, membrane fouling and NOM removal in drinking water treatment.

Therefore, a hypothesis is proposed: The performance of UF membranes may be improved by changing membrane characteristics via the addition of surface modifying macromolecules (SMMs) to the casting solution and by controlling other manufacturing variables.

The specific objectives of this research are:

- To develop a test protocol for the study of membrane fouling,

- To evaluate the effect of the membrane preparation variables on:
 - the final characteristics of the membrane and
 - the membrane performance
- To analyze the feasibility of improved NOM removal from water using surface modified membranes in the ultrafiltration process.

These objectives are of particular interest because of the cost savings that could be achieved by using a new ultrafiltration membrane that is less susceptible to fouling. DBP precursors removal to comply with the more stringent drinking-water regulations is also of great concern. To achieve the above objectives the following tasks need to be undertaken: membrane preparation, membrane characterization, and membrane testing. The testing will concentrate on the evaluation of the performance of the experimental membranes in terms of fouling and NOM removal from surface water.

This thesis is organized as a paper-format thesis, the main results, presented in Chapter 4 to 7, were prepared in a journal manuscript format. Chapter 4, which presents the results of the first stage of the study (i.e., membrane apparatus and test protocol), has been accepted for publication by the Journal of Environmental Engineering (ASCE). Chapter 5 presents part of the results of the second stage of the study, focusing on the effect that some membrane manufacturing conditions have on the final characteristics of the membranes. This manuscript was submitted for publication to the Journal of Membrane Science. Chapter 6 focuses on the effect of the same manufacturing conditions on the ultrafiltration performance and it has been accepted for publication by the journal Separation and Purification Technology. Finally, the results of the third stage of the study are presented in Chapter 7, and study the impact of the additive polyvinylpyrrolidone and the impact of NOM fractionation on the treatment of surface water using surface-modified membranes. This manuscript was submitted for publication to the Journal of Environmental Engineering.

CHAPTER 2

LITERATURE REVIEW

The following literature review will discuss current problems in drinking water treatment (i.e., humic substances, DBPs), membrane applications in water treatment, ultrafiltration, membrane fouling, and surface-modified membranes.

2.1 Current problems in drinking water treatment

At the same time as population grows, the quality of water resources decreases progressively, and the sources of water become more and more scarce. It also becomes more difficult to find a source water that does not have some contamination requiring treatment. Some contaminants are quite easily removed; whereas others may be so difficult to treat that an alternative source may be the best solution. Also some adverse properties may be tolerated, whereas other contaminants pose dangers to health and must be removed (McGirr, 1993).

Because of the different contaminants, the approaches to groundwater and surface water treatment are basically different. Sometimes, groundwater can be distributed without treatment or after disinfection only; in other cases, removal of iron, manganese or hydrogen sulphide may be required. Although softening may occasionally be necessary, this is often done at the point of use in Canadian practice. More recent concerns with groundwater have centred on synthetic organic chemicals (SOCs), particularly volatile compounds (Huck et al., 1993).

In the case of surface water, according to Huck et al. (1993), the most significant steps are normally particulate removal and disinfection. The latter plays a very important role in drinking water treatment, since the United States Environmental Protection Agency (USEPA) Science Advisory Board have concluded that exposure to microbial contaminants is one of the most important environmental risks (USEPA, 1998).

2.1.1 Removal of microbial threats

While classic waterborne diseases have been controlled, a residual of waterborne disease remains transmitted by newly recognized agents such as viruses, certain bacteria (*Campylobacter*, *Yersinia*, or *Mycobacteria*, for example), and protozoans (Haas, 1990). The U. S. Centers for Disease Control and Prevention indicated that, between 1980 and 1996, 401 waterborne disease outbreaks were reported, with over 750,000 associated cases of disease (Craun et al., 1998), and it is believed that these reports may substantially understate the actual number of waterborne disease outbreaks and cases in the United States. In Canada, the most recent case is the Walkerton tragedy in May 2000, where 7 people died and over 2,000 were ill as a result of the *E. Coli* 0157 contaminated drinking water supply (Holme, 2001). Acute health effects from exposure to microbial pathogens can range from mild to moderate cases lasting only a few days, to more severe infections that can last several weeks and may result in death for those with weakened immune systems, including infants, pregnant women, the elderly, but especially AIDS patients, those patients receiving treatment for certain types of cancer, organ-transplant recipients and people on immunosuppressant drugs (USEPA, 1998).

This kind of experiences led to the promulgation of the Surface Water Treatment Rule (SWTR) on June 29, 1989 by the USEPA to prevent waterborne diseases caused by resistant microorganisms such as viruses, *Legionella*, and *Giardia lamblia*. Nine years later, the Interim Enhanced Surface Water Treatment Rule (final rule was published on December 16, 1998) added *Cryptosporidium* to the list of concerns. The SWTR requires disinfection and filtration for all public water systems that use surface water or a source that is groundwater under the direct influence of surface water and that does not meet specified criteria for watershed protection, coliform bacteria, and turbidity.

Traditionally, water disinfection was considered successful if it eliminated coliform indicator bacteria, however *Giardia* and *Cryptosporidium* are much more resistant to chlorine and other chemical disinfectants. While chlorine is by far the most common disinfectant used in drinking water applications, it does not always results in 100% inactivation of *Giardia* cysts. Inactivation rates depend on a number of factors (i.e., type

of disinfectant, dose, temperature and pH); to achieve inactivation longer contact times and/or higher chlorine doses are usually required. For example to reach 100% *Giardia* inactivation at 5°C the necessary chlorine concentration is 2 mg/L and contact time of 1 h at pH 6 (McDonald et al., 1993).

The higher disinfectant doses and longer contact times required to control these resistant microorganisms have also led to an increased formation of disinfection by-products.

2.1.2 The formation of disinfection by-products

When selecting a disinfectant, one has to be aware that undesirable disinfection by-products can be formed (Lykins and Clark, 1994). Every major disinfectant (ozone, chlorine dioxide, chloramines, chlorine) has some concerns. For ozone, by-products such as aldehydes, ketones, and carboxylic acids can be produced. These by-products can also be produced by other oxidants, such as chlorine, but usually at lower concentrations. Of greater concern with the use of ozone, is the formation of bromate ions when bromide ions are present in the source water. For chlorine dioxide (ClO_2), the concern is the inorganic by-products of chlorite and chlorate ions. For chloramines (NH_2Cl), the concerns are the formation of cyanogen chloride (CNCl), and the fact that this is a weak disinfectant (Miltner, 1993). For chlorine (Cl_2), the major concern is the production of chlorinated by-products.

These disinfection by-products are formed when disinfectants react with the organic matter present in the water. The vast majority of organic material present in water is comprised of naturally occurring humic material, a complex, difficult to separate mixture of similar macro-organic molecules. Humic materials (or humus) are natural organic matter (NOM) formed from the chemical and biological degradation of plant and animal residues and from synthetic activity of certain microorganisms and may approach levels of several parts per million (mg/L or ppm) (Montgomery, 1985).

Humic materials have a broad molecular weight distribution ranging from about 300 to 100,000 g/mol (Zeman and Zydney, 1996) and can be divided in three main fractions, fulvic and humic acids, both with an amphiphilic character, and humin. It is worth noting

that the major components of organic colour in surface waters are the fulvic acids (Wilson, 1959).

Rook (1977) determined that both humic and fulvic acids are precursors of haloforms when treated with chlorine, and these haloforms possess carcinogenic properties. Toxicological studies have shown several DBPs to cause adverse reproductive or developmental effects in laboratory animals, and numerous epidemiological studies have suggested an increased cancer risk to individuals exposed to chlorinated waters (Roberts et al., 2002). In animals, chloroform has been shown to be carcinogenic after oral exposure, resulting in an increase in kidney and liver tumours (ATSDR, 1997).

Given that humic and fulvic acids are precursors of DBPs (primarily trihalomethanes (THMs), halo ketones (HKs), haloacetonitriles (HANs) and haloacetic acids (HAAs)), potential treatment processes must also control the formation of disinfection by-products (DBPs) (Tan and Amy, 1991).

In 1992, the U. S. Regulatory Negotiating Committee on microbial pathogens, disinfectants and DBPs concluded that there was considerable uncertainty in this regard and additional information was needed to assess the potential health problems created by the presence in drinking water, not only of pathogens, but also of DBPs (USEPA, 1998). To assess the extent and severity of the risks in order to make sound regulatory and public health decisions, the Information Collection Rule (ICR) was promulgated on May 14, 1996. The purpose of the ICR is to collect occurrence and treatment information to help evaluate the need for possible changes to the SWTR and existing microbial treatment practices, and to help evaluate the need for future regulation of DBPs.

Under the ICR, the public water systems had to monitor water quality factors affecting DBP formation and DBPs within their treatment plants and in the distribution system on a monthly basis for 18 months. A subset of the public water systems must conduct bench or pilot studies of granular activated carbon or membrane processes, to evaluate DBP precursor removal and control of DBPs (Krasner et al., 1995). These technologies were selected by a Negotiating Committee based on process experience, expected performance, and limitations of several technologies available for DBP precursors

removal (Carlson, 1991). This committee was integrated by representatives of state and local regulatory and public health agencies, local elected officials, consumer groups, public water systems (PWSs), environmental groups, and USEPA.

In an effort to strengthen protection against microbial contaminants, especially *Cryptosporidium*, and at the same time, reduce potential health risks of DBPs, in December 1998, USEPA announced a new rule: The Stage 1 Disinfectants and Disinfection By-products Rule (D/DBPR). It was developed to balance the risks between microbial pathogens and disinfection by-products (DBPs). In January 2002 the Stage 1 D/DBPR became effective for all community water systems with surface or groundwater under the influence of surface water and serving over 10,000 persons, with limits of 80 $\mu\text{g/L}$ for THMs and 60 $\mu\text{g/L}$ for HAAs. For all other community systems it will become effective in January 2004 (Dowbiggin, 2001).

All this explains why the removal of microbial threats and the formation of DBPs are the most current concerns in drinking water treatment. In order to solve these two main problems, it has been demonstrated that membrane treatment is an effective way of disinfecting drinking water without the creation of disinfection by-products (Tan and Amy, 1991; Aoustin et al., 2001; Clark et al., 1994; for more details refer to Section 2.1.1). Madaeni (1999) summarizes the advantages of using membranes for drinking water treatment, compared with conventional treatment as follows: a) water of constant and superior quality, b) less addition of chemicals, c) lower energy requirement, d) feasibility of small scale systems, e) possibility to fully automate the process (Bodzek and Konieczny, 1998), f) capability of removing a wide range of substances, and g) solution to the problems of water of variable quality.

2.2 Membrane processes

Several types of membrane processes for water and wastewater treatment are commercially available (AWWA, 1998). Reverse osmosis (RO), electrodialysis (ED) (or its variant, electrodialysis reversal (EDR)) and nanofiltration (NF) have been increasingly applied in municipal water treatment (Hamann et al., 1990). Microfiltration (MF) and ultrafiltration (UF) processes, which are already extensively used in industry, are being

implemented as proprietary systems, much like the desalination industry saw 30 years ago with RO membranes, except today membranes are used primarily for microbial control in municipal treatment (Duranceau, 2000) (Table 2.1).

MF, UF, NF and RO are pressure-driven processes with varying degrees of separation capabilities:

- MF membranes operate at about 30 to 210 kPa (5 to 30 psi) transmembrane pressure (TMP) and can be used to remove particulates (turbidity, Giardia and Cryptosporidium protozoa, bacteria, and under some circumstances, viruses) (Bergman and Lozier, 1993).
- UF membranes have smaller pores than MF membranes, which result in a higher TMP (typically ranges from 140 to 520 kPa (20 to 75 psi)). Due to the smaller pores, UF membranes reject all the same solutes as MF plus viruses and dissolved organics, depending on size (commonly with molecular weights down to about 10,000 Daltons) (Fig. 2.1). UF can be defined as a clarification and disinfection membrane operation in water treatment (Aptel and Buckley, 1996).
- NF membranes usually operate with TMPs from 340 to 860 kPa (50 to 125 psi). NF, which is also called low-pressure reverse osmosis or membrane softening, lies between RO and UF in terms of membrane selectivity. They are designed for removal of multivalent ions (calcium and magnesium) in softening operations (Bergman and Lozier, 1993). They reject mono- and polyvalent ions very differently, the former being poorly rejected by the NF membrane, which explains why NF leads to a much lower osmotic backpressure than that experienced with RO (Aptel and Buckley, 1996). More recently, NF has been employed for organics control (Fu et al., 1994; Tan and Sudak, 1992).

Table 2.1 Summary of the membrane operations in water treatment

Membrane operation	Driving force	Flux (LMH = L/m ² -h) (gfd = gal/ft ² -day) ^b	Pores	Molecular Weight	Water Treatment Application	Capacity of largest facility
Microfiltration	Pressure difference 30 – 210 kPa (5 – 30 psi ^a) 70 – 340 kPa (10 – 50 psi ^b)	170 – 1700 LMH 5 – 50 x 10 ⁻⁵ m ³ /m ² -s 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 140 – 520 kPa (20 – 75 psi ^a) 340 – 690 kPa (50 – 100 psi ^b)	35 – 500 LMH 10 – 140 x 10 ⁻⁶ m ³ /m ² -s 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 340 – 860 kPa (50 – 125 psi ^a) 690 – 1380 kPa (100 – 200 psi ^b)	25 – 40 LMH 7 – 10 x 10 ⁻⁶ m ³ /m ² -s 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 690 – 8270 kPa (100 – 1200 psi ^a) 1380 – 4140 kPa (200 – 600 psi ^b)	5 – 35 LMH 1 – 10 x 10 ⁻⁶ m ³ /m ² -s 3 – 20 gfd ^b	Dense media ^c	> 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)

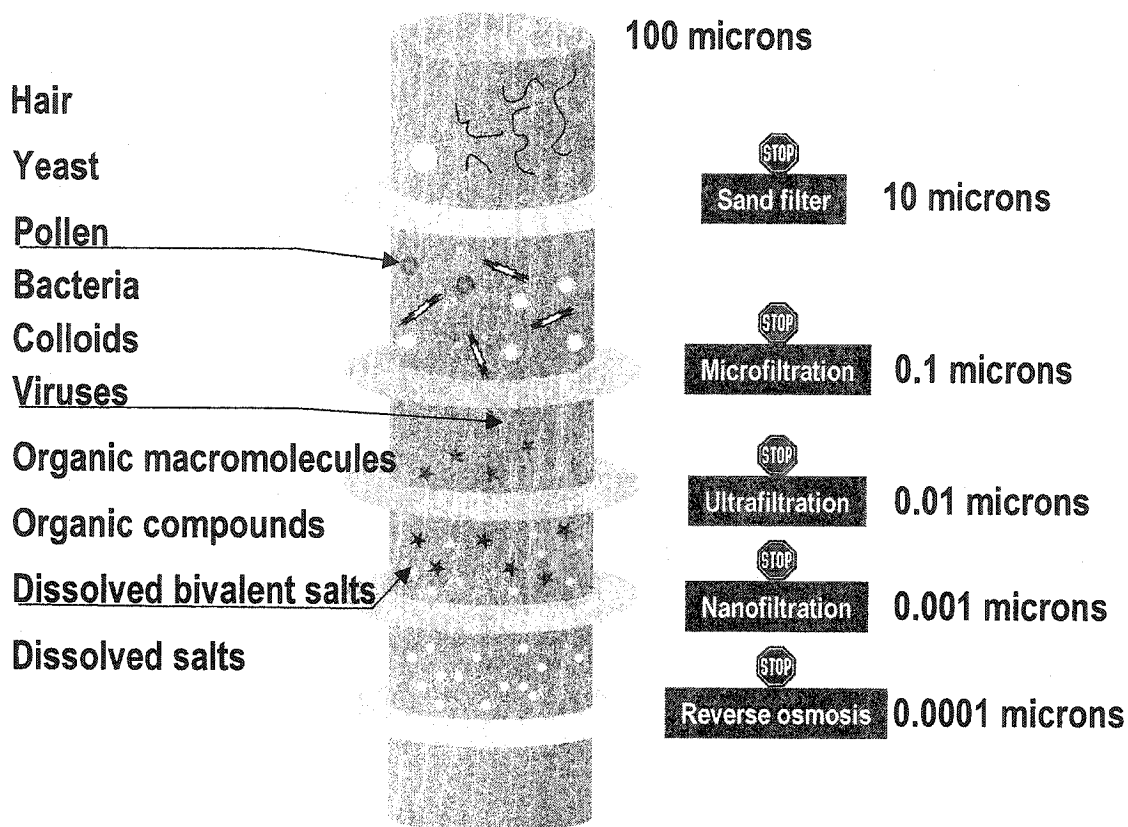


Fig. 2.1 Ranges of separation (Buckley and Hurt, 1996)

- RO membrane pressures typically range from 690 to 4140 kPa (100 to 600 psi) when treating fresh or brackish water (TDS up to about 10,000 mg/L) and from 5510 to 8270 kPa (800 to 1,200 psi) for seawater desalting applications (total dissolved solids (TDS) in the 35,000 to 45,000 mg/L range). In RO membrane operation the solvent of the solution is transferred through a dense membrane tailored to retain salts and low-molecular-weight solutes. If a concentrated saline solution is separated from pure water by such a membrane, the difference in chemical potential tends to promote the diffusion of water from the diluted compartment in order to equalize the concentrations. At equilibrium, the difference in the levels between the two compartments corresponds to the osmotic pressure of the saline solution (Aptel and Buckley, 1996).

While pressure-driven processes use a membrane barrier to separate the feed stream from the product stream (permeate or filtrate), in ED and EDR technology an electrical potential induces dissolved ions to pass through anion- and cation-permeable membranes, leaving a demineralized “dilute” stream. Treated water does not pass through a membrane barrier and, consequently, uncharged or weakly charged contaminants remain in the dilute (product) stream (Bergman and Lozier, 1993).

In addition to pressure driven and electropotential driven membrane processes there are permeation operations where the driving force is the activity difference across the membrane. Permeation processes are applied to solutions or mixtures. When applied to solutions, it is the solvent that is transferred through the membrane. For instance, in pervaporation the activity difference is generally maintained by creating a partial vacuum on the permeate side in such a way that the pressure is kept below the vapour pressure of at least one component of the liquid in contact with the upstream face of dense membranes. Pervaporation is mainly used for the dehydration of alcoholic azeotropes and more recently in the removal of VOC from drinking water and wastewater (Aptel and Buckley, 1996).

In general, the nature of the feed to be treated by a membrane process will determine the best membrane for each specific application. Figure 2.1 is an example of the selection of the membrane technology most suitable for a particular application.

The development of anisotropic membranes led to the breakthrough in industrial applications. Anisotropic membranes consist of a very thin top dense layer, called the skin or active surface layer, because it is responsible for the separation (Matsuura, 1994), supported by a thicker and more porous supporting sublayer. Membrane technology has not been used just in water treatment, but also in areas of water scarcity, where upgrading of treated municipal wastewaters for indirect potable and direct industrial reuse, as well as for industrial water recycling (Malleval et al., 1996).

2.2.1 Membrane preparation and materials

In the previous section anisotropic membranes were introduced as the reason why membranes started to be used in industrial applications. Figure 2.2 shows the two different layers that constitute an anisotropic membrane. The skin has the main functions of the membrane, since the overall flux and selectivity depend only on the structure of the skin. According to Aptel and Buckley (1996), its thickness is in the range of 0.1 to 0.5 μm , roughly 1 percent of the thickness of the porous sublayer. The supporting layer possesses negligible resistance to mass transfer and is present for mechanical support only. It is usual to distinguish two types of anisotropic membranes: asymmetric and composite.

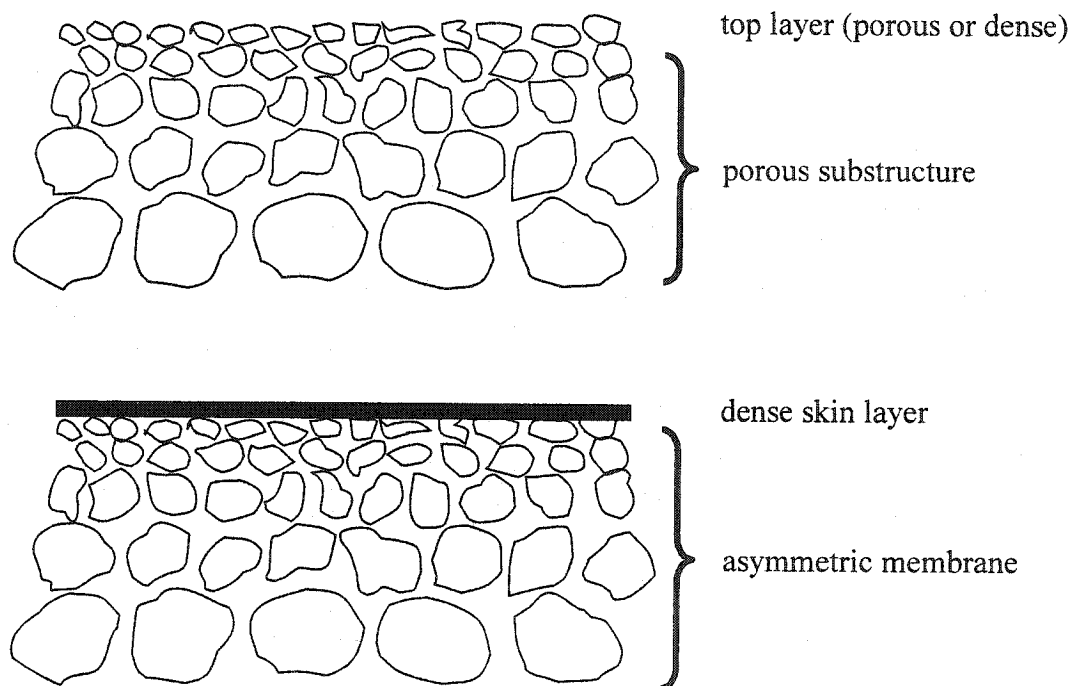


Fig. 2.2 Schematic drawing of an asymmetric membrane and a composite membrane (Aptel and Buckley, 1996)

Asymmetric membranes are prepared from the same material, whereas in composite membranes the top layer and sublayer originate from different materials. Therefore, composite membranes have the advantage that each layer can be optimized independently. Generally, the porous layer is already an asymmetric membrane (Fig. 2.2) (Aptel and Buckley, 1996). Although the basic design concept for composite membranes was introduced for RO membranes, later the same concept was extended to the UF and MF range.

Now that the morphology of the membranes has been briefly described, the most common techniques to prepare and the materials used to create this morphology will be discussed. In spite of the differences among the various methodologies used in the preparation of membranes, the goals are always to control the pore size and the pore size distribution and to decrease the thickness of the surface layer (Matsuura, 1994). One method to manufacture asymmetric membranes is the phase inversion technique. Kesting (1985) explains that this technique is called phase inversion because the polymer solution (continuous phase: the solvent) inverts into a swollen three-dimensional macromolecular network or gel (continuous phase: polymer); thus the polymer essentially goes out of solution at the surface forming the skin layer (Cheryan, 1986). Cheryan (1986) described this process as follows: the polymer is dissolved in a suitable solvent and a swelling agent. The solution is cast onto a film by placing it on a large flat surface and the solvent starts to evaporate at the surface increasing the polymer concentration at the solution/air interface, thus the polymer forms the skin layer. The solvent that remains in the bulk of the mixture, the polymer, and the swelling agent, start to form two phases: the polymer-solvent and the swelling agent. As the solvent evaporates, the polymer forms a coat around the swelling agent. When the solvent and the swelling agent depart the coat ruptures forming the porous sublayer. There are two variations of the phase inversion technique, the wet process and the dry process. In the wet process the casting solution is fairly concentrated, and the solvent is allowed to evaporate only partially. The skin layer is formed after the partial evaporation, when the membrane is immersed in water in the step known as gelation. Sometimes, afterwards, the membrane is heated to produce smaller pores. On the other hand, in the dry process the casting solution is diluted and the solvent is allowed to evaporate completely (Kesting, 1985).

The membranes formed using the wet method must be kept wet all the time, since during the gelation solvent diffuses out and water diffuses in, therefore water forms an integral part of the membrane and if it evaporates in the air, the asymmetric porous structures could collapse because of the capillary forces generated during drying. A multiple-stage solvent exchange can be applied to dry these membranes. In this technique, the water in the membrane is replaced progressively, using different solutions of water-miscible solvent (nonsolvent for the membrane polymeric material) with increasing concentration. Then, another solvent, this time a volatile one, may be used to replace the first solvent (Matsuura, 1994).

As can be seen, there are several variables involved in the phase-inversion technique that would impact the characteristics of the membrane formed. They include the composition of the casting solution, the solvent evaporation temperature and time, the nature and the temperature of the gelation media, and the nature of the different solvents used during the solvent exchange technique (Matsuura, 1994).

While asymmetric membranes are made in a one-step procedure, composite membranes are made by a two-step procedure. In the latter case, the basic concept is to deposit a very thin selective layer on top of a highly permeable substrate (Zeman and Zydney, 1996). Cadotte (1985), the developer of the "thin-film composite" membrane, described the following four general methods to prepare this kind of membranes:

- 1) Casting of the thin-film separately, from a dilute solution of a preformed polymer, in a surface-active "spreading" solvent, upon a water surface. Then the membrane is removed from the water by lamination onto the porous support layer (Cadotte, 1985 and Kesting, 1985).
- 2) Dip coating of the substrate in a polymer, monomer or prepolymer solution, followed by curing with heat or radiation. This procedure avoids the difficulty of handling the thin films, however it has the disadvantage that only solutions that do not interact with the porous support may be utilized in the application of the skin layer (Kesting, 1985).

- 3) Plasma coating occurs when a substrate membrane is subjected to glow-discharge plasma that consists of various ions, radicals, electrons and molecules. The glow discharge is generated inside a tubular reactor when a high frequency field is applied outside (Matsuura, 1994). Plasma reactions include polymerization, depolymerization and modification of functional groups. Organic compounds with adequate vapour pressure may be used to deposit a thin layer on top of the porous support (Cadotte, 1985).
- 4) In-situ polymerization, the support layer is immersed in an aqueous solution containing a reactive monomer or prepolymer, then it is immersed in a second bath containing a water-immiscible solvent with another monomer. Thus, the reaction takes place at the interface to form the skin layer. 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).

There are many more techniques, both old (Carnell and Cassidy, 1961) and new, used in membrane preparation, but their description is not included in this thesis because they are not as widely used. Zeman and Zydney (1996) give a good description of the technologies presently used in industrial membrane manufacturing. The discussion of membrane characteristics continues with a brief introduction of the materials used in membrane preparation.

Just as the techniques used in the preparation of synthetic membranes vary significantly, so do the materials. They include both organic (polymers) and inorganic (metal, ceramics, glasses, etc.) materials. Ceramic membranes (oxides, nitrides, or carbides of metals such as aluminium, zirconium, or titanium) represent the main class of inorganic membranes. Inorganic membranes generally have superior mechanical, chemical and thermal stability relative to organic membranes, however they are brittle and more expensive.

Zeman and Zydney (1996) explain why the number of polymers used in typical membrane preparation is considerably smaller than the number of available polymers. According to them, to be successful in membrane manufacturing the polymer must: 1)

have suitable properties for the targeted applications, 2) be compatible with the selected membrane formation technology, 3) be available and affordable, and 4) be a good membrane former.

The largest class of polymers used is the hydrophilic cellulose and its derivatives, due to their low cost and low tendencies for adsorption (Aptel and Buckley, 1996). In water treatment applications cellulose esters (mainly di and triacetate) derived membranes are frequently used because they are relatively resistant to temperature, to biological degradation, and to chlorine. They are, however, sensitive to acid or alkaline hydrolysis. Polyamides were developed to overcome the limitations with cellulose acetate membranes, they are thermically and chemically more stable, however their free chlorine tolerance is almost zero (Cheryan, 1986).

Polyvinylidene fluoride (PVDF) membranes have high chemical resistance, and can be repeatedly autoclaved. Polytetrafluorethylene (PTFE) membranes are very stable to strong acids and alkalis, and can be used at a wide range of temperatures (Cheryan, 1986). These polymers are used to prepare macroporous membranes, together with the following hydrophobic polymers: polyethylene (PE), polycarbonate (PC) and polypropylene (PP) (Aptel and Buckley, 1996).

Cheryan (1986) presents a list of the polymeric materials used in the manufacture of MF, UF and RO membranes. While Zeman and Zydney (1996) present an updated version for MF and UF membranes. The focus of this thesis is UF membranes; therefore more attention will be paid to the materials used in their preparation. UF membranes are generally prepared from amorphous polymers, in contrast to those used for MF membranes that are crystalline polymers. The latter polymers show high chemical resistance, thermal stability and less compaction, due to the cross-linking effect between amorphous domains and the hindrance of the free rotation of polymers segments. On the other hand, amorphous polymers are generally used for UF membranes because with these materials pores of a small size can be generated, regulated and controlled with relative ease (Anselme and Jacobs, 1996).

Polymeric material such as polysulfone (PS), polyethersulfone (PES), and polyacrylonitrile (PAN), are recommended because of their high glass transition temperature, which allow a higher maximum service temperature (Kesting, 1985). Other materials also used in membrane manufacture are PVDF and cellulosic polymers.

Hydrophobic PS membranes are widely used in UF applications (Cheryan, 1986), because of their wide temperature limit and pH tolerance, in addition to their fairly good chlorine resistance and the wide range of pore sizes available. Their main limitation is the apparent low-pressure limit. The use of hydrophobic materials is more suitable when mechanical strength and thermal stability are prime requirements, since water molecules act as plasticizers for hydrophilic materials. For this reason, membranes fabricated from hydrophobic materials tend to have greater chemical, mechanical and thermal stability (Anselme and Jacobs, 1996).

PES is a derivative of polysulfone that is slightly more hydrophilic, has a higher glass transition temperature (225°C) and does not contain aliphatic hydrocarbon groups (Hamza et al., 1997) (Fig. 2.3). It is an excellent UF membrane material because of its film and membrane forming properties together with its high compatibility with other polymers (Zeman and Zydney, 1996) and high mechanical and chemical stability (Hamza et al., 1997). 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). In addition, PES is commercially available and relatively inexpensive. These characteristics make PES one of the most widely used polymers for manufacturing UF membranes (Hamza et al., 1997).

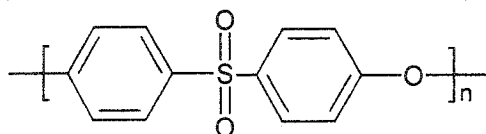


Fig. 2.3 Chemical structure of PES

In membrane development, many membranes are manufactured under different preparation conditions and they need to be evaluated for the above-mentioned properties, as well as for their resistance to fouling. By definition fouling resistance has to be

assessed via permeation (filtration) tests, in which the permeate flux is measured over time. Thus, it is highly desirable to have a testing procedure that is short in duration, utilizes a minimum amount of test solution, and requires only a small piece of membrane, which is representative of a large membrane sheet.

2.2.2 Membrane permeation experiments

In general, there are two main types of devices used in membrane permeation experiments: cross-flow and dead-end (Zeman and Zydney, 1996). In the cross-flow geometry the feed flow is parallel to the membrane and perpendicular to the filtrate flow, resulting in three different streams: feed, permeate and retentate. On the other hand, dead-end devices only have a feed and permeate stream and the main flow direction is perpendicular to the membrane surface (Pellegrino, 2000). The following paragraphs will discuss the type of cells used in membrane permeation experiments.

Matsuura (1994) described three different permeation cells: a reverse osmosis cell, an ultrafiltration cell and a static cell. The first two types are used in experiments with continuous cross-flow flow operation while the latter is used for the batchwise dead-end operation. Zeman and Zydney (1996) listed several dead-end devices used in UF and MF test, vacuum filtration being the simplest of these. In these vacuum filtration devices the flat sheet membrane is placed between a support plate and an open glass funnel/feed reservoir. The feed solution is drawn through the membrane applying a vacuum. In the syringe-end filters the feed is manually driven through the membrane from a syringe. In this case, the control over the applied pressure is minimal and over the flow rate is very crude. Another dead-end device described by Zeman and Zydney (1996) is the pleated sheet cartridge. In this device the membrane is sandwiched between two nonwoven fabric supports and pleated into an accordion-like array (not all membranes are pleatable) formed into a single cylindrical unit with a plastic core in the middle and inserted in a plastic or a stainless steel housing. Yet another type of system is the plate-and-frame device, which uses multiple flat sheet membranes in a sandwich arrangement consisting of the support plate, the membranes, and the channel spacer or separator. This type of module has a cross-flow geometry.

Cheryan (1986) gave a list of apparatus used in laboratory UF evaluations. Stirred UF cells are a popular test module in which agitation is provided with a magnetic stirring bar placed as close as possible to the membrane surface, and the pressure is supplied by air or nitrogen, avoiding the possible damage of highly labile products due to pumping. He warned that their use in the evaluation of engineering parameters is not recommended since the flux obtained with these cells is not a good indication of the results from a large-scale module, however they might be used, under limited conditions, in the evaluation of rejection properties. He also presents several Amicon thin-channel devices. In this case, the retentate is pumped at high shear rate through narrow channels on top of the membrane; it can be used in both dead-end and cross-flow filtration. Centrifugal forces can also be used to provide the TMP necessary to perform the filtration, like in the case of the centrifuge tube devices described by Pellegrino (2000). The designs include membrane inserts for microcentrifuge vials or self contained devices, which are placed in a centrifuge and the force vector drives permeate through the membrane. Diffusion devices are yet another type of test modules. They consist of tubular membrane sleeves that can be filled with a solution and clamped at both ends, immersed in a large vessel that contains another fluid, where the membranes properties control the permselective diffusion between the two fluids.

Several test cells have been used in the laboratory when studying UF membrane fouling, due to both proteins and natural organic matter. However, by far, the most widely used are the Amicon stirred batch UF cells, used with or without stirrer (Nicolas et al., 2000). O'Melia and coworkers (Bonner and O'Melia, 1991 and Jones and O'Melia, 2001) used the 50-mL (model 8050) Amicon cell to study some aspects of the fouling of UF membranes by natural organic matter and proteins. While Brink et al. (1993) used an older style (model 202) to carry out their experiments of reduction of susceptibility due to protein fouling and Borneman et al. (1997) used the 200-mL (model 8200) for their UF studies of apple juice. Aoustin et al. (2001) used a 110 mL-magnetically stirred batch cell, whose brand was not indicated, to evaluate the effects of surface water composition on rejection and fouling of two UF membranes. Another dead-end module was used by Jönsson (1995) to study concentration polarization and fouling by silica sol, octanoic acid

and sodium octanoate. This module, manufactured by ABB Flootek, Sweden, was equipped with one membrane above and one below a rotor blade.

Cross-flow cells have also been used in fouling evaluations. They include Millipore's MiniTan cells (Cho et al. (1998, 1999a, 1999b, 2000a, and 2000b)), Millipore's 4 GPM Pellicon Cassette System (Peuravuori and Pihlaja, 1997) and Osmonics' SEPA cells (DiGiano et al., 2000; Bodzek and Konieczny, 1998; and Allgeier and Summers, 1995). The latter has been designated by the USEPA as the standard cell for evaluating the potential of membrane processes as part of the Information Collection Rule (ICR) (USEPA, 1996).

2.3 Ultrafiltration membrane performance

This section synthesizes and completes the information about the UF characteristics that has been mentioned in previous sections. UF membranes are effective in removing particulate material from water, including microorganisms, such as protozoa (*Giardia* and *Cryptosporidium*), bacteria and viruses (Crozes et al., 1993). Because of its large pore structure, UF fluxes are in the range of 10 to 35 x 10⁻⁶ m³/m²-s (20 to 80 gfd) (Singh, 1997). In contrast to the rejection of contaminants by RO membranes (where it is mainly a function of the relative chemical affinity of the contaminant for the membrane vis-à-vis water) or rejection by MF (which is almost entirely due to physical sieving of materials at the membrane surface), UF and NF membranes reject contaminants via a combination of physical sieving and contaminant-membrane chemistries (Wiesner and Buckley, 1996). Therefore, rejection in an UF membrane for one of the compounds in a solution can be determined either by porosity (average pore diameter and distribution of pore size on the membrane surface), the membrane's cutoff threshold, or the physicochemical characteristics of the compound or solution (Anselme and Jacobs, 1996).

As mentioned, UF membranes are produced from polymeric material such as PS, PES, and PAN, PVDF and cellulosic polymers, as well as ceramic membranes made by sintering inorganic materials.

Industrial applications of UF are found in: metallurgy, paper, textile, leather, food and dairy, pharmaceutical and chemical industries, etc. It is used for fractionation, purification, separation and concentration of water-soluble solutes or water-dispersible materials (Hamza et al., 1997).

2.3.1 Ultrafiltration in municipal drinking water treatment and NOM removal

Another application that is recently receiving a lot of attention is the removal of natural organic matter in drinking water treatment. Thorsen (1999a, 1999b) mentioned how this procedure is particularly important in northern countries, including Canada, United States, Great Britain, Scandinavia, Russia and Norway, due to the predominance of highly coloured waters. As explained earlier, humic substances are the responsible for the brown colour characteristic of these waters, and they are also DBP precursors. Rouhomäki et al. (1999) mentioned that sixty percent of the Finnish lakes are described as humic waters. According to Thorsen (1999b) the first of several full-scale plants aiming for colour removal, was started in 1989 in Norway using spiral-wound cellulose acetate membranes, which is the most common type used in these plants. However, in Sweden they have used spiral polyamide membranes, and in Scotland tubular cellulose acetate membranes. Thorsen (1999b) 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. Though pilot studies in the United States have been presented as early as 1987 (Taylor et al., 1987), none of the 194 municipal membrane plants in the survey by Morin (1994) were designed with NOM removal as their primary purpose. The seventeen low-pressure membrane plants at that time were designed for water softening (NF). Anselme and Jacobs (1996) presented another list of 32 UF membrane plants in operation; nine of them treat surface water, however they did not indicate if these plants were designed for NOM removal.

These pilot studies and full-scale units have demonstrated, that nanofiltration membranes may achieve NOM removals greater than 90% (see Table 2.2). The possibility of replacing them by UF membranes which do not require pretreatment, have higher water

production rates and lower operating pressure and the concomitant reduction in operational costs seems very attractive. However, published results of pilot studies with 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. Recently, Osmonics has 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. The removal achieved by G-20 is slightly odd i.e., smaller than the looser membranes G-50 and G-80; moreover, operating pressure is reported for some membranes as a range and in others as an average value, however there are no independent confirmation tests reported in the literature.

Studies have shown that combinations of UF with coagulation pretreatment and/or PAC additions are capable of TOC removals up to 90% (Best et al., 2001a; 2001b; Manning et al., 2001; Zhang et al., 2001). However, such high removals are not always achieved and the additional treatment has additional costs plus additional waste material (i.e., sludge and saturated PAC). This thesis concentrates on UF without pretreatment.

In spite of the wide industrial acceptance of UF for more than two decades, existing synthetic membranes still have a number of shortcomings. One of the major obstacles that hinders more widespread application of UF and MF is decline of the flux with time. This phenomenon is commonly termed as membrane fouling (Song, 1998).

Table 2.2 NOM removal by NF membranes as cited in the literature

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)	TFC5 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)	Moustick 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)	Moustick 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
Taylor et al. (1987)	N50, Film Tec	Pilot	Groundwater, ACME Improvement District	93% DOC

Table 2.3 NOM removal by UF membranes as cited in the literature

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
Lainé et al. (1989)	XM100, Amicon Inc.	Lab	Lake Decatur (Ill.)	42% TOC
Lainé et al. (1989)	YM100, Amicon Inc.	Lab	Lake Decatur (Ill.)	43% TOC
Lainé et al. (1989)	PM30, Amicon Inc.	Lab	Lake Decatur (Ill.)	47% TOC
Lainé et al. (1989)	YM5, Amicon Inc.	Lab	Lake Decatur (Ill.)	41% TOC
Lainé et al. (1991)	Cellulosic Derivative	Pilot	Boise River (Idaho)	23% TOC
Lainé 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

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

The term fouling includes the totality of phenomena responsible for decrease of the permeate flux over a period of time and modify rejection, except those linked to membrane compaction and mechanical characteristics modification (Anselme and Jacobs, 1996). Membrane compaction is the phenomenon that results when a polymeric membrane is put under pressure, causing the polymers to be reorganized and the structure to be changed with a consequent reduction in porosity, increased membrane resistance and eventually flux reduction (Persson et al., 1995). As Cheryan (1986) declared, in its strictest sense the flux decline occurs when all operating parameters, including pressure, flow rate, temperature and feed concentration are kept constant. According to Madaeni (1999), in a constant pressure process membrane fouling results in a flux decline, while in a constant flow rate filtration, fouling causes an increase in pressure drop across the membrane. Membrane fouling is due to the deposition and/or accumulation of submicron particles on the membrane surface and/or crystallization and precipitation of smaller solutes on the surface and within the pores of the membrane itself (Cheryan, 1986). The materials that produce the reduction in permeate flux are collectively referred to as foulants. Fouling increases the complexity of membrane filtration operations since the system has to be halted frequently to restore the flux (Song, 1998). It may also affect the quality of the water that is produced from the membrane system (Tracey, 1996). Since fouling results in lower-than expected fluxes, this is usually considered in the design of the plant, increasing the surface area and consequently increasing the capital costs. In addition, operational costs are increased because of the reduction in product water flux

and/or the increased operational pressures necessary to maintain the flux. The cost of membrane cleaning to remove foulants includes not only the costs of the chemicals, but also: (a) the opportunity cost of not generating a product while the unit is being cleaned, (b) labour costs for personnel to clean the unit, (c) management time involved in trying to solve the system problems, (d) shortened membrane life, as the powerful cleansing agents may damage the membrane to some extent, resulting in increased frequency of membrane replacement (Tracey, 1996) and (e) the production of wastewater (Boerlage et al., 1998).

Though sometimes, both reversible and irreversible decreases in permeate flux decline are referred to as membrane fouling (Wiesner and Aptel, 1996), Zeman and Zydney (1996) made a distinction between membrane fouling and concentration polarization. Concentration polarization is a reversible boundary layer phenomenon arising from the bulk mass transfer limitation in the membrane that results in a localized increase of the solute concentration at the membrane surface that lowers the flux because of either an increased hydrodynamic resistance in the boundary layer or a higher local osmotic pressure decreasing the driving force (Cheryan, 1986). Therefore, adjusting the device design and operating conditions can control concentration polarization. Its effects can be reduced or even eliminated by decreasing the transmembrane pressure or lowering the feed concentration. Jönsson (1995) mentioned that increasing the shear rate at the membrane wall will increase the rate at which the retained solutes can be transferred from the membrane wall into the bulk of the fluid, increasing the flux. In contrast to concentration polarization, membrane fouling occurs because of specific physical or chemical attractive interactions between the various macrosolutes or particles and the membrane (Zeman and Zydney, 1996) and perhaps between adsorbed solute and other solutes in the feed stream (Cheryan, 1986). The process is very complex, because each component of the feed stream will react differently with the membrane, and the porosity, charge, and zeta potential are just some of the factors that will 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 influence on membrane fouling. The term irreversible with respect to fouling is relative. The changes in membrane properties caused by fouling can often be reversed by backflushing, by

application of very high cross-flow velocities, or by chemical cleaning. This procedure of flux recovery is performed in separate cleaning cycles. On the other hand, sometimes a loss in permeate flux that is truly irreversible is termed membrane poisoning. Membrane poisoning eventually requires replacement of the membrane (Wiesner and Aptel, 1996).

Membrane fouling can be attributed to phenomena occurring either within the membrane module or to phenomena occurring in and on the membrane. Tracey (1996) indicated that membrane fouling within the membranes modules is due to: particulates, colloids, biological activity, and chemical scaling. Loose NF and UF membranes, as opposed to RO and tight NF membranes, do not suffer from chemical scale formation since the inorganic salts pass through the membrane. Porter (1990) mentioned the use of prefilters or screens to remove large particles that block thin channels or accumulate in stagnant areas of the module, as a preventive measure that could be taken to avoid or reduce membrane fouling. This project, however, will focus on the fouling that occurs in and on the membrane.

2.4.1 Fouling mechanisms

As discussed, there are many potential foulants, since the feed characteristics can be very different and the mechanisms responsible for membrane fouling will vary accordingly. Thus, if the solute molecules are large enough to be retained by the membrane, they may be deposited at the surface of the membrane. On the other hand, low-molecular solutes, small enough to enter the membrane pores, may be deposited in the membrane matrix (Jönsson, 1995).

As if the diversity of mechanisms was not complicated enough, the terminology has changed over time and from one research group to another. In his study, Hermia (1966) 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 resistance; and standard blocking or direct adsorption (internal adsorption). In a filtration experiment, it is reasonable to expect a complex succession of these fouling mechanisms (Bowen et al., 1995). The first three fouling mechanisms may occur when the membrane retains the solute, whereas the last one can

appear when the solute molecules are smaller than the membrane pores (Jönsson et al., 1997). However, in order to analyze experimental data, the practice consists of assuming only one of the fouling mechanisms takes place, frequently standard blocking or cake filtration (Bowen et al., 1995).

Complete blocking occurs when each particle arriving to the membrane causes blocking of some pore or pores with no superposition of particles. Intermediate blocking takes place when each particle settles on a previously-arrived particle that already blocks some pores or directly blocks some membrane area. In contrast, during cake filtration, each particle locates on (or attaches to) other already arrived particles that already block some pores and there is no room for the newly arrived particle to directly obstruct some membrane area. When each particle arriving to the membrane is deposited into the internal pore walls, leading to a decrease in the pore volume, the mechanism is called standard blocking (Fig. 2.4).

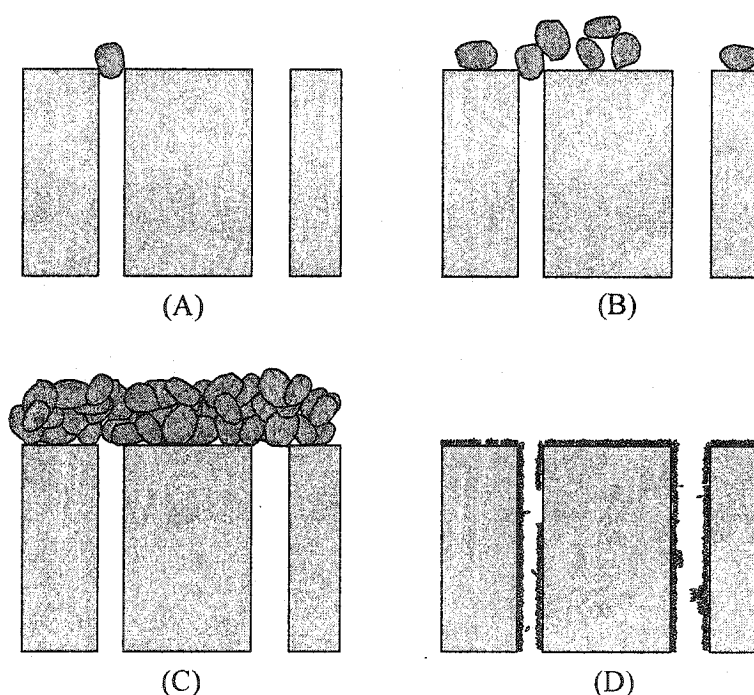


Fig. 2.4 Fouling mechanisms according to Bowen et al. (1995): (A) complete blocking, (B) intermediate blocking, (C) cake filtration, (D) standard blocking

Song (1998) described a typical flux-time curve of dead-end filtration as the flux continuously decreasing until it reaches a zero value. In contrast, in the case of cross-flow

UF and MF, the flux-time curve starts with a rapid initial drop from the flux of pure water filtration (I), followed by a long-term gradual flux decrease (II), and ends with a steady-state flux (III) (Fig. 2.5) (Song, 1998). He attributed the rapid initial drop from the flux of pure water filtration to the quick blocking of membrane pores. The pores are more likely to be blocked partially and the degree of pore blockage depends on the shape and the relative size of the particles and the pores. The blockage will generally be more complete when the particles and pores are similar in both shape and size. He mentioned that pore blocking is a quick process compared with cake formation since less than one layer of particles will be sufficient to achieve the maximum blocking (because the porous area is smaller than the whole membrane area). Song (1998) calculated that for suspensions of particle radius of 0.01, 0.1 and 1 μm , the time required for cake formation are about 4, 5, to 6 orders of magnitude longer, respectively, than those for pore blocking under the same operating conditions. For instance, for the 1 μm particles the pore blocking and cake formation were achieved at 10 min and 2.21×10^7 min, respectively, when the feed particle concentration was 10^{-4} (as volume fraction) and the initial permeate flux through the clean membranes was 10^{-4} m/s.

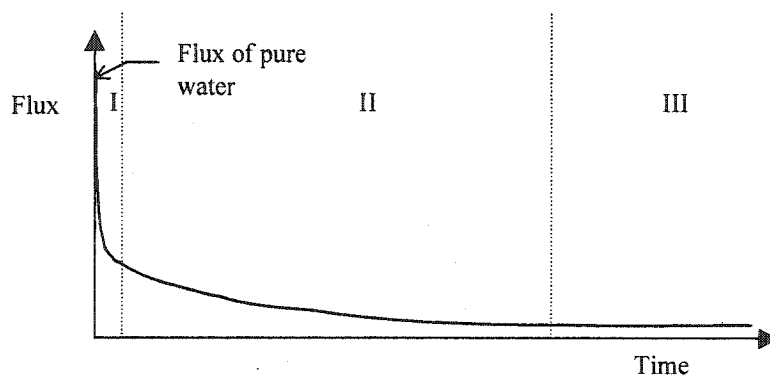


Fig. 2.5 A schematic presentation of the three stages in flux decline according to Song (1998)

The flux will reach a steady state when the cake layer has grown to the equilibrium thickness (Song, 1998). This equilibrium thickness of the cake layer increases with the applied pressure because to absorb a higher pressure a thicker cake layer is needed. Both organic and inorganic types of foulants follow the same kind of flux-reduction-with-time curve.

2.4.2 Inorganic fouling

According to Anselme and Jacobs (1996), UF processes (unlike NF and RO) do not generally allow sufficient dissolved salt retention, which can lead to mineral precipitation on the membrane due to concentrations higher than solubility products. However, one of the causes of fouling that has been identified is the precipitation of certain mineral salts. In water treatment, precipitation phenomena are especially due to calcium carbonate precipitation or to precipitation of dissolved metals such as iron and manganese due to oxidation and hydrolysis during the filtration process. Thus, one important way of controlling fouling is by adjusting the pH, which controls the solubility of the salts, decreasing the chance of deposition on the membrane and increasing the chance of permeating through the membrane (Cheryan, 1986).

Dissolved metal precipitation, which leads to the formation of an iron oxide and manganese cake on the membrane, is the phenomenon that has been identified most frequently in operating treatment plants (Anselme and Jacobs, 1996). 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 is reversible by backwashing, but due to an increase of the cake thickness an increase in longitudinal head loss of the module is generally observed, which can induce an increase in energy consumption for concentrate recycling (Anselme and Jacobs, 1996).

2.4.3 Organic fouling

The most frequently cited types of organic foulants of membranes are proteins and NOM. Among proteins, bovine serum albumin is one of the most studied proteins. Since proteins are rejected by the membrane, they tend to have high concentrations at the membrane surface (Cheryan, 1986). Strong influences of pH and ionic environment are expected since they affect protein charge, stability and tendency to aggregate (Fane and Fell, 1987). Since the chemistry of proteins is relatively simple, in drinking water treatment membranes, sometimes protein fouling models are used as a reference for other organic foulants, like NOM.

NOM has been implicated as a mayor foulant in drinking water treatment (Hong and Elimelech, 1997). As mentioned previously, NOM is a very complex solute with a broad spectrum of functional groups, sub-structures and molecular weight distribution that depends on its origin (Aoustin et al., 2001); therefore, NOM characteristics will change from site to site. The actual charge, configuration and chemical potential of the NOM in solution depend on the characteristics of the environment (Cho et al., 1999a, Hong and Elimelech, 1997). According to Braghetta et al. (1998) the polyelectrolyte solution theory of Ghosh and Schnitzer establishes two hypothetical extreme macromolecular configurations for NOM. The first is flexible linear macromolecules, which occur at very low ionic strength (salt content), and low humic substances concentration, at pH ranging between 6.5 to 9.5 (Aoustin et al., 2001), when intramolecular charges are high and repulsive. The second configuration is that of a rigid, compact and spherocolloidal structure, which occurs at high ionic strength, low pH, and high solution concentration, when intramolecular electrostatic repulsion decreases because the charge (functional) groups are neutralized (Ruohomäki et al., 1999). These two cases are the extreme points of the NOM molecular configuration and depending on the particular environmental conditions the molecular configurations will be in between these extremes.

According to Amy and Cho (1999), NOM characteristics that affect its interactions with membrane are: a) molecular weight distribution and shape (Cho et al. 2000b), b) hydrophobic (or hydrophilic) character and c) functional group content. The inorganic water quality, including pH, ionic strength (I), and calcium content may also affect NOM-membrane interactions. Amy and Cho (1999) found that though steric exclusion plays some role in NOM rejection, the role of electrostatic exclusion (repulsion) is more significant, when using UF membranes, together with aromaticity/hydrophobicity interactions (Cho et al., 1999a). On the other hand, Braghetta et al. (1998) ascribed the rejection of Suwannee River organic matter macromolecules by a nanofiltration membrane, to a combination of electrostatic charge repulsion and size exclusion effects.

One common practice is to use a XAD-8 resin to isolate hydrophobic and hydrophilic fractions of NOM to use as separate membrane feeds (Braghetta et al., 1998; Nilson and DiGiano, 1996; and Cho et al., 2000b). In her study, Braghetta et al. (1998) found that

unfractionated NOM produced a more substantial flux decline than either hydrophobic or hydrophilic fractions. They attributed this result to interactions between hydrophobic and hydrophilic materials that probably influence the foulant behaviour of the total NOM solution. Amy and Cho (1999) showed that the nature of the foulants was of a hydrophilic character, particularly polysaccharide-like material (bacterial cell fragments). In general, the more hydrophilic the NOM, the lower is its apparent molecular weight (Aoustin et al., 2001). This contradicts the interpretation made by Aoustin et al. (2001) who attributed irreversible pore adsorption and plugging to large hydrophobic UV-absorbing molecules (UV absorbance at 254 nm is a water quality parameter which can be used to characterize aromaticity of TOC in water) (Anselme and Jacobs, 1996). On the other hand, Cho et al. (2000a) concluded that the initial water composition is the factor that determines which NOM fraction will constitute the most important foulant in the adsorption layer.

Aoustin et al. (2001) and Anselme and Jacobs (1996) mentioned the mechanisms through which membrane fouling by NOM occurs: a) accumulation of solute and gradual irreversible changes to the polarized layer (such as cake formation), (b) surface adsorption or deposition of solutes, or c) adsorption or deposition of solutes in the bulk of the membrane (pores, backup structure). Cho et al. (2000b) mentioned pore mouth adsorption and subsequent narrowing of the pores as fouling mechanisms caused by small species (in comparison with pore size). When the solubility of the NOM is exceeded within the concentration polarization layer, the rejected NOM precipitates and may form a new phase on the membrane surface, increasing the hydraulic resistance across the membrane and limiting the permeate flux. This kind of fouling is generally reversible (Aoustin et al., 2001). Fouling due to adsorption depends mainly on the affinity that the NOM components have for the membrane's polymers, therefore, characteristics of both the NOM and the membrane play a role in this interaction, together with the operational conditions. The key NOM characteristics were discussed above, the key membrane characteristics include surface properties, chemistry (charge, hydrophobicity), and morphology (MWCO, pore distribution and geometry, roughness, etc.) (Aoustin et al., 2001; Amy and Cho, 1999). Thus, when the degree of chemical complexity of NOM is combined with the membrane characteristics, the filtration process becomes more and more difficult to understand and predict.

2.4.4 Fouling reduction

Cheryan (1986) explained that the most effective way to minimize fouling depends on the nature of the fouling process. Pretreating the feed is the most effective way to minimize fouling when it results from specific membrane-solute interactions. On the other hand, when no significant specific membrane-solute interactions are occurring, adjustment of the operating conditions (especially, cross-flow velocity, together with pressure, and temperature) should make fouling manageable. Increasing cross-flow velocity decreases the degree of polarization by increasing mass transfer and other back transport mechanisms (Fane and Fell, 1987). However, because the chemical nature of the membrane and the membrane-solute interactions are the factors that influence the nature and extent of membrane fouling, surface chemistry, solute-solute and solute-membrane interactions are the key parameters in the fouling phenomenon. Therefore, a potential way to reduce membrane fouling is the modification of the surface of the membrane.

2.5 Membrane surface modification

In order to have the proper surface characteristics, membrane chemistry can be modified to improve performance in targeted applications. According to Zeman and Zydney (1996), almost 50% of all MF/UF membranes marketed today are surface-modified. It is very difficult to differentiate between the preparation of a composite membrane, with methods like the ones described in Section 2.2.1 and membrane surface modification. In general authors use the terms without distinction, because there is no clear definition of these two terms. However, a somewhat clearer distinction could be defined as follows (Matsuura, 2002). A composite membrane is formed when there is no physical surface modification of the original membrane, but just the addition or attachment of a coat on top of the support membrane. A composite membrane cannot be formed in a single step procedure. In the case of the surface modification, the characteristics of the surface of the membrane are permanently altered and it is possible to manufacture a surface modified membrane using a single casting step.

Some practical examples of surface modification are described as follows. Brink et al. (1993) preadsorbed two water-soluble polymers, methylcellulose and poly(vinyl

methylether) to several UF polycarbonate and polysulfone membrane achieving a membrane fouling reduction. They attributed the polymers protection action to the fact that they occupy adsorption sites and they are hard to displace. In addition, the preadsorbed polymers partly seal off the pore entrance avoiding internal adsorption by steric repulsion.

Polysulfone UF membranes were modified by Nyström and Järvinen (1991) by UV irradiation in an aqueous solution alone or together with hydrophilicity increasing agents, i.e., dextrans. They found that it is the direct irradiation that induces the primary increase in hydrophilicity of the membrane, and not the transmission by small molecules or macromolecules in the irradiation bath. UV irradiation increased the water flux (PWP) up to 4 times compared with the unmodified membranes. This increase is due to the etching effect of oxygen (chain scissions) and the resulting enlargement of the pores during stirring conditions, however no loss in protein retention was observed. After one hour of filtration of a whey solution, flux reduction of the UV-irradiated membranes was very similar to that of the unmodified membranes.

Lindau and Jönsson (1999) studied the anti-fouling behaviour of two modified membranes. The first was a PVDF membrane modified by chemical binding (grafting) of a cellulosic polymer onto the surface of a pre-formed support PVDF membrane. The second was a polyamide membrane modified prior to casting by blending the polymer solution with a hydrophilic copolymer. The fouling of the modified PVDF membrane was more pronounced than the fouling of its unmodified counterpart. They ascribed this effect to the small size of the octanoic acid, used as the test solution, which is not retained by the membrane, but passes into the membrane pores where it is adsorbed; therefore, the modified surface layer cannot exert its effect of steric impediment. Only when the octanoic acid concentrations were decreased to below 60% of the saturation concentration, the modification was effective, since the flux reduction of the modified polyamide membrane was lower than that of unmodified membrane.

Combe et al. (1999) also came to unexpected results when they tried to reduce fouling by adsorption of soil humic acid (supplied by Aldrich) by modifying the surface of cellulose

acetate membranes, using different methods to increase the hydrophilicity. First, they used a 0.1 M NaOH solution with 1% MeOH for different contact times to break the ester link between cellulose and acetyl groups (hydrolysis). Another way they used to reduce hydrophobicity was by surface oxidation with 35% H₂O₂. After hydrolysis and oxidation, membranes were annealed using a water bath with temperatures in the range of 40 and 80°C. In a third approach, they modified the surface charge of the membranes by contacting them with a dilute solution of "Colloid 189" (vinyl acetate/acrylic acid copolymer). They determined the surface charge by measuring the streaming potential and calculating the zeta potential with the Helmholtz-Smoluchowski equation. In the case of the hydrolysis, the hydrophilicity was increased but the negative charge of the membrane was reduced canceling the beneficial effect of the hydrophilicity. However, with oxidation, both hydrophilicity and negative charge increased, and yet adsorption of humic acid was increased. They attempted to explain this behaviour by the role of calcium in adsorption, and the measurement and interpretation of charge by zeta potential. They achieved a decrease of adsorption of humic acid only in the case of pre-adsorption of the anionic polymer on the membrane surface.

Mok et al. (1994) studied the effect of surface modification of PES hollow-fiber membranes by grafting polyethylene glycol (PEG) polymer on the internal surface using gamma-ray irradiation. They were able to reduce the amount of protein adsorbed during the UF of porcine albumin solution. They used the difference in weight before and after the experiments to determine adsorption. The reduction was more significant when the solution was dilute, and when the pore size of the PES membranes was larger. They also observed a fouling (adsorption) reduction when increasing the feed flow velocity, but just in the case of the unmodified membranes. On the other hand, both the PWP and the solution separation were decreased by grafting. Apparently, the main cause of the PWP reduction is the gamma-irradiation.

Though Kasemura et al. (1993) modified the surface of an epoxy resin and not a membrane, this case is relevant to this project, as it will be seen later, because they used fluorine-containing methacrylic ester copolymers. Epoxy resins are very easily contaminated because they absorb organic materials, and they are affected by water

because of the hydroxyl group in their structure. The copolymers were composed of methyl methacrylate, glycidyl methacrylate and heptadecafluorodecyl acrylate. The results showed a clear enhancement of oil and water repellency. In addition, the amount of fluorine measured by X-ray photoelectron spectroscopy at different angles decreased with the sampling depth. Later, using the same principle, Uragami et al. (1999), modified the surface of poly[1-(trimethylsilyl)-1-propyne] membranes (PTMSP) using fluorine-containing additives. These additives were synthesized by graft-copolymerization of heptadecafluorodecyl acrylate and methyl methacrylate with oligo dimethylsiloxane. Different amounts of polymer additives were added to the casting solution containing 2 wt % PTMSP solution in toluene causing the membrane surface to become remarkably water-repellent. Both contact angle measurements and XPS, indicated that the polymer additives had migrated to the air-side membrane surface. They tested the pervaporation performance of these membranes with a 10 wt % aqueous solution of ethanol. There was no significant change of flux compared with the unmodified membranes, however the ethanol/water selectivity increased. As observed in these examples, sometimes the results from time-consuming membrane surface modification are unexpected, and in most of the cases there is a trade-off between permeability, selectivity, and fouling reduction.

2.5.1 Surface Modifying Macromolecules (SMMs)

Mahmud (1996) and Pham (1995) mentioned some of the disadvantages that the surface modifying techniques might encounter. Plasma techniques and surface fluorination cannot be easily controlled, and may cause irreversible surface damage. 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. As can be seen, many of the techniques used in surface modification are both complicated and require at least an additional step in the membrane preparation process (Suk et al., 2002a). An excellent option would be a technique with characteristics such as: 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. The technique used by Kasemura et al. (1993), possesses these characteristics.

Since the early 90s our research group have been involved in the manufacture and application of surface-active polymeric additives capable of modifying surfaces. Therefore, these polymers have been called “Surface Modifying Macromolecules” or SMMs. The theory behind the SMM preparation has been thoroughly discussed by Pham (1995), and Tang et al. (1996). The main feature of the SMMs is that they have a lower surface free energy than that of a base polymer; therefore, they have the ability to migrate preferentially toward a polymer-air interface (Fang, 1997). The SMM is blended with a membrane casting solution made of a solvent and the base polymer, and when the solution is cast into a membrane in the air, produces a surface-modified membrane using a single casting step. Figure 2.6 illustrates the migration of the lower surface free energy SMM molecules (i.e., the black circles) with time. The white circles represent the base polymer and solvent molecules.

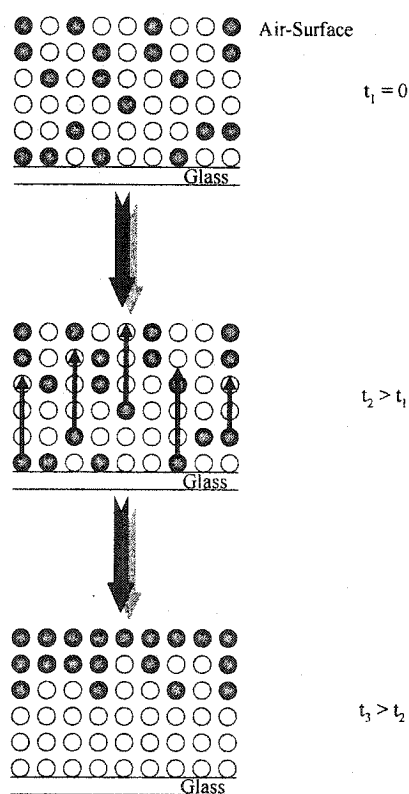


Fig. 2.6 Migration of SMM to the membrane surface (Fang, 1997)

According to Kasemura et al. (1993), the most effective surface-active additives have an amphiphatic structure with both polar and non-polar polymer blocks. ZonylTM

2.5), and the glass transition temperature. He also determined the solubility of the SMMs in PES.

Table 2.5 Bulk properties of SMMs used for PES membrane surface modification

SMM polymer	$M_n/10^4$ ^a	$M_w/10^4$ ^b	PD ^c	wt % F	Reference
MPB322HN	1.6 ($\pm$ 6%) ^d	2.7 ($\pm$ 10%)	1.6 ($\pm$ 5%)	13.6 ($\pm$ 10%)	Pham (1995)
MPB322HR	1.4 ($\pm$ 4%)	2.2 ($\pm$ 7%)	1.6 ($\pm$ 2%)	11.4 ($\pm$ 69%)	Pham (1995)
MPB212HN	1.1 ($\pm$ 6%)	1.6 ($\pm$ 11%)	1.5 ($\pm$ 6%)	19.8 ($\pm$ 27%)	Pham (1995)
MPB212HR	1.1 ($\pm$ 6%)	1.8 ($\pm$ 9%)	1.6 ($\pm$ 7%)	12.1 ($\pm$ 20%)	Pham (1995)
MPB322LN	1.5 ($\pm$ 11%)	2.5 ($\pm$ 15%)	1.6 ($\pm$ 4%)	5.8 ($\pm$ 61%)	Pham (1995)
MPB322LR	1.3 ($\pm$ 3%)	1.9 ($\pm$ 5%)	1.5 ($\pm$ 2%)	7.9 ($\pm$ 13%)	Pham (1995)
MPB212LN	0.9 ($\pm$ 5%)	1.3 ($\pm$ 9%)	1.4 ($\pm$ 5%)	17.1 ($\pm$ 6%)	Pham (1995)
MPB212LR	1.0 ($\pm$ 2%)	1.5 ($\pm$ 13%)	1.5 ($\pm$ 8%)	11.6 ($\pm$ 20%)	Pham (1995)
MDI-PPO-BAL	2.0 ($\pm$ 24%)	2.5 ($\pm$ 18%)	1.3 ($\pm$ 6%)	11.4	Ho (1997)
MDI-PPO-FSO1	1.3 ($\pm$ 4%)	1.8 ($\pm$ 3%)	1.4 ($\pm$ 1%)	21.0	Ho (1997)
MDI-PPO-FSO2	1.4 ($\pm$ 7%)	1.8 ($\pm$ 4%)	1.3 ($\pm$ 2%)	16.3	Ho (1997)
MDI-PPO-FSO3	1.5 ($\pm$ 8%)	1.9 ($\pm$ 5%)	1.3 ($\pm$ 4%)	14.2	Ho (1997)
MDI-PCL-BAL	2.3 ($\pm$ 1%)	2.9 ($\pm$ 3%)	1.3 ($\pm$ 2%)	8.6	Ho (1997)
MDI-PCL-FSO1	1.6 ($\pm$ 3%)	2.0 ($\pm$ 5%)	1.3 ($\pm$ 2%)	17.2	Ho (1997)
MDI-PCL-FSO2	1.6 ($\pm$ 4%)	2.1 ($\pm$ 5%)	1.3 ($\pm$ 2%)	16.7	Ho (1997)
MDI-PCL-FSO3	2.5 ($\pm$ 28%)	3.1 ($\pm$ 21%)	1.3 ($\pm$ 6%)	10.8	Ho (1997)
MDI-DEG322	1.2 ($\pm$ 8%)	1.4 ($\pm$ 7%)	1.2 ($\pm$ 8%)	22	Mandeep (2001)
MDI-DPS432	0.5 ($\pm$ 20%)	0.6 ($\pm$ 17%)	1.2 ($\pm$ 8%)	21.1	Mandeep (2001)
MDI-PPO322	2.0	2.5	1.3	13.4	Mandeep (2001)
DDI-DPS-BAL	0.7	0.8	1.1	17.2	Mandeep (2001)

^a M_n = number-average molecular weight,

^b M_w = weight-average molecular weight,

^c PD = polydispersity

^d Standard deviation

M_n is the total weight of all polymer molecules divided by the total number of polymer molecules in a sample. M_w is the weighted average of the molecular weight of all polymer molecules in a sample. PD is the ratio between M_w and M_n . The numbers in brackets in Table 2.5 represent the % of standard deviation of the different measurements. At the end, Pham (1995) concluded that the most reproducible formulation 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. Just two of the SMMs were partially miscible with 25% PES, MPB212HR and MPB322LR (Pham, 1995).

At the same time Tang et al. (1996) synthesized very similar SMMs using twelve different chemical formulations, in order to modify segmented polyurethanes, i.e., elastomers used in medical applications. They used 1,6-hexanedi-isocyanate (HDI) instead of MDI, and they employed polytetramethylene oxide (PTMO) in addition to PPO. Tang et al. (1996) used three different mole ratios: 2:1:2, 3:2:2 and 4:3:2. They simply named their SMMs with numbers from 1 to 12, and described them by the nature of the polyol, the stoichiometry and the fraction of BA-L employed, by the following nomenclature: PPO/PTMOijkX. Ho (1997) also prepared another set of eight SMMs in order to study the influence of SMM composition on its miscibility with PES. She used polycaprolactone diol (PCL) in addition to PPO, and she tried the three distillation fractions of the fluoro-alcohol FSO-100, together with the low fraction of BA-L. For all her synthesis she used the same stoichiometric ratio, 3:2:2. From calorimetric determinations, they concluded that base polymer-SMM mixtures retained the properties of the base polymer in the bulk (Pham, 1995; Ho, 1997). Ho (1997) named her SMMs: MDI-PPO or PCL-BAL or FSO, 1, 2 or 3 depending on the boiling fraction used in the synthesis (Table 2.5).

When Ho et al. (2000) and Minnery (2000) used several microscopy techniques to study the morphology of the PES-SMM membranes, they observed spherical microstructures constituted by aggregates of SMMs in the form of micelles. These microstructures were produced due to the relative immiscibility of the SMMs in PES, and their concentration at the surface was greater, corroborating the SMM migration.

Later, Mandeep (2001) tried to improve the miscibility of PES-SMM, synthesizing three new SMMs with PES-like characteristics, in an attempt to generate materials with a more uniform distribution of fluorine at the membrane surface. She used reagents with sulfone, aromatics and ether groups, similar to the PES structure. She employed: a) MDI and trimethyl- 1,6 diisocyanate (aromatic groups); b) diethylene glycol (DEG) (ether group) and dihydroxy diphenyl sulfone (DPS) (sulfone group) as polyols; and c) the low boiling fraction of Zonyl BA-L as fluoroalcohol (as previously demonstrated to increase the reproducibility). Mandeep (2001) named her SMMs: MDI-DEG322, MDI-DPS432 and THDI-DPS652. She employed 3:2:2, 4:3:2, and 6:5:2 stoichiometries, respectively. In

microscopy studies she observed two phases in the mixture PES/MDI-DPS432, while the presence of a dispersed phase was less evident with PES/MDI-DEG322. Mandeep (2001) synthesized an extra SMM that she used as a control MDI-PPO322. It is worth noting that the latter SMM is the same SMM as Ho's SMM MDI-PPO-BAL, and Pham's MBP322LR, and later is referred to as SMM41 (Fang, 1997; and Minnery, 2000). The solvent used in all SMMs synthesis was N,N-dimethylacetamide. The reproducibility of all these syntheses, as it was mentioned before, was evaluated measuring the main bulk properties of the polymers, and determining the % of standard deviation between SMMs prepared in different batches, as presented in Table 2.5. The shaded rows represent the same SMM41 polymer prepared by Pham (1995), Ho (1997), and Mandeep (2001). It is observed how the average bulk properties were different, and the percentage of standard deviation of Ho's SMM was higher than Pham's. Mandeep (2001) prepared just once her SMM41 and it was very similar to Ho's, although the wt % F is slightly higher.

When membrane films were cast adding SMM in the PES-based casting solution, a significantly increase in both the water advancing and the receding surface contact angles was observed compared to the unmodified surface (Table 2.6). Values of advancing contact angle for the PES/SMMs films are very high and approach those of Teflon i.e., 116° (Pham et al., 1999). However, their receding contact angles are not as close to that of Teflon (i.e., 92°) (Pham et al., 1999). The advancing and receding angles of these PES/SMMs films are very different indicating that the surface is heterogeneous (Ho et al. 2000). Thus, they concluded that the PES/SMM membrane has a more hydrophobic surface than the PES membrane (Pham, 1995; Ho, 1997; and Mandeep, 2001). At the end, all of them arrived to the same conclusion: "We have created membrane surfaces enriched with fluorine groups that resulted in more hydrophobic surfaces, confirming the selective migration of SMMs to the polymer surface".

Table 2.6 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 (1997)
PES+MDI-PPO-BAL	107.3 ± 1.8	58.2 ± 4.5	49.1 ± 4.8	Ho (1997)
PES+MDI-PPO-FSO1	102.9 ± 2.0	32.9 ± 5.3	70.0 ± 5.7	Ho (1997)
PES+MDI-PPO-FSO2	106.3 ± 2.3	24.2 ± 4.6	82.1 ± 5.1	Ho (1997)
PES+MDI-PPO-FSO3	97.5 ± 1.6	12.4 ± 3.3	85.1 ± 3.7	Ho (1997)
PES+MDI-PCL-BAL	113.2 ± 1.1	30.5 ± 3.8	82.7 ± 4.0	Ho (1997)
PES+MDI-PCL-FSO1	119.4 ± 0.8	17.5 ± 1.5	101.9 ± 1.6	Ho (1997)
PES+MDI-PCL-FSO2	112.2 ± 0.7	21.0 ± 1.2	91.2 ± 1.4	Ho (1997)
PES+MDI-PCL-FSO3	99.7 ± 2.8	29.0 ± 6.9	70.7 ± 7.4	Ho (1997)
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)

2.5.2 SMMs applications

Pham (1995) used the SMMs that were miscible with PES in a membrane casting solution (also containing PVP) to prepare membranes for pervaporation. He expected an enhancement in the performance of PES pervaporation membranes and believed his experiments confirmed that the surface modified membranes were selective towards chloroform. However, it was later found that ethanol, used in the drying of the membranes by solvent exchange, was mistaken for chloroform (Mahmud et al., 2001). Mahmud (1996) used SMM41 and SMM58 (Pham's MPB212HN) to develop pervaporation membranes for volatile organic chemical removal. Mahmud (1996) investigated the impact of PES/SMM membrane preparation parameters on the separation

of chloroform from aqueous solutions via pervaporation. These parameters included polyvinylpyrrolidone (PVP) addition levels, solution mixing period, solution age and membrane age. He could not conclude if an enhancement on the pervaporation performance was a result of the modifications. However, he was able to conclude that PES membranes are water selective in pervaporation separation of the chloroform/water mixture, as a significant depletion of chloroform was achieved (Mahmud et al., 2001). Fang (1997) also used SMM41 in the preparation of pervaporation membranes. He found that a longer evaporation period led to a higher separation and to a lower permeation rate for the chloroform/water mixture. Thus, he was able to conclude that, though the membranes prepared from polyethersulfone solutions containing SMM can be asymmetric, by varying the solvent evaporation period, membranes with different structures can be obtained. Minnery (2000) also used SMM41 to prepare pervaporation membranes for the separation of ethanol/water solutions. He concluded that his results did not reveal a significant difference in the pervaporation performance, in terms of flux and selectivity, of modified and unmodified PES membranes.

In her study of the membrane materials to be used in biomedical applications, Ho (1997) concluded that the SMMs were shown to migrate and concentrate at the surface in the form of spherical microdomains dispersed in the top 12 μm of the membranes. Presumably, because of donor variability and the presence of surface contaminants on the membrane, she was not able to draw any conclusion on the relative activation of platelets and leukocytes by PES hollow fibre membranes. However, she clearly observed a reduction in the adsorption of fibrinogen (one of the blood proteins, linked directly to platelet activities, activation of the intrinsic coagulation pathway and interaction with leukocytes) when using the surface modified PES hollow fibers. Mandeep (2001) found that her novel SMMs with PES-like structure performed poorer than Ho's SMM41, as the latter adsorbed the least amount of proteins. She found that the central segment backbone chemistry of her SMMs played an important factor on their compatibility with PES.

Hamza et al. (1997) reported that polyethersulfone UF membranes surface-modified with Pham's MPB212L SMM generally had lower pure water permeation rates than the unmodified counterparts, possibly due to their increased hydrophobicity. However, the

former membranes proved to be less susceptible to fouling by oil/water emulsions as observed from their higher product rates compared with the unmodified membranes. Later, Suk et al. (2002a) studied the kinetics of the migration of SMM41 to the surface, using the elemental analysis from the X-ray photoelectron spectroscopy. They observed that the complete migration of the SMM was accomplished in about 10 minutes of evaporation, under the particular experimental conditions of the study, however the trend presents an initial time lag of approximately 10 minutes. They observed as well that the contact angle increased with the evaporation time, and this increase was faster when the films were thinner.

2.6 Summary

NOM in surface waters is not only a precursor of toxic DBPs during drinking water treatment, but it is also a very important membrane-fouling agent (Yuan et al., 2002; Cho et al., 1999a; and Hong and Elimelech, 1997). The drop in productivity associated with fouling has hindered a more widespread use of membranes, not only in water treatment but also in other industrial applications (Song, 1998).

PES is one of the most widely used polymers in the manufacturing of UF membranes due to its ease of generation, regulation and control of small pores (Anselme and Jacobs, 1996) and compatibility with other polymers, together with its high mechanical, thermal, and chemical stability (Hamza et al., 1997) and low cost. However, PES membranes are easily fouled (Zeman and Zydney, 1996).

Fouling by NOM depends on the interaction between NOM and the membrane. Therefore, characteristics of both the NOM and the membrane play an important role in this interaction, together with the operational conditions. The key NOM characteristics include its molecular weight distribution, shape, hydrophobic (or hydrophilic) character, and functional group content. At the same time, water quality (pH, ionic strength and calcium content) may also affect the NOM-membrane interaction. On the side of the membrane characteristics, it is important to mention, surface properties, chemistry (charge, hydrophobicity), and morphology (MWCO, pore distribution and geometry, roughness, etc.). Given the complexity of NOM-membrane interactions, it is very hard to

make any predictions. This thesis focused on the study of the impact that the membrane preparation variables, including the addition of SMM to the PES casting solution, had on the final characteristics of the membranes, and in turn in the performance of the UF of a natural water.

CHAPTER 3

MATERIALS AND METHODS

The research in this dissertation was divided into three different stages: The first one concentrated on the apparatus selection and establishment of the membrane test protocol. The second stage was an evaluation of the impact of using three different SMMs, while varying some preparation variables, on membrane performance. And in the third stage, the most promising SMM from the second stage was used in a more detailed study of the effect of several parameters on membrane performance. Figure 3.1 shows a flow diagram of the general methodology followed in this thesis.

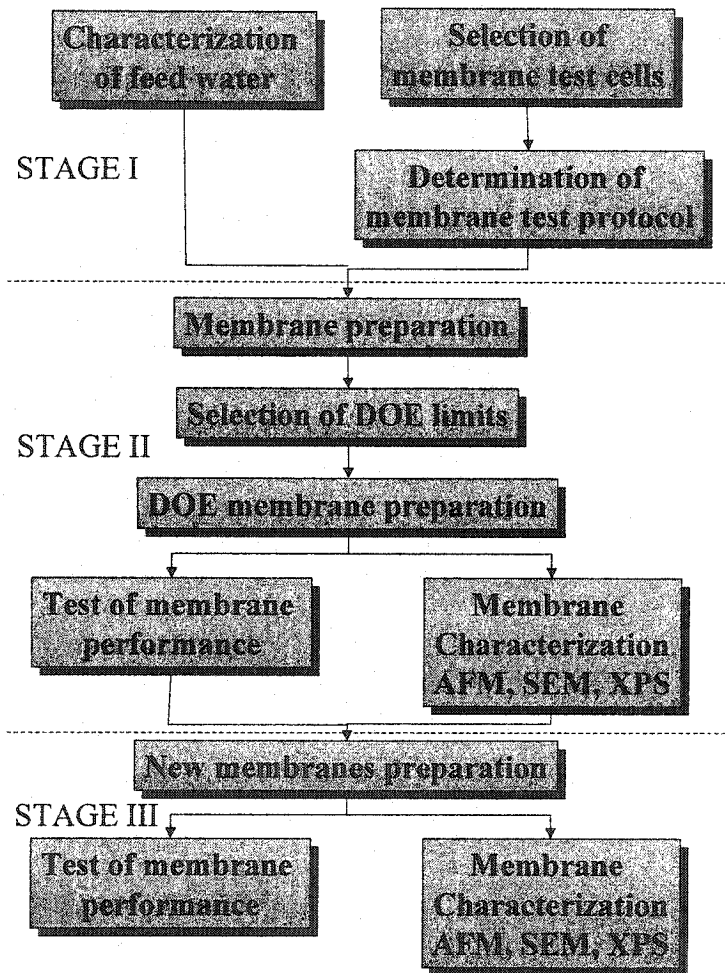


Fig. 3.1 Methodology overview. (DOE = Design of Experiments)

This chapter describes the chemicals employed during this research, and the techniques used in a) feed water characterization; b) selection of the apparatus; c) membrane test protocol; d) membrane preparation and modification; and e) membrane characterization.

3.1 Chemicals

Unless otherwise stated, the chemicals used in this project were of analytical grade without any further modification. The base polymer used in the membrane preparation was polyethersulfone (PES, 4100P) supplied by ICI Advanced Materials (Billingham, Cleveland, England). Polyvinylpyrrolidone (PVP) powder with an average molecular weight of 10,000 Daltons was supplied by Aldrich Chemical Company, Inc., (Milwaukee, WI) as well as the N-methyl pyrrolidone (NMP) used as a solvent. Two of the surface modifying macromolecules (SMMs) (DPS and DEG) were synthesized by Mandeep (2001). The third SMM used (SMM41) was synthesized by Ho (1997) and by the author. It is worth noting that SMM41 was synthesized for the first time by Pham (1995), and has been used in several other studies (Mahmud, 1996; Minnery, 2001; Fang, 1997). The probe solutes for the solute transport method were either polyethylene glycol (PEG) (Sigma Chemical, St. Louis, MO), or polyethylene oxide (PEO) (Aldrich Chemical, Milwaukee, WI). The molecular weight of the different PEG fractions used ranged from 300 to 35,000 Daltons, while for PEO it was 100 or 200 kDaltons. Ethyl alcohol 99% (BDH Inc., Toronto, ON) was used to dry membranes.

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 (BDH Inc., Toronto, ON) was used as a reagent during the organic carbon oxidation in the presence of ultraviolet light, and orthophosphoric acid (BDH Inc., Toronto, ON) was used to acidify the samples, in order to convert carbonates to CO₂.

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 Stage I: Apparatus selection and determination of the membrane test protocol

The goal of the 1st stage of this study was to find a testing procedure that is short in duration, uses a minimum amount of test solution, only requires a small membrane coupon, and is representative of the large-scale process. First, it was necessary to evaluate and compare the performance of different apparatus, and then to examine the test protocol most suitable to achieve the above objective. In the development of new membranes, it is easier to produce defect-free small membrane coupons rather than large ones, so the smaller cells are more attractive from this point of view. Also a six-cells in series set-up allows for the evaluation of six membrane coupons simultaneously. On the other hand, given the variability in the performance of coupons taken from the same membrane sheet, the larger cells may give a better indication of the average performance of a given membrane sheet. In this study, it was of particular interest to determine if all the cells perform similarly to the cell currently recommended by the USEPA so that they could be reliably used for testing newly prepared membranes.

Prior to the determination of the membrane test protocol, the feed water was characterized.

3.2.1.1 Characterization of feed water

As mentioned in the previous chapter, in order to evaluate the performance of the membranes, it was necessary to determine some of the characteristics of the test solution. In this case the test solution was the highly coloured (rich in natural organic matter, NOM) Ottawa River water (ORW), which is the source for the city of Ottawa, Canada. This water was collected at the intake of the Britannia Water Treatment Plant on June 6, 2000. The water was prefiltered through an extra fine pore filter cartridge (sediment) (from the local hardware store) and stored in a freezer room at 0°C to eliminate the potential for further biological degradation. Prior to the use of the water, it was moved to a cold room at 4°C, to have it in liquid form and one day before the test it was allowed to reach room temperature. The characteristics of the surface water were measured before

and after freezing. These characteristics were statistically the same. This is not surprising, since the water was frozen for very short time.

As discussed in Appendix A, a second NOM laden water was also considered during a preliminary screening. It performed fairly similarly to CORW, and as a matter of convenience ORW was selected for the remaining evaluations.

The general chemical and physical characteristics of this water were measured as follows. TOC concentration was measured using the Dohrman Total Carbon Analyzer (Model DC-180, Santa Clara, CA) with the persulfate-ultraviolet oxidation method and infrared spectrometry as described in the standard method 5310 C, (Standard Methods, 1995). 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, ultra pure water was used as a blank. UV absorbance was used as TOC surrogate since they are linearly related (see Appendix N). 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 nephelometer DRT 100B by HF Scientific, Inc (Method 2130 B, Standard Methods, 1995). Alkalinity was determined by titration with H₂SO₄ (Method 2320 B, Standard Methods, 1995). To calculate hardness, titrations with EDTA were performed (Method 2340 C, Standard Methods, 1995).

Schäfer (2001) described different techniques used in the determination of the molecular distribution of NOM, including gel permeation chromatography (GPC), UF, ultracentrifugation, dynamic light scattering, among others. In this study, the apparent molecular weight distribution (AMWD) of the organic matter within the 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 (by Millipore, Bedford, MA) with four different nominal molecular weight cut-offs (MWCO): 5,000, 10,000, 30,000 and 300,000 Daltons. According to the manufacturer, these membranes have a nonionic character, they are hydrophilic and exhibit a rejection efficiency of >98% for specific compounds above the nominal MWCO. Clark and Jucker (1993) found that

these membranes were relatively unaffected by change in solution pH and ionic strength. Mulder (1991) explained that another way to operate the UF cells, which allows a better fractionation is diafiltration. Diafiltration consists on diluting the retentate with solvent (water) causing the low molecular weight solutes to be washed out. However, this type of operation is continuous and the equipment available did not allow the use of the stirred UF cell in this mode. The batch UF fractionation technique is detailed by different authors: Nilson and DiGiano, 1996; Chadik et al., 1991; Collins et al., 1986; Amy et al., 1987; Cai, 1999; Logan and Jiang, 1990; and Braghetta et al., 1997. This technique proved to give very similar results to those obtained in previous studies for the fractionation of the Ottawa River water (Jacangelo et al., 1994).

The AMWD apparatus consisted of the UF cell, a stirring table and a nitrogen pressure source. Membranes were preconditioned by the following steps suggested by the manufacturer. First, the membranes were rinsed by floating skin-side down in a beaker with Milli-Q water for 90 min changing the water twice. Second, the membranes were soaked in a 5-wt % NaCl solution for 30 min, followed by another 30 min soaking in Milli-Q water. Third, the rinsed membranes were stored in 10% by volume ethanol/water solution and they were kept refrigerated (Aiken, 1984). Fourth, prior to use the membranes were rinsed several times by filtering Milli-Q water through them (three to eight reservoir volumes). Six 50-mL sample aliquots were processed for each molecular weight. The samples were at room temperature and were not buffered, other than by the natural alkalinity of the water sample (Amy et al., 1987). The pressure ranged from 69 to 414 kPa (10 to 60 psig), depending on the flow rate recommended by the manufacturer for each membrane. For the 300,000 Daltons membrane the applied pressure was 69 kPa (10 psig); 241 kPa (35 psig) for the 30,000-Dalton membranes; 345 kPa (50 psig) for the 10,000-Dalton membrane, and 414 kPa (60 psig) for the 5,000-Dalton membrane. The first 3 mL of filtrate were wasted. When 70% of the volume was filtered, filtrates and retentates were collected and combined in pairs filtrate with filtrate, and retentate with retentate, to have 3 different samples per molecular weight. Next, they were analyzed for TOC. As Nilson and DiGiano (1996) indicated, the TOC concentration of a particular molecular weight fraction was calculated by subtracting the TOC concentration of the

filtrate from one membrane from the TOC concentration of the filtration from the membrane of the next larger nominal MWCO.

For some experiments the river water was pre-concentrated on-site up to 5 times using a portable Reverse Osmosis System by RealSoft (Norcross, GA). This system included a prefilter and a FT30 composite membrane (Filmtec Membranes, Midland, MI). The concentrated Ottawa River water, which will be referred to as CORW, was used to accelerate the fouling process. Reagent-grade water was used as a blank in all pure water permeation rate (PWP) determinations.

3.2.1.2 Apparatus tested

Five different test cells were evaluated, including dead-end and cross-flow cells. The membrane test cells used are illustrated in Fig. 3.2, i.e., reverse osmosis cells RO (Fig. 3.2a), ultrafiltration cells UF (Fig. 3.2b), a batch cell (Fig. 3.2c), a stirred UF cell (model 8050, Amicon®), and a commercial cross-flow cell (SEPA® CF Membrane cell by Osmonics®, Minnetonka, MN). The RO, UF, and batch cells (Fig. 3.3) were manufactured at the Dept. of Civil Engineering machine shop using 316 stainless steel, based on designs described in the literature (Sourirajan and Matsuura, 1985). The Amicon UF stirred cell (Fig 3.2d) and the Osmonics CF (Fig. 3.2e) are both commercial cells. The former cell is made of polysulfone, and the body of the latter is made of polypropylene.

The RO, UF and CF cells operate in a cross-flow type of geometry, while the batch cell and the stirred UF cell operate in dead-end mode. The results of the performance of the dead-end “batch” cell shown in Figures 3.2 and 3.3 are presented in Appendix C.

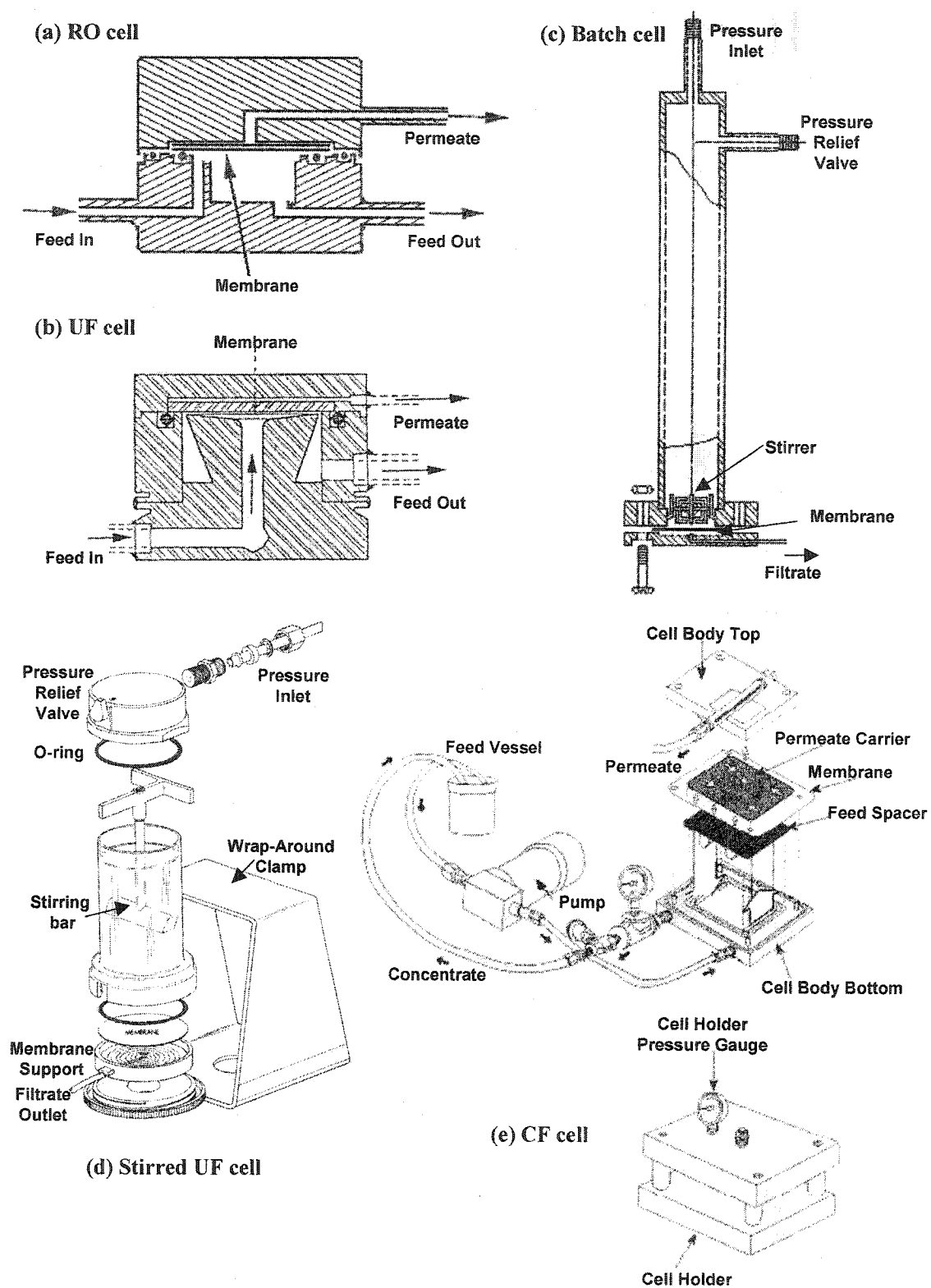
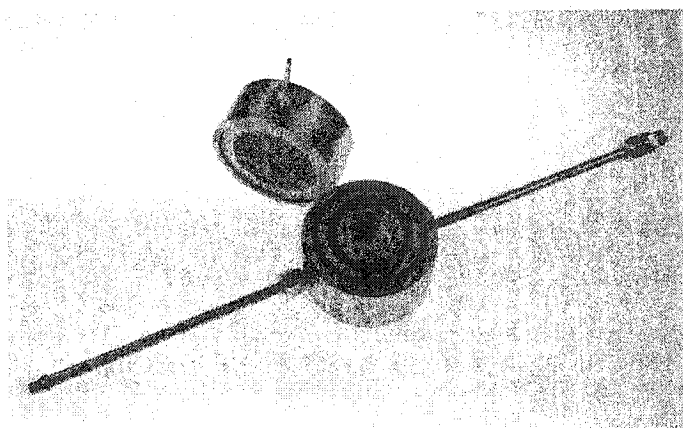
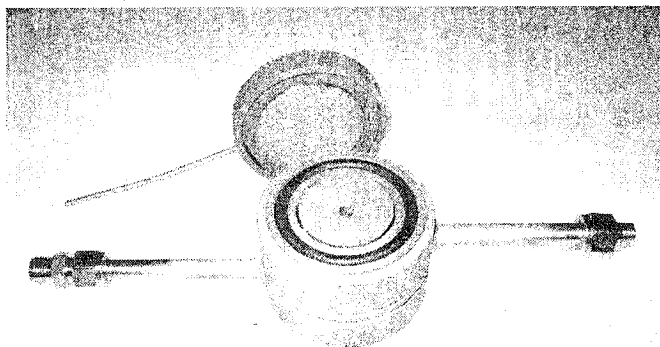


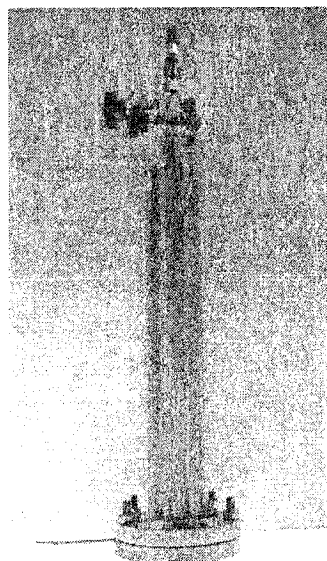
Fig. 3.2 Test cells



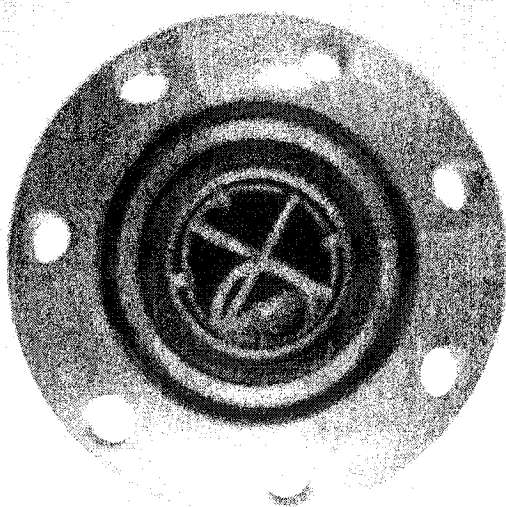
RO cell



UF cell



Batch cell

**Fig. 3.3 Photos of the non-commercial test cells**

Cross-flow cells

The UF cells have a relatively high cross sectional area for fluid flow at the entrance and the exit, thus the pressure drop across the cell is less than 7 kPa (1 psig) per cell. The UF cell also has a thinner channel flow design above the membrane surface, which allows a relatively high fluid velocity parallel to the membrane surface (Fig. 3.2b). The volume in this channel and the inlet and outlet openings are approximately the same. Sourirajan and Matsuura (1985) claimed that these two changes in the design from that of the RO cell (Fig. 3.2a), allow the UF cell to handle viscous fluids and simulate the flow conditions in larger size devices. The CF cell was especially chosen because it is currently recommended by USEPA for evaluating membrane performance for water treatment (DiGiano et al., 2000), and is also recommended by Osmonics® to simulate the flow dynamics of larger commercially available membrane elements such as Osmonics® spiral-wound membrane elements. These cells were operated within a recirculation system consisting of a feed reservoir, a high pressure pump, a pressure regulator, the membrane test cell(s) and the recycling lines that return both the permeate and concentrate streams back to the reservoir to maintain the feed concentration constant. In average, the feed concentration from the beginning to the end of the experiment changed less than 5%. This system allowed the operation of up to six RO and UF cells connected in series. The system is described in more detailed in the next section.

Dead-end cells

The batch cell and the UF stirred cell were operated in a batch dead-end filtration mode with a pressure of 345 kPa (50 psig) derived from a gas cylinder (Fig 3.4). The set-up was similar to the one used in the AMWD determination. The volume of the filtrate was continuously monitored using a balance and a stopwatch.

The membrane coupons necessary for the CF cell were 168 cm² in area, while those for the other cells were less than 20 cm² in area.

The results of the comparison test using the RO, UF, CF and UF stirred cells are presented in Chapter 4, while those for the batch dead-end filtration are presented in Appendix C.

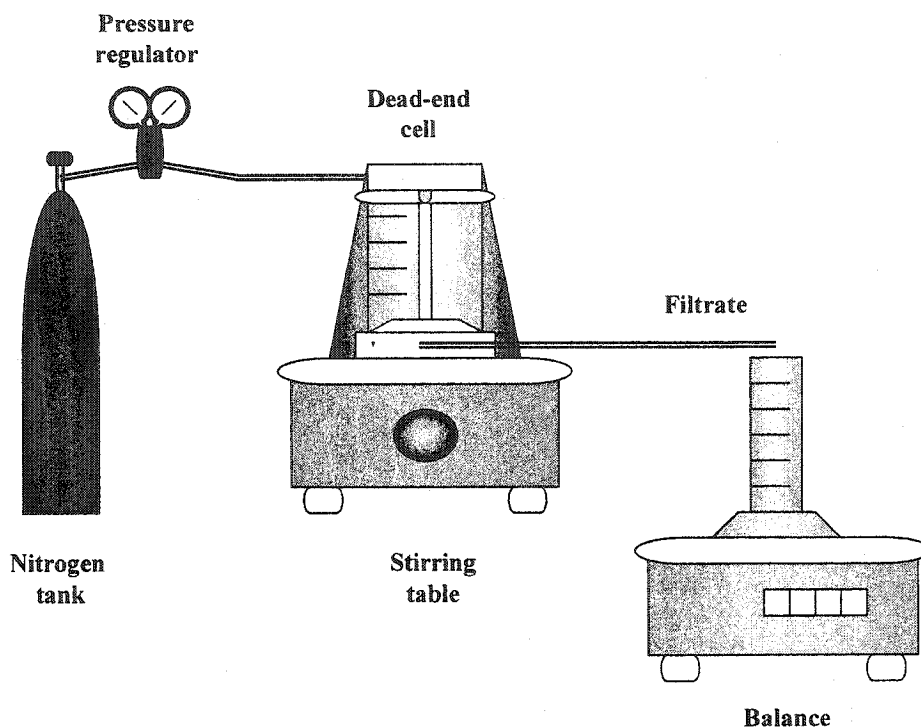


Fig. 3.4 Dead-end system

3.2.1.3 Continuous-flow experimental set-up

The experimental set-up (Fig. 3.5) used for the cross-flow cells employed a 10-L low-density polyethylene carboy (Nalgene) working as water reservoir that feeds a diaphragm Hydracell pump (Model M-03, Wanner Engineering, Inc., Minneapolis, MN). A bypass line was installed to help control the flow delivered by the pump. The flow of the feed stream was measured by a flowmeter (P-32025-20 rotameter, Gilmont Instruments, Barrington, IL), and the inlet pressure was measured by a pressure gauge (MG-68027-06, Cole-Parmer, Vernon Hills, IL). Next, either six UF cells or six RO cells were connected in series or the CF cell alone, and then, the outlet pressure was determined by a second pressure gauge. The backpressure valve was used to set the operating pressure at 345 kPa (50 psig). The concentrate stream passed through a concentric tube heat exchanger where

a 13 L heated/refrigerated circulator unit (Model 1150A, VWR, West Chester, PA) helped to cool the concentrate down to room temperature prior to recirculation to the feed reservoir. The temperature of the cooling water in the refrigeration unit was adjusted to maintain it between 10 and 15°C, depending on the season and the time of the day. To avoid drastic changes in temperature due to the sunlight, Styrofoam insulation covers were installed in the windows of the room. It was essential to have temperature control since the high-pressure pump caused a significant increase in the water temperature. The permeate stream was also continuously recycled to the feed reservoir, except when samples were collected for TOC analysis (sample size is 5 mL). After the permeate flux was measured by weighing, it was returned to the feed tank. At the beginning of the runs the permeate flux was measured every 10 or 15 minutes, then every 30 minutes, and as time went on, measurements were taken less frequently. All tubing was clear PVC (Nalgene); valves, and flowmeter were made of stainless steel 316.

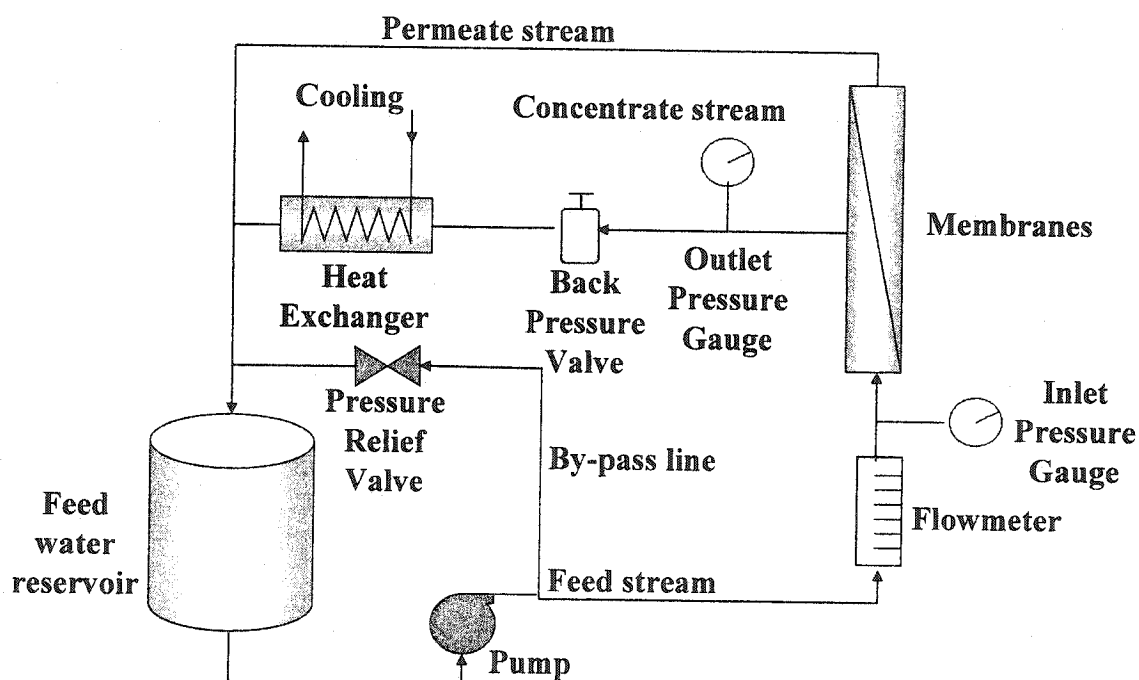


Fig. 3.5 Experimental set-up used in the test of continuous flow cells

3.2.1.4 Membranes tested and MWCO determination

The membrane used in the first stage of the work was a PES UF membrane, HO51, donated by Osmonics (Minnetonka, MN). This membrane was chosen because it has similar characteristics to the membranes prepared and evaluated in the second and third phases of this work. The MWCO of this membrane was determined in triplicate using the solute transport technique detailed by Singh et al. (1998), which used the UF recirculation system described above. First, the membrane coupons were compacted for 4 h at 482 kPa (70 psig). Then the PWP was monitored for 18 h. PEG molecules with molecular weights 300, 1,500, 4,000, 6,000, 8,000, 10,000, 12,000 and 14,000 Daltons were used to prepare eight different solutions, all of them with a concentration of 100 ppm. Each solution, starting from the lower molecular weight, was circulated through the systems at a flow rate of 0.9 Lpm for 1 h. Feed and permeate samples were then collected and analyzed for TOC using a Total Carbon Analyzer (Model DC-190, Dohrman, Santa Clara, CA) with the combustion-infrared method as described in the standard method 5310 B, (Standard Methods, 1995). The system was flushed with distilled water, and then, using Milli-Q water, the PWP was monitored for another hour between the uses of each PEG solution. At the end, the PWP was measured to corroborate that it had remained constant throughout the whole process of MWCO determination.

3.2.1.5 Testing protocol

The precompaction protocol used in this stage prior to each run, in the case of the dead-end cells (laboratory made batch cell and stirred UF cell) consisted of filtering at 482 kPa gauge (70 psig) a volume of Milli-Q water equivalent to three or four cell volumes prior to determining the PWP. For the PWP measurements the transmembrane pressure was set to 345 kPa gauge (50 psig) and the duration depended on the volume of the cell, in the case of the Amicon UF cell the volume is 50 mL, while the volume of the batch cell is 380 mL. Afterwards, the permeation rate (PR) of the ORW or CORW was measured, in this case only 80% of the cell volume was filtered.

Similarly, for the continuous-flow cells, the precompaction protocol consisted of installing the membrane coupons in the test cells and filtering Milli-Q through each new coupon at 482 kPa gauge (70 psig) for 50 h. Then the PWP was determined repeatedly

during a period of 28 h while operating at 345 kPa gauge (50 psig). After this step, the PR of the ORW or CORW was measured for membranes in the RO, UF, and CF cells at a feed flow rate of 0.9 Lpm and an operating pressure of 345 kPa gauge (50 psig) during 6 days of continuous operation. This feed flow rate was selected to have a laminar flow inside of the cells, and it allowed the operation of six cells in series with a pressure drop of less than 14 kPa gauge (2 psig) from the first to the last cell. The duration of the run was established after some testing, the objective being to reach a steady state in terms of permeate flux. The pressures used were chosen in the UF-operating range, not too high to reduce costs, and not too low so as to insure reasonable permeate flux.

At the end of every experiment, the actual permeation area was checked, using a Manostat caliper by IQ Instruments (Switzerland). Permeation rate was measured by weighing the permeate sample collected during a predetermined period. The NOM concentration was assessed by the measurement of dissolved organic carbon (DOC) using the Model DC-180 Dohrman Total Carbon Analyzer (Santa Clara, CA), with the persulfate-ultraviolet wet oxidation method and an infrared detector.

3.2.2 Stage II: Evaluation of the impact of membrane preparation variables on the membrane performance

In this stage the impact of several membrane preparation variables were evaluated using statistical analysis. The membrane testing experimental set up used in this stage was described in section 3.2.1.3.

3.2.2.1 SMM synthesis

Three different SMMs were used in the preparation of new membranes to evaluate the effect of the chemistry of each one. The SMMs used in this study were synthesized using the methodology developed by Pham (1995). It basically consisted of a two-step process. First, the diisocyanate was allowed to react with a polyol in N,N-dimethylacetamide (DMAC) solvent to form a urethane prepolymer solution. The reaction was terminated through the addition of the low molecular weight fraction of an oligomeric fluoro-alcohol, resulting in a solution of surface modifying macromolecules that had to be precipitated. The low molecular weight fraction of the oligomeric fluoro-alcohol (BAL)

was obtained by the distillation at 2.5 kPa (0.025 mm Hg) of the commercial polyfluoroalcohol (DuPont Chemicals), which yielded three different fractions. Basically, the difference among the three SMMs used was the polyol employed in the first stage of the SMM synthesis and the molar ratio of the reagents. The procedure was described by Mandeep (2001). The three SMMs were evaluated to see if they resulted in improved miscibility with PES and improved membrane performance. 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 at 25°C and lasted 24 h. Table 3.1 shows the reagents employed in the synthesis of the SMMs used in this study. Table 3.2 indicates the SMM nomenclature, together with the reagent stoichiometry used in their synthesis.

Table 3.1 Materials for SMM synthesis (Ho, 1997; Mandeep, 2001)

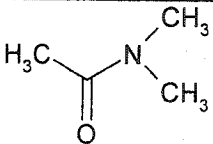
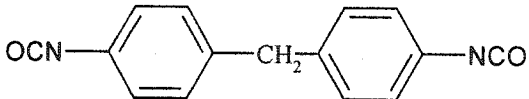
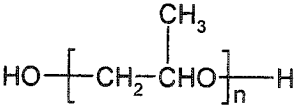
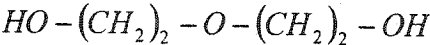
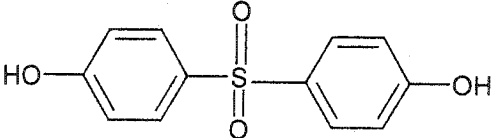
Reagent	Chemical structure	Molecular Weight	Acronym
Solvent: N,N-Dimethylacetamide		87	DMAC
Diisocyanate: Methylene bis-p-phenyl diisocyanate		250	MDI
Polyol: Polypropylene diol		425	PPO
Diethylene glycol		106	DEG
Dihydroxy diphenyl sulfone		250	DPS
Oligomeric fluoroalcohol: BAL low boiling fraction	$F(CF_2)_nCH_2CH_2OH$	~ 443	BAL

Table 3.2 SMM Nomenclature and stoichiometry

SMM	Reagents	Stoichiometry
DEG	MDI-DEG-BAL	3:2:2
DPS	MDI-DPS-BAL	4:3:2
SMM41	MDI-PPO-BAL	3:2:2

To verify the preparation of the SMMs after the synthesis, the polymer molecular weight was determined using GPC. Polystyrene polymer standards with narrow molecular weight distributions were used in the GPC calibration (Ho, 1997). Another important characteristic of the SMMs in this study was the fluorine content. The fluorine content of all the samples were analyzed by Galbraith Laboratories, Inc. (Knoxville, TN), an external laboratory.

The SMMs used in the various parts of this thesis originated from a few different batches. Appendix L shows that although there were differences in the % F of the SMM from various batches, the performance of the membranes containing these SMMs was essentially the same.

3.2.2.2 Membrane preparation

All membranes were prepared using the phase inversion technique as described by Matsuura (1994). Casting solutions were prepared using different amounts of the following components: PES, used as the base polymer; PVP, used as a pore former; SMM, and NMP, used as a solvent. NMP was used as opposed to the DMAC employed in the SMM preparation because NMP is less toxic. PES and the SMMs were stored in a dessicator under vacuum. All the components were weighed and the SMM was the first powder added to the NMP in a 150 mL glass bottle with narrow mouth and Teflon lined caps. After the SMM was dissolved, PES and PVP were added, and next, the bottle was capped, and sealed with Teflon tape and electric tape. Low-concentration (low-viscosity) solutions were mixed using a mixer that consisted of two parallel spinning rollers and the bottles were placed on top of the spinning roller. The bottles were spun for several hours, usually overnight. Very viscous solutions were mixed in an environmental incubator

orbital shaker (model G24, New Brunswick Scientific Co., Inc., Edison, NJ) operating at 50°C. Usually 24 to 48 h were required for complete dissolution.

After the solutions were homogeneous, they were 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 at pressures ranging from 69 to 276 kPa gauge (10 to 40 psig) (depending on the viscosity of the solution). After filtering, the filtrate was placed 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 the membrane was cast with a metal rod with side runners to get a thickness of 250 μm (10 mils). The size of the casting area is 28 cm by 22 cm. Second, the glass plate was placed inside a 95°C oven for the evaporation period. Third, the glass plate was immersed into ice-water at 4°C for at least 1 h. This step is called gelation and leads to the hardening of the membrane. The hardened membranes eventually peeled-off by themselves from the glass plate and after the gelation period they were cut into 65 mm diameter coupons and were stored at 5°C in Milli-Q water until they were used.

After the preparation of each type of new membrane, to permit membrane characterization, some sheets were dried by the following procedure. First, the membranes were sequentially submerged 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.

3.2.2.3 Selection of the factorial design limits

A factorial experimental design was conducted to evaluate the impact of preparation variables on the membrane performance. First, it was necessary to find the limits of the factorial design for the variables studied: the composition of the casting solution, and the solvent evaporation time. In the first attempt to establish the conditions for the factorial

design, two different membranes were prepared with the following compositions: 15 wt % PES, 5 wt % PVP with 1 min evaporation time and 10 wt % PES, 3 wt % PVP with 3 min evaporation time. The membrane testing protocol was the same as that used for the HO51 membranes. The performance of these membranes was evaluated, together with the time necessary for the test. Almost 93 h of PWP measurement (at 345 kPa gauge (50 psig)) were necessary to obtain a stable flux, after 50 h of precompaction at 482 kPa gauge (70 psig). Later, it was necessary to determine the maximum concentration of PES in the casting solution that could be mixed with 1.5 wt % of DPS, since DPS was the only SMM (of the three SMMs used) that produced turbid solutions when it was mixed with high PES concentrations. It was found that 18 wt % was the maximum PES concentration that yielded a clear solution. SMMs DEG and specially DPS, using a long evaporation time created sheets of membrane filled with holes, resembling Swiss cheese. Therefore, it was necessary to establish a maximum evaporation time. Several trials were made increasing progressively evaporation time and it was determined that 3 min was the longest time that could be used in order to produce an acceptable sheet of membrane. However, based on the results of the kinetic study presented by Suk et al. (2002a), a solvent evaporation of 3 min limits the SMM migration to the membrane surface.

To isolate the effect of the SMM, a second preliminary set of membranes was prepared without using the pore former PVP. Five replicates were performed of a membrane prepared with 18 wt % PES, and 3 min evaporation time (without PVP or SMM). In this case the precompaction was performed at higher pressure (655 kPa gauge (95 psig)) for 50 h to reduce the time necessary to achieve a stable flow when measuring the PWP. Once steady flow was reached, the PWP was monitored for 24 h. Steady flux was reached when there was less than 1% variation between readings taken 1.5 h apart. The MWCO and flux reduction with CORW (and Milli-Q water) were determined following the same procedure as in Stage I. Then the same procedure was repeated with another set of membranes with 15 wt % PES and 3 min evaporation time (without PVP or SMM). The time to reach the steady flow was also monitored. Results of these preliminary tests are presented in Appendix D.

With all this information the conditions for the factorial design were established. The maximum PES concentration was 18 wt %, and the minimum 12 wt %. The levels of evaporation time were: 0 and 3 min. A central point with 15 wt % PES and 1.5 min solvent evaporation time was also included. Three surface modifying macromolecule options were used: DEG, DPS, SMM41 and no SMM. Therefore, twelve different casting solutions were prepared in total. The concentration of SMM in the polymer solution was kept constant for all membranes at 1.5 wt %, and the remaining percentage was the solvent, NMP. Since there were two levels for the PES concentration, as well as for the evaporation time (in addition to the central points), in the case of the SMM type (4 levels) it was necessary to introduce a “dummy variable” to be able to accommodate four different types of SMM (Table 3.3).

Table 3.3 Setting the dummy variable to the additive type

B ₁	B ₂	Additive	
-1	-1	1	No SMM
1	-1	2	DEG
-1	1	3	DPS
1	1	4	SMM41

The test of each membrane was performed in a particular order, determined by a graeco-latin square design, a statistical tool that allows elimination of extraneous sources of error (specifically different runs and different test cells). For the graeco-latin square used each membrane received a name, according to Table 3.4.

Table 3.4 Membrane nomenclature used in the graeco-latin square design

Membrane ID	Evaporation Time	PES Conc.			Evaporation Time	PES Conc.	Additive
	x_1	x_2	B_1	B_2	x_1	x_2	
A1	-1	-1	-1	-1	0 min	12%	No SMM
B1	1	-1	-1	-1	3 min	12%	No SMM
C1	-1	1	-1	-1	0 min	18%	No SMM
D1	1	1	-1	-1	3 min	18%	No SMM
E1	0	0	-1	-1	1.5 min	15%	No SMM
F1	0	0	-1	-1	1.5 min	15%	No SMM
A2	-1	-1	1	-1	0 min	12%	DEG
B2	1	-1	1	-1	3 min	12%	DEG
C2	-1	1	1	-1	0 min	18%	DEG
D2	1	1	1	-1	3 min	18%	DEG
E2	0	0	1	-1	1.5 min	15%	DEG
F2	0	0	1	-1	1.5 min	15%	DEG
A3	-1	-1	-1	1	0 min	12%	DPS
B3	1	-1	-1	1	3 min	12%	DPS
C3	-1	1	-1	1	0 min	18%	DPS
D3	1	1	-1	1	3 min	18%	DPS
E3	0	0	-1	1	1.5 min	15%	DPS
F3	0	0	-1	1	1.5 min	15%	DPS
A4	-1	-1	1	1	0 min	12%	SMM41
B4	1	-1	1	1	3 min	12%	SMM41
C4	-1	1	1	1	0 min	18%	SMM41
D4	1	1	1	1	3 min	18%	SMM41
E4	0	0	1	1	1.5 min	15%	SMM41
F4	0	0	1	1	1.5 min	15%	SMM41

The fouling evaluation was made using the five-fold concentrated Ottawa River water (CORW). The UF membranes were placed in a six-cell in-series system, as described above. The order in which the membranes were installed in the different cells during four different runs is detailed in the Table 3.5.

Table 3.5 Membrane location during the four runs

Cell Run	I	II	III	IV	V	VI
1	B4	A3	D2	C1	E2	F3
2	D3	B1	A4	C2	E3	F4
3	C3	A1	D4	B2	E1	F2
4	D1	A2	C4	B3	E4	F1

Prior to each run the membranes were subjected to a precompaction protocol (similar to the previous stages, see the flow diagram in Fig. 3.6) filtering Milli-Q water through each new coupon at 620 kPa gauge (90 psig) for 52 h. Next, the PWP was determined during a period of 50 h under the operating pressure, 345 kPa gauge (50 psig). After its completion, the membranes were ready to be tested, either with CORW, Milli-Q water, PEG solution, or PEO, depending on the type of experiment. The permeation rate of the CORW was measured at a feed flow rate of 1.1 Lpm and an operating pressure of 345 kPa gauge (50 psig) during 6 days of continuous operation. The permeation rates were measured at different intervals. The TOC removal was assessed with the persulfate-ultraviolet oxidation method and infrared spectrometry (Model DC-180 Dohrman Total Carbon Analyzer, Santa Clara, CA).

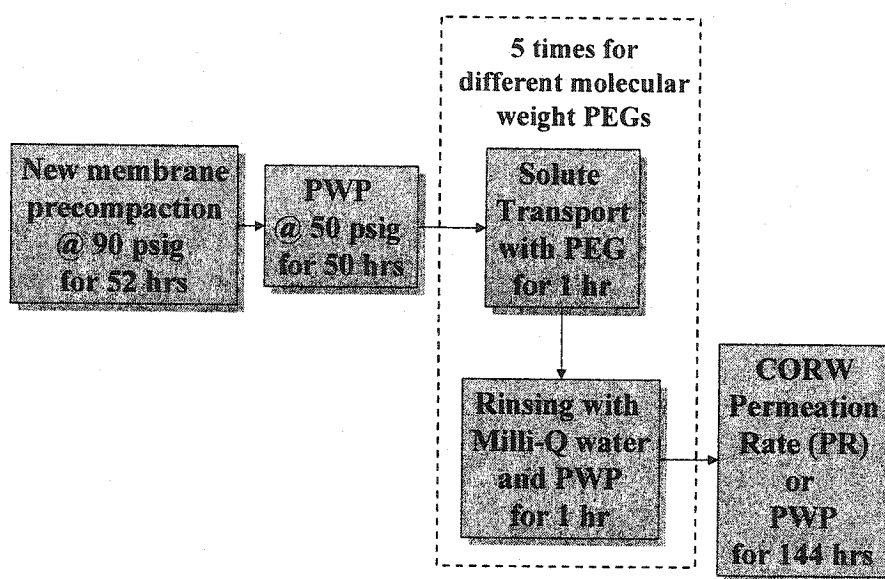


Fig. 3.6 Membrane test protocol

To isolate the fouling effect of the CORW, an identical coupon was tested following the same protocol, except for using Milli-Q water instead of using CORW for the 6-day permeation experiment. The difference between the flux reduction with CORW and Milli-Q water was considered to be the fouling effect of the CORW.

After the precompaction protocol, the UF membranes were characterized based on solute transport data, as described in the methodology of the first stage. The molecular weight

cut-off (MWCO) of each membrane was calculated from the transport data with PEG of molecular weights from 300 to 30,000 Daltons and PEO in the range of 100,000 to 200,000 Daltons. Using the results of the solute transport test and the proper equations, the pore distribution together with pore density and surface porosity of each membrane were computed.

The amount of NOM accumulated on top of the individual membranes at the end of the six-day test (referred 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, all the beakers were baked in an air-circulated oven at 105°C for 24 h, together with two of blanks (with just 25 mL of NaOH solution). Afterwards, the beakers were allowed to reach room temperature inside of the 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 dry weight of the average of the blanks.

3.2.2.4 Membrane characterization

Representative membrane samples were characterized after they had been dried. An Atomic Force Microscope (AFM) (Nanoscope III from Digital Instruments) operated in the tapping mode was used to obtain the topological information of the membrane surface measuring roughness. Small squares of approximately 0.5 cm² area were cut from each type of membrane prepared (Khulbe et al., 1996), and were glued on metal disks using two-sided tape. Dust particles and impurities were removed from the surface using a small dropper to blow air over the sample. The membrane surfaces were imaged in at least two different scan sizes, 5 x 5 µm and 1 x 1 µm. Roughness parameters were calculated with the microscope software using the small images.

A model JSM-6400 JEOL (Japan Electron Optics Limited, Japan) Scanning Electron Microscope was used to observe the cross-sectional area of the membranes. Dry samples

were submerged in liquid nitrogen and then they were torn using tweezers and mounted in chair-shaped sample holders for the SEM with double-sided tape; then, samples were coated under vacuum with a thin layer (60% gold and 40% palladium) in a Hummer VII sputting system (Anatech, Springfield, VA).

The chemical analysis of the membrane surface was determined using a Kratos Axis X-ray photoelectron spectrometer (Kratos, Manchester, UK). Each sample was analyzed at take-off angles of 0° and 60° , which corresponded to X-ray penetration depths of 6.3 and 3.15 nm, respectively (Suk et al., 2002a). However, since the 3.15 nm depth better represents the composition of the membrane surface, the data used in the analysis corresponded to the take-off angle of 60° . The 0° readings were helpful in providing a measure of the migration of the SMMs to the membrane surface, when compared with the 60° readings.

In all these techniques several spots of each sample were analyzed and the results presented in this document correspond to an average of the information obtained.

Contact angle was determined using the sessile drop technique with a 20- μ L droplet of distilled water and a standard goniometer apparatus (Ramé-Hart, model 100, Mountain Lakes, NJ). Advancing and receding angles were measured at least 10 times, and the contact angle hysteresis was calculated as the difference between the two of them.

3.2.3 Stage III: Fine-tuning with the most promising SMM

In the third stage of the project, a new series of membranes was prepared using the SMM41 from the second stage (which will be referred to as SMM41_0) and SMM41 from a new batch, named SMM41_1. The use of these two SMM41s was compared with the use of SMM-free membrane. Furthermore, the impact of pore former PVP additions to the casting solution was evaluated at two different PVP:PES ratios (i.e., 1:3 and 1:1). These two levels were chosen based on the results from Lafrenière et al. (1987). They studied the effect of polyvinylpyrrolidone additive on the product rate, pore size, and the separation of PEG-6000. They obtained the highest permeation rate when the weight ratio PVP/PES was unity, when they used PES concentrations in the casting solution in the

range of 15 to 30 wt %. They also found that increasing the PES concentration beyond 20 wt % started a drastic decrease in the product rate, while the solute separation increased.

Thus, the PES concentration was increased from 18 wt % (i.e., the maximum concentration used for the membranes in the second stage) to 21 wt %. The amount of SMM in the casting solution was kept constant at 1.5 wt %. No evaporation period was used during the preparation. The data were gathered in different groups of 2 or 3 variables to verify their effect, separately. The order of testing was randomized in two different systems as shown in Tables 3.7 and 3.8.

Table 3.6 Randomization of the order of testing

PES Conc. x_1	PVP/PES x_2	SMM41 x_3	$x_1x_2x_3$	System	PES Conc. x_1	PVP/PES x_2	SMM41 Additive
-1	-1	-1	-1	I	18%	1:3	No SMM
1	-1	-1	1	II	21%	1:3	No SMM
-1	1	-1	1	II	18%	1:1	No SMM
1	1	-1	-1	I	21%	1:1	No SMM
-1	-1	1	1	II	18%	1:3	SMM41_1
1	-1	1	-1	I	21%	1:3	SMM41_1
-1	1	1	-1	I	18%	1:1	SMM41_1
1	1	1	1	II	21%	1:1	SMM41_1
-1	1			I	18%	1:1	SMM41_0
1	1			II	21%	1:1	SMM41_0

Table 3.7 Order and chronology of membranes tested during the second stage of this study. Runs 1 and 4 were performed in system I and 2 and 3 in systems II

Cell Run	I	II	III	IV
1	No SMM 18/6	No SMM 21/21	SMM41_1 21/7	SMM41_1 18/18
2	SMM41_1 18/6	No SMM 21/7	SMM41_1 21/21	No SMM 18/18
3	SMM41_1 18/6	No SMM 21/7	SMM41_1 21/21	No SMM 18/18
4	No SMM 18/6	No SMM 21/21	SMM41_1 21/7	SMM41_1 18/18

In Appendix L it is demonstrated that the performance of the membranes did not significantly change with the batch of SMM used for their preparation. Therefore, for the rest of the thesis no differentiation between SMM41 batches will be made.

3.2.3.1 Test of different molecular weight fractions of NOM

In order to evaluate more deeply membrane fouling by NOM, membranes from the second and third stages with 18 wt % PES were tested using two different molecular weight fraction of NOM from the CORW as a feed i.e., the low molecular weight fraction (LMW) and the high molecular weight fraction (HMW). Therefore prior to the test, a LMW fraction was separated from the CORW using YM3 membranes (MWCO = 3 kDaltons). YM3 membranes were rinsed for one hour with Milli-Q water. PWP was measured for 1 h and afterwards, the fractionation of the CORW was performed for 165 h at 345 kPa gauge (50 psig). The same experimental set-up described in Section 3.2.2.2 was used to evaluate the performance of six different membranes, three surface modified with 1.5 wt % of SMM41, and three unmodified. No evaporation period was used during the preparation. The previous PVP/PES ratios (i.e., 1:3 and 1:1) were compared with no addition of PVP.

CHAPTER 4

APPARATUS EVALUATION

D. B. Mosqueda-Jimenez¹, R. M. Narbaitz², T. Matsuura³

4.1 Abstract

Flux decline with time is one of the most serious shortcomings of microfiltration and ultrafiltration membranes. It is highly desirable to have a membrane (fouling) testing procedure that is short in duration, utilizes a minimum amount of test solution, only requires a small membrane area, and is representative of the large-scale process. The objective of this study was to compare the results of the testing of a given membrane using a number of different test units (reverse osmosis, ultrafiltration, dead-end and cross-flow cells) and testing procedures. It was of particular interest to determine if smaller cells used in the literature perform similarly to the SEPA cross-flow cell, as it is a standard.

During 6-day runs the flux decline of the polyethersulfone membrane tested was mainly caused by membrane compaction and much less due to fouling. As various membrane materials compact to different extent, studies into the fouling characteristics of different types of membranes should incorporate precompaction and pure water testing to quantify the contribution of membrane compaction and true fouling to the overall flux decline. The dead-end cell performed very differently from continuous cells, so their use is not recommended. The six-day continuous flow tests showed that the reverse osmosis (RO), ultrafiltration (UF), and cross-flow (CF) cells yielded very similar DOC removals and flux decline, despite UF and RO cells using membrane coupons eight times smaller than CF cells.

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Key words

Fouling, ultrafiltration, crossflow cell, dead-end cell, precompaction

4.2 Introduction

During the last 40 years, interest in membrane processes for water and wastewater treatment has grown and these technologies are now the subject of an intensive research and development effort, as well as many full-scale applications. However membrane processes face a continuing challenge: membrane fouling, which is the reduction in flux with time. Membrane fouling occurs because of specific physical or chemical interactions between the various macrosolutes/particles and the membrane (Zeman and Zydney 1996). Jönsson et al. (1997) identified three major causes: the build-up of a cake layer, pore plugging and adsorption. Membrane fouling excludes the phenomena linked to membrane compaction, which is defined as the densification of the porous structure of the membrane due to the high pressure of the feed. Novel membrane materials, pretreatment, effective cleaning regimes, or process operation modifications are potential avenues to control membrane fouling (Anselme and Jacobs 1996).

In membrane development, many membranes are prepared under different preparation conditions and their fouling performance needs to be evaluated. Thus, it is highly desirable to have a testing procedure that is short in duration, utilizes a minimum amount of test solution, and requires only a small area of membrane, which is representative of a large membrane sheet.

Several test cells have been used in the laboratory when studying ultrafiltration membrane fouling, due to proteins and natural organic matter. However, by far, the most widely used is the Amicon stirred batch UF cell with different volumes, used with and without a stirrer (Nicolas et al. 2000; Bonner and O'Melia 1991; Jones and O'Melia 2001; Brink et al. 1993; Borneman et al. 1997; among others). Jönsson (1995) used another module, manufactured by ABB Flootek, (Sweden), which was equipped with one membrane above and one below a rotor blade. Cross-flow cells have also been used in

fouling evaluations. They include Millipore's MiniTan cells (Cho et al. (1998, 1999a, 1999b and 2000)), Millipore's 4 GPM Pellicon Cassette System (Peuravuori and Pihlaja 1997) and Osmonics' SEPA cells (DiGiano et al. 2000; Bodzek and Konieczny 1998; and Allgeier and Summers 1995). The latter has been designated by the USEPA as the standard cell for evaluating the potential of membrane processes as part of the Information Collection Rule (ICR). On the other hand, in his book, Matsuura (1994) described three different permeation cells: a reverse osmosis cell and ultrafiltration cell and a static cell. The first two types are used in experiments with continuous flow, while the latter is used for the batchwise operation.

The objective of this study was to determine the impact of membrane testing cells and testing procedures on the test duration, as well as membrane performance. Commercially available testing cells, including the EPA recommended Osmonics' SEPA and an Amicon stirred cell, were compared with two of the cells described by Matsuura (1994). Although our motivation was to standardize the testing procedure for small coupons of experimental membrane materials, the results are equally relevant for those interested in comparing the performance of alternative commercial membranes for a given application.

4.3 Experimental methods and analysis

4.3.1 Water sources

This study concentrated on evaluating the effect of the testing cell and operating conditions (including the test river water concentration and membrane precompaction), on membrane fouling. The study was made using highly coloured Ottawa River water (ORW), which is the source of supply for the city of Ottawa, Ontario, Canada. It was collected on June 6, 2000. This was a clear, low alkalinity, low hardness and highly coloured water (Table 4.1), typical of northern rivers (Thorsen 1999a, and 1999b). The river water was used after prefiltration (through a fine pore filter cartridge (rust and sediment) from the local hardware store) as water feed or, in some experiments, was concentrated up to 5 times using a portable Reverse Osmosis System by RealSoft

(Norcross, GA). This system included a FT30 membrane composite (Filmtec Membranes, Midland, MI). The concentrated Ottawa River water, which will be referred to as CORW, was used to accelerate the fouling process. The general chemical and physical characteristics of both types of feed, ORW and CORW, were determined as follows. TOC concentration was measured using a Dohrman Total Carbon Analyzer (Model DC-180, Santa Clara, CA) with the persulfate-ultraviolet oxidation method and infrared spectrometry as described in the standard method 5310 C, (Standard Methods 1995). Colour was determined using a colour comparator Aqua Tester by Orbeco Analytical Systems Inc. (Farmingdale, NY). A pH meter Accumet by Fisher (Pittsburgh, PA) was used to read pH (Method 4500-H⁺ B, Standard Methods 1995). Turbidity was determined using a nephelometer DRT 100B by HF Scientific, Inc (Method 2130 B, Standard Methods 1995). Alkalinity was determined by titration with H₂SO₄ (Method 2320 B, Standard Methods 1995). To calculate hardness, titrations with EDTA were performed (Method 2340 C, Standard Methods 1995).

Table 4.1 Ottawa River water quality characteristics.

<i>Parameter</i>	<i>ORW^a</i>	<i>CORW^b</i>
DOC ^c concentration (mg/L)	7	28
SUVA ^d (m ⁻¹ mg ⁻¹ L)	3.4	3.9
Colour (cu)	30	180
pH	7.6	8.2
Alkalinity (mg/L as CaCO ₃)	26	120
Turbidity (NTU)	0.8	0.3
Total hardness (mg/L as CaCO ₃)	30	153
Calcium hardness (mg/L as CaCO ₃)	22	122

^aORW = Ottawa River water

^bCORW = Concentrated Ottawa River water

^cDOC = Dissolved organic carbon

^dSUVA= UV absorbance at 254 nm (1-cm cell)/DOC

Reagent-grade water was used as a blank. A Milli-Q Water System by Millipore (Bedford, MA) consisting of mix bed ion exchange resins, synthetic activated carbon,

organic scavengers and membranes was used to prepare this ultrapure water, referred in this paper as mQ water. The supplier claims that the organic concentration of this water is less than 10 ppb. The average TOC of the mQ water measured in our laboratory was 30 ppb.

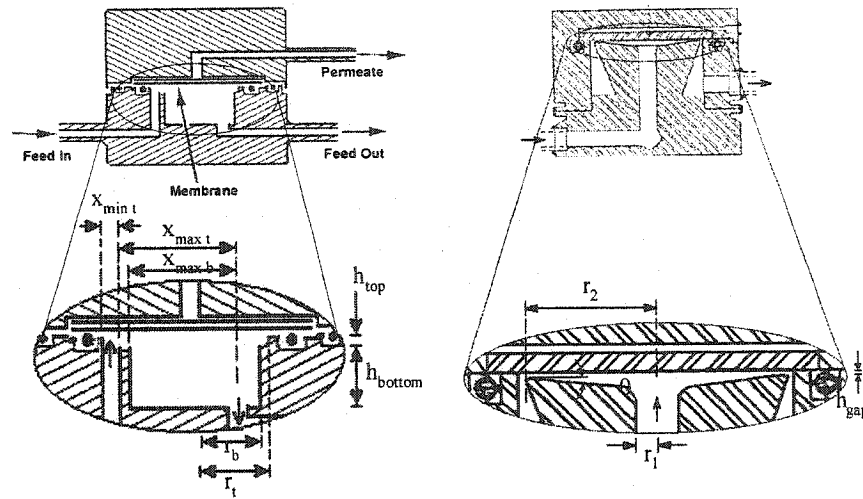
4.3.2 Membranes

The membrane used in the apparatus evaluation was a polyethersulfone (PES) ultrafiltration membrane, HO51, obtained from Osmonics (Minnetonka, MN). Membrane coupons were cut from flat sheet rolls. This membrane was chosen because it has similar characteristics to the membranes fabricated and tested in the second and third phases of this work. The molecular weight cut-off (MWCO) (defined as the molecular weight of a solute whose retention is 90%) was calculated from the transport data with polyethylene glycol (PEG) of molecular weights from 300 to 14,000 Daltons. The procedure was described in detail by Singh et al. (1998). The MWCO was determined to be approximately 7,000 Daltons. A second membrane made of regenerated cellulose (YM3 by Millipore, Bedford, MA) was also used for a limited number of comparative tests. Some additional results are presented in Appendix A. The latter membrane has a MWCO of 3,000 Daltons according to the membrane manufacturer. This membrane was tested with the small cells since it was commercially available in discs with diameters of less than 150 mm.

4.3.3 Test cells

The membrane test cells used are illustrated in Table 4.2 and Fig. 4.1, i.e., reverse osmosis cells (RO), ultrafiltration cells (UF), a stirred UF cell (Amicon® model 8050, Amicon Corp., Danvers, MA), and a crossflow cell (SEPA® CF Membrane cell by Osmonics®). As was mentioned previously, the last cell was especially chosen because it is currently recommended by USEPA for evaluating membrane performance for water treatment (DiGiano et al. 2000), and is also recommended by Osmonics® to simulate the flow dynamics of larger commercially available membrane elements such as Osmonics® industrial separators (spiral-wound membrane elements).

Table 4.2 Test cells dimensions (in mm)



a) RO cell

b) UF cell

RO cell		UF cell		CF cell	
h_{top}	1.7	r_1	3.175	$w_{membrane}$	80
h_{bottom}	12.2	r_2	25.5	δ_{spacer}	0.8
r_{top}	18.25	θ	4.5°		
r_{bottom}	14.2	h_{gap}	0.6		
$x_{max\ t}$	30				
$x_{min\ t}$	2.8				
$x_{max\ b}$	25				

The RO and UF cells were manufactured at the Dept. of Civil Engineering machine shop using 316 stainless steel, based on designs described in the literature (Sourirajan and Matsuura, 1985). The UF cells has a relatively high cross sectional area for fluid flow at the entrance and the exit, thus the pressure drop across the cell was less than 7 kPa gauge (1 psig) per cell. The UF cell also has a thinner channel flow design above the membrane surface, which allowed a relatively high fluid velocity parallel to the membrane surface (Table 4.2). The volume in this channel and the inlet and outlet openings are approximately the same. It is claimed (Sourirajan and Matsuura 1985) that these two changes in the design from that of the RO cell allow the cell to handle viscous fluids and simulate the flow conditions of large scale units.

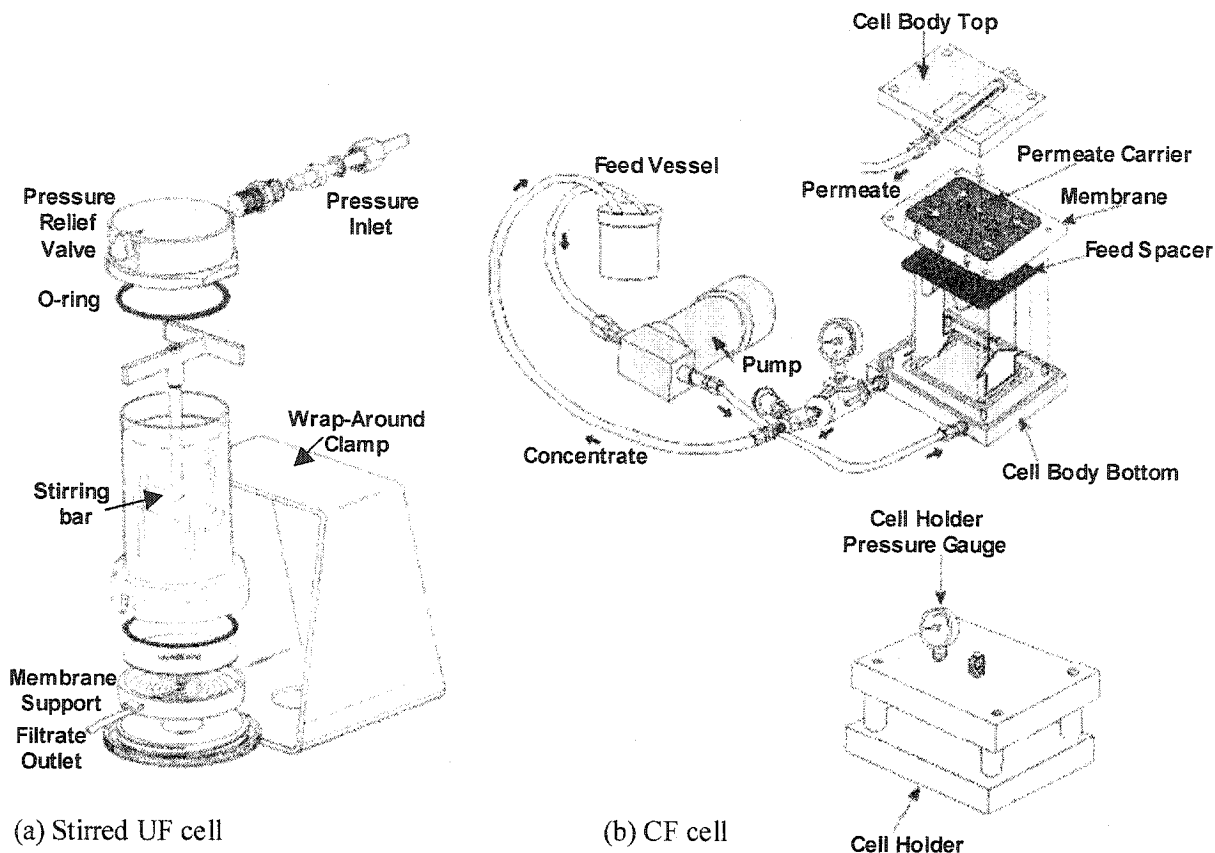


Fig. 4.1 Test Units.

The Amicon UF stirred cell (Fig. 4.1a) is made of polysulfone, and the cell body of the Osmonics CF cell is made of polypropylene (Fig. 4.1b). This stirred cell was operated in a batch dead-end filtration mode with a pressure of 345 kPa gauge (50 psig) derived from a gas cylinder. The remaining cells were operated within a recirculation system consisting of a feed reservoir, a high pressure diaphragm pump (Hydra-Cell, Wanner Engineering, Inc.; Minneapolis MN), a pressure regulator, the membrane test cells and the recycling lines that returned both the permeate and concentrate stream back to the reservoir to maintain the feed concentration constant (Fig. 4.2). This system allowed operating the Osmonics CF cell or up to six RO (or UF) cells connected in series. The membrane coupons necessary for the CF cell (Fig. 4.1b) were 155 cm² in area, while for the other cells the coupons were less than 20 cm² in area. However to allow the

comparison between cells the cross-flow velocity for the different types of cells was set at 0.2 m/s, a velocity similar to that used in full-scale operation of membrane elements (Rudie et al., 1990).

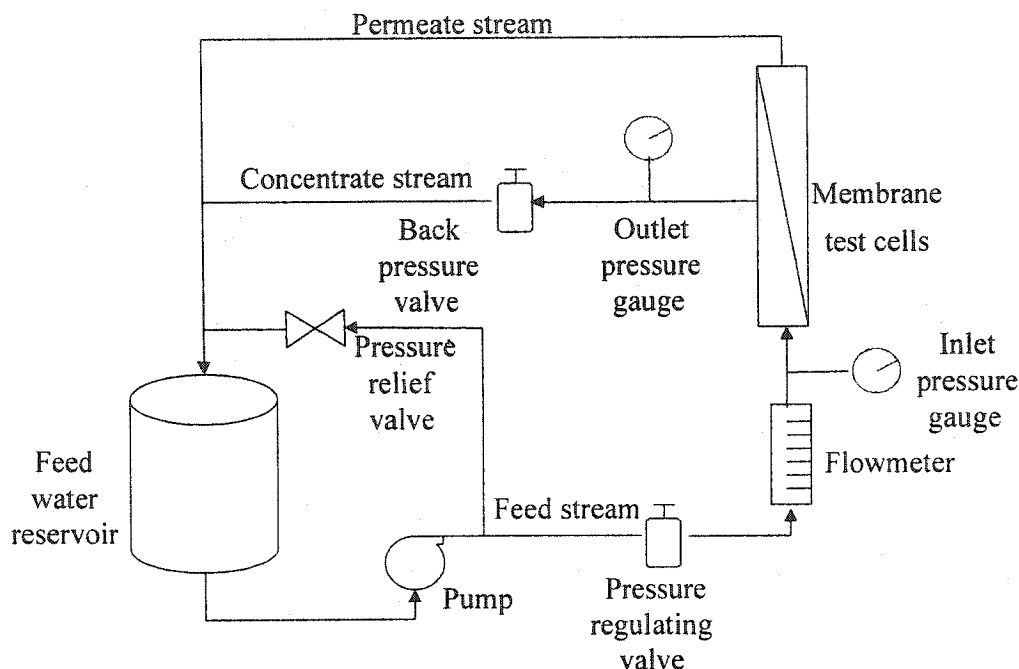


Fig. 4.2 Recirculation system.

In the development of new membranes, it is easier to produce defect-free small membrane coupons rather than large ones, so the smaller cells are more attractive from this point of view. Also the six-cells in series set-up allows for the evaluation of six membrane coupons simultaneously. On the other hand, given the variability in the performance of coupons taken from the same membrane sheet, the larger cells may give a better indication of the average performance of a given membrane sheet. In this study it was of particular interest to know if the RO and UF cells perform similarly to the CF cells so that they could be reliably used for testing newly prepared membranes.

4.3.4 Test protocol

The precompaction protocol used prior to each run consisted of installing the membrane coupons in the test cells and filtering mQ water, through each new coupon, at 483 kPa gauge (70 psig) for 50 h. The precompaction pressure was higher than the operating

pressure to accelerate the compaction. Then the pure water permeation rate (PWP) was determined repeatedly during a period of 28 h under an operating pressure of 345 kPa gauge (50 psig). After this step, the permeation rate (PR) of the ORW was measured for membranes in the RO, UF, and CF cells at a feed flow rate of 0.9 Lpm and an operating pressure of 345 kPa gauge (50 psig) during 6 days of continuous operation. In the case of the dead-end cell (stirred UF cell) the transmembrane pressure was set also at 345 kPa gauge (50 psig) and the test duration depended on the volume of the cell (50 ml). Permeation rates were measured by weighing the permeate sample collected during a predetermined period.

4.3.5 Determination of removal

The solute concentration was assessed by both the measurement of dissolved organic carbon (DOC) and the ultraviolet (UV) absorbance at $\lambda = 254$ nm. The amount of sample necessary to use the TOC instrument autosampler was 20 mL (to have at least 4 repeats). Therefore, in order to reduce the amount of permeate extracted from the system and keep the concentration nearly constant throughout the experiment, UV absorbance at 254 nm was used as a TOC surrogate, since the UV analysis only requires 1 or 2 mL of sample. One fifth of the samples were analyzed by both TOC and UV analysis to be able to prepare a calibration curve and confirm it regularly. It was observed that TOC and UV absorbance data were correlated linearly almost perfectly (see Appendix N). UV absorbance was measured at 254 nm using a Beckman DU-40 Spectrophotometer with a 1-cm quartz cell. In this case, reagent grade water was also used as a blank. According to Edzwald et al. (1985), UV absorbance is a good technique to measure the concentration of NOM because humic substances contain aromatic moieties that, together with conjugated double bonds, absorb light in the UV wavelength region.

4.4 Results and discussion

4.4.1 DOC removal

The apparent molecular weight distribution (AMWD) of the organic matter within the ORW was determined by UF fractionation using the stirred UF cell and regenerated cellulose membranes (Millipore, Bedford MA) with different nominal MWCOs (Fig. 4.3). The procedure is described elsewhere (Nilson and DiGiano, 1996). Almost 60% of the natural organic matter (NOM) was in the molecular weight range from 10,000 to 30,000 Daltons, while close to 30% of the NOM was lower than 5,000 Daltons and the remaining 10% was distributed in the ranges 5,000 to 10,000 and higher than 30,000 Daltons. Jacangelo et al. (1994) performed an analogous TOC fractionation of the ORW that they collected on two consecutive days, November 20th and 21st, 1991. Their results and those presented in this paper match exactly (i.e., 30%, 64%, 3% and 5% for the < 5,000, 5,000 - 30,000, 30,000 - 100,000, and > 100,000 Dalton-fractions, respectively). This was rather surprising given that the samples were collected years apart and during different seasons.

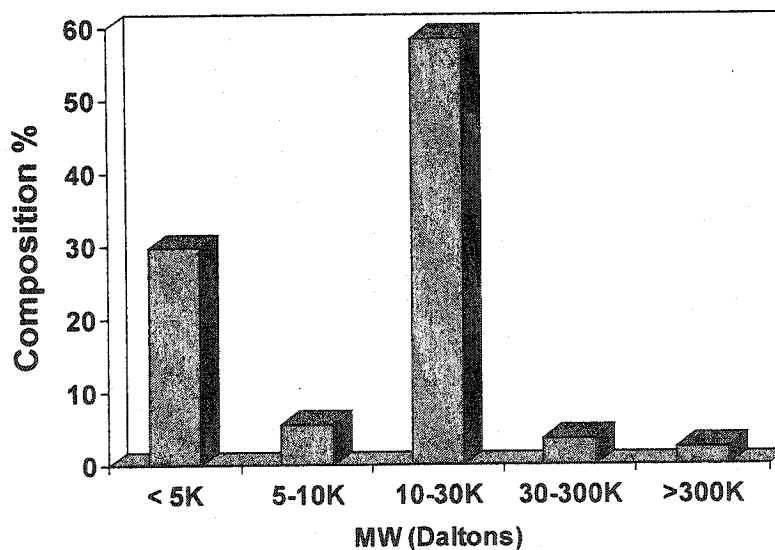


Fig. 4.3. Apparent molecular weight distribution of organic matter in the Ottawa River water.

The ORW was further subjected to continuous UF experiments using Osmonics PES membranes in the RO and UF cells. Based on size exclusion, the DOC removal should be about 65%, since MWCO of the latter membrane is 7,000 Daltons; however, the DOC separations were nearly 90% (Fig. 4.4). This shows that the MWCO of a membrane sometimes is not a reliable indicator of its DOC removal capabilities. The additional factors for the higher separations may include cake formation, pore adsorption, and difference in solute-membrane interaction. The first two factors are fouling mechanisms, this means that fouling may increase NOM removal while also decreasing flux. A compromise based on the maximum flux decline allowed for the process and the desired NOM removal has to be made in each case, according to the particular needs and costs.

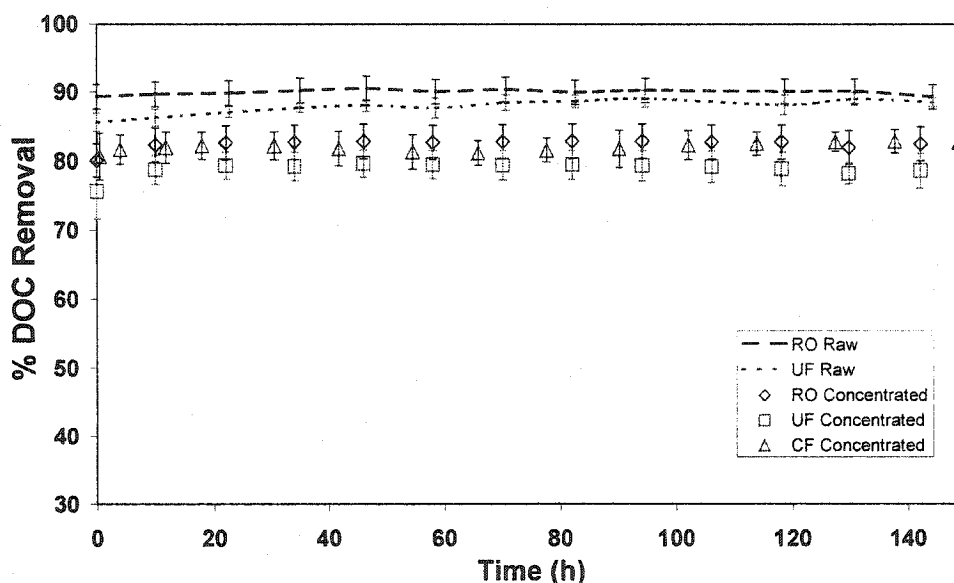


Fig. 4.4 DOC removal of different feed solutions obtained by continuous flow cells. PES HO51 membrane. Operating pressure: 345 kPa gauge (50 psig).

Figure 4.4 shows that the DOC removals (e. g., for ORW it was close to 90% while for CORW it was about 80%) were almost constant with time. The reason for the lower DOC removal for the CORW is unknown. However, it is believed that the difference is mainly due to the concentration process performed to obtain CORW. This concentration process not only modified the molecular weight distribution of the organic matter when the dissolved solids with the smallest molecular weight were removed by the RO membrane, but it also increased the concentration of mono and divalent ions, which contributed to a decrease in DOC removal (Hong and Elimelech 1997; Bouchard et al. 1997; Taylor et al.

1987). Thus, the lower DOC removals from CORW were consistent with the observed higher hardness of CORW (Table 4.1). The cake formed during the ultrafiltration of the ORW was more compact due to the smallest particles, which also promoted higher DOC removals. The CF cell's percent DOC removal was between those of the RO and UF cells. The experimental data presented are the average values of two to six replicates; the Y bars showed in the figures represent the confidence interval at a 95% level. Based on the overlapping confidence intervals, the UF, RO, and CF cells performed statistically the same in terms of DOC removal.

Since the dead-end cell was operated in a batch mode, the concentration in the cell increased with time according to the following equation (Jones and O'Melia 2001):

$$C_{b(t)} = C_0 \left(1 + \frac{V_t}{V_0} \right) \quad (4.1)$$

where $C_{b(t)}$ is the concentration of the NOM solution inside of the cell (bulk concentration) at time t , V_t is the total volume permeated through the membrane at the same time, C_0 is the initial NOM concentration, and V_0 is the initial volume. In the case of the stirred UF cell, V_0 is 50 mL.

The DOC rejection was then calculated as follows:

$$DOC \text{ rejection} = 100 \left(1 - \frac{C_{p(t)}}{C_{b(t)}} \right) \quad (4.2)$$

where $C_{p(t)}$ is the permeate concentration at time t .

On the other hand, DOC removal was calculated with the following equation (also used in the case of the continuous cells):

$$DOC \text{ removal} = 100 \left(1 - \frac{C_{p(t)}}{C_f} \right) \quad (4.3)$$

where C_f is the feed concentration.

Figure 4.5 presents the variation of permeate and bulk concentrations with time, together with the percentage of DOC removal and DOC rejection for CORW. The difference between these two percentages was due to the increase of the bulk concentration inside of the cell because the permeate (with relatively low DOC concentration) was extracted from the system. The relationship between them is described by equation 4.1. As time proceeded, the permeate concentration increased together with the increase of the bulk concentration. Thus, the percent DOC rejection remained almost constant along the test. After more than 70% of the volume of CORW had been filtered, the rejection started to decrease drastically, as the effect of the bulk concentration became more important. On the other hand, the percent DOC removal of CORW achieved by the stirred UF cell was almost 70%, at the beginning of the test, which was close to the initial removal achieved by the continuous cell. However, the percent DOC removal decreased very rapidly, as the bulk concentration increased inside the cell. It was therefore concluded that the DOC removals achieved with these dead-end systems operated in batch mode were not representative of the cross-flow systems within the time scale studied.

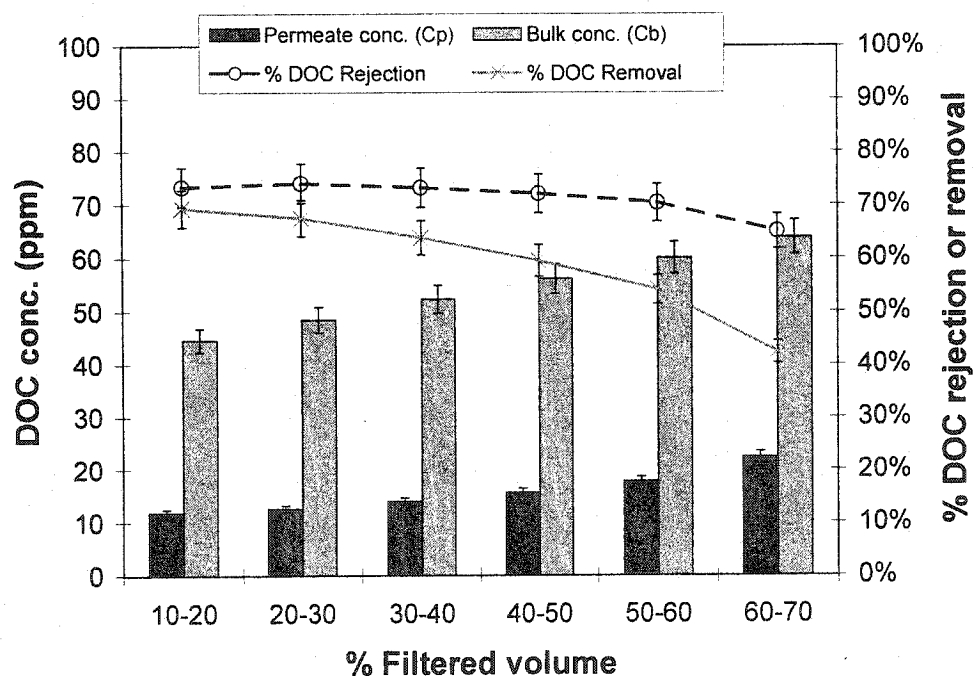


Fig. 4.5 DOC concentrations, and removal for CORW by the dead-end cell. PES HO51 membrane. Operating pressure: 345 kPa gauge (50 psig).

4.4.2 Flux reduction

4.4.2.1 Impact of precompaction

During the precompaction procedure (using mQ water as feed) that preceded all the tests, the PES HO51 membranes were subjected to flux reductions of up to 60% after the 50-h run (Fig. 4.6); while for regenerated cellulose membranes (YM3) this reduction was less than 18%. Persson et al. (1995) explained this difference in the compaction behaviour as a function of the structure of the membrane. While PES membranes have a structure with macrovoids below the thin separation layer, cellulose membranes have a continuous sponge-like structure, which make them less susceptible to compaction. Thus, the PES membranes used in this evaluation were more compressible than regenerated cellulose membranes. The three types of continuous flow cells followed the same trend. However, the flux decline during the precompaction of the PES membranes inside the three different kinds of cells was not the same, i.e., 38 ± 2 , 55 ± 5 , and $73 \pm 5\%$, for RO, UF and CF cells, respectively. Unfortunately, there is the risk that during this long precompaction the minute amounts of solute present in mQ water might have caused some flux decline, as explained in Section 4.4.3. For the regenerated cellulose membranes the various cells also yielded different levels of precompaction. During another 28-h period where the feed pressure was 345 kPa gauge (50 psig) instead of 483 kPa gauge (70 psig), the flux declined an extra 3 and 5% for the regenerated cellulose and PES membranes, respectively. The variation in initial flux as observed for the various cells and coupons might have been caused by differences among the coupons that were taken from different parts of a membrane sheet. It is then concluded that because the level of compaction depends on the membrane material, when testing a membrane it is important to determine the actual degree of compaction.

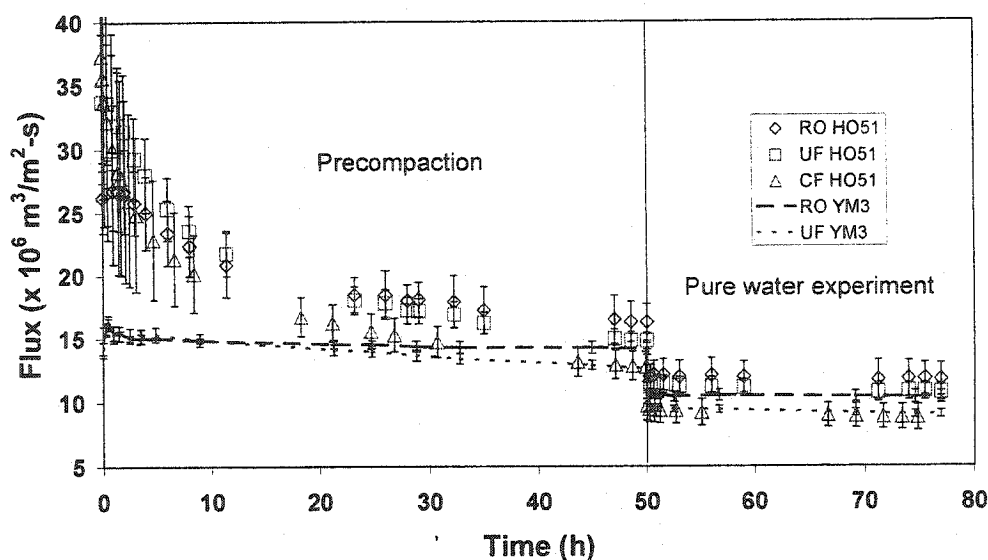


Fig. 4.6 Pure water permeation flux (PWP) during precompaction period (483 kPa gauge, 70 psig) and the following pure water experiment (345 kPa gauge, 50 psig). Markers: PES HO51 membrane; lines: Regenerated cellulose YM3 membrane.

4.4.2.2 Impact of NOM concentration

When the feed solution was switched to ORW or to CORW (after precompaction and the PWP determination), the flux declined further. In the case of raw ORW, after 144 h (6 days) of operation the flux decreased by 50 and 58%, for the RO and the UF cells, respectively (Fig. 4.7b). In the case of the CORW, the flux decreased by 45, 58 and 52% for RO, UF and CF cells, respectively. The difference in flux reduction between ORW and CORW was relatively small (in the case of the UF cells the flux reductions caused by ORW and CORW are statistically the same). However, it is observed in Fig. 4.7a that the absolute fluxes were not the same, due to the initial difference of permeate flux among membrane coupons. For this particular surface water preconcentration did not significantly accelerate fouling (relative flux reduction). However, the higher concentrations result in higher precision in DOC analysis. Cho et al. (1999a) found that 24-fold concentrated surface water resulted in a 20% higher flux decline than the diluted water for one type of membrane, while it had no effect for another type of membrane. Although the reason for the lack of impact of five-fold preconcentration in this study is not known with certainty, it is believed that it may be due to the membrane type or the lower degree of preconcentration used by Cho et al. (1999a). Perhaps, the chosen

operating conditions were not the best to emphasize the difference between the NOM concentrations in the feed. It is believed that a higher feed flow would have increased the differences. However, finding the best operating conditions to emphasize the difference of NOM concentration in the feed was not one of the objectives of this thesis.

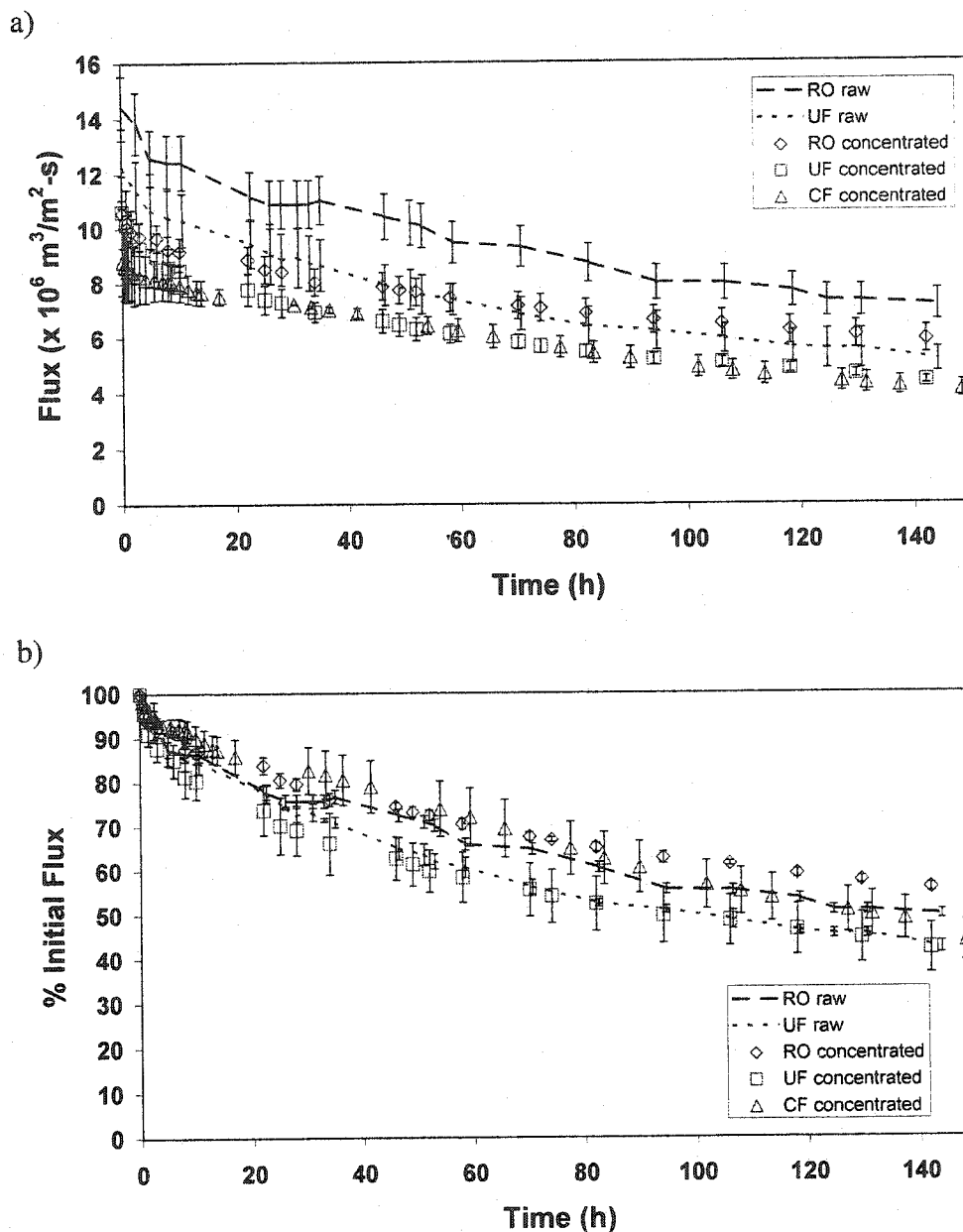


Fig. 4.7 Flux decline with raw ORW and CORW obtained by continuous flow cells. PES HO51 membrane. Operating pressure: 345 kPa gauge (50 psig).

4.4.3 Fouling

Even after precompaction, the flux declined continuously when mQ water was used as the feed. Figure 4.8 shows that decline was 27% for the RO cells and about 35% for UF and CF cells. In Fig. 4.8, the data for CORW given in Fig. 4.7 were reproduced to permit the comparison between flux decline for CORW and PWP. It is worth noting that the initial fluxes were different, however, they were statistically the same. Figure 4.7b shows

that when treating ORW a large part of the flux decline was due to further membrane compaction. Rudie et al. (1985) claimed that what initially was believed to be membrane compaction was a type of membrane fouling associated with the deposition of airborne particulates or microorganisms or corrosion of metal components present in trace amounts in the feed water.

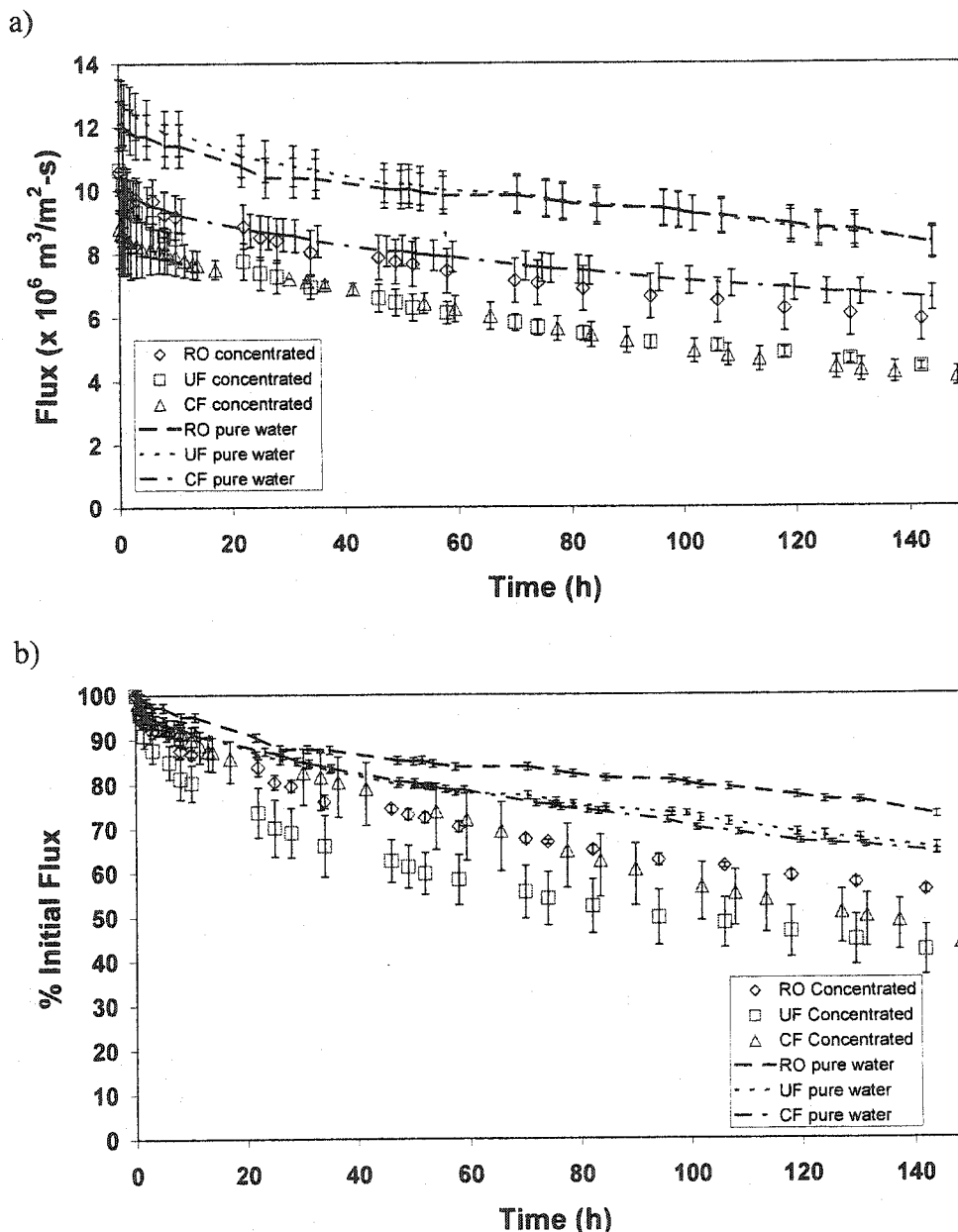


Fig. 4.8 Flux decline with pure water and CORW feed. a) absolute and b) relative flux decline. PES HO51 membrane. Operating pressure: 345 kPa gauge (50 psig).

Therefore, to eliminate the effect of these potential extraneous sources of fouling and the actual effect of compaction, the runs with mQ water were considered as blanks. Subtracting the blank pure water flux from the CORW flux, one can estimate the true flux decline due to the presence of contaminants in river water as shown in Fig. 4.9. It is worth noting that because the initial permeate flux affects the fouling rate, it was necessary to check that the initial values were statistically the same in each case for the mQ water test and for the CORW test, before comparing them. After 6 days, the true fouling resulted in flux declines of $16 \pm 3\%$ for the RO cells, while for the UF and CF they were 23 ± 2 and $19 \pm 8\%$, respectively. Thus, membrane fouling in the CF cell is statistically the same to that achieved in the RO and CF cells. It is observed that RO and UF cells seem to reach a stable state after 80 h, compared with CF cells where this plateau was not reached in 6 days. However this trend was not conclusive since the variations in the CF results were higher compared with RO and UF cells. It was surprising that membranes in the UF cells fouled more quickly than those in the RO cells, because the UF cells had a thin flow channel above the membrane surface, which allowed higher fluid velocity parallel to the membrane surface (Sourirajan and Matsuura 1985). This was supposed to increase the shear and reduce membrane fouling.

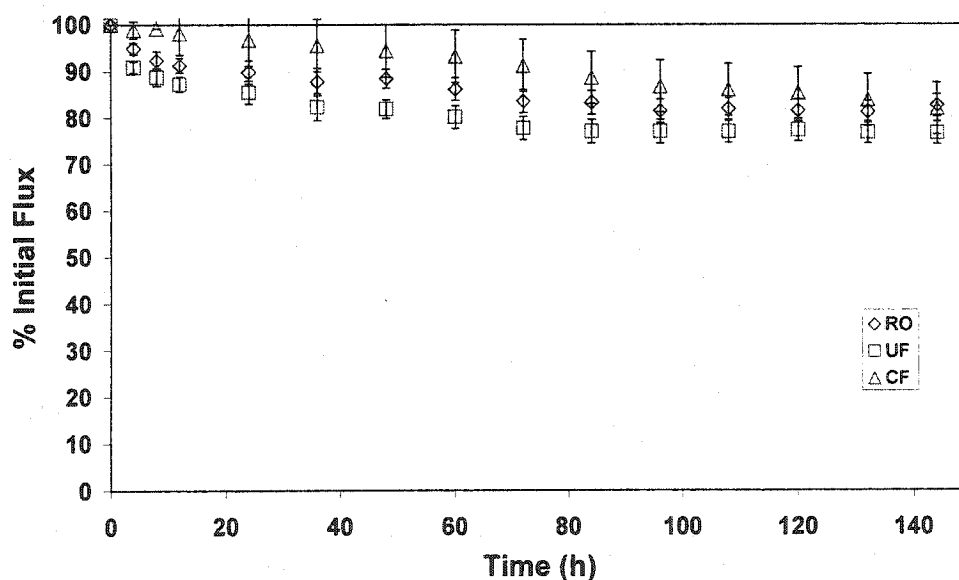


Fig. 4.9 True fouling effects of CORW for continuous flow cells. PES HO51 membrane. Operating pressure: 345 kPa gauge (50 psig).

There are different hydrodynamic parameters that can be used when studying the transport of material toward and away from the membrane wall, such as mean cross-flow velocity, the shear stress or the shear rate at the membrane wall (Carrère 2000). The most commonly employed are the cross-flow velocity, and the Reynolds number; for this reason experiments were planned so that two cells had the same cross-flow velocity (UF and CF) and two cells had the same Reynolds number (UF and RO). The mean cross-flow velocity was easily calculated in the case of the cells with rectangular geometry, like CF-SEPA, by dividing feed flowrate by inlet effective area (membrane width $\times$ spacer thickness) (Cho et al. 1998):

$$U_c = \frac{Q}{w_{\text{membrane}} \times \delta_{\text{spacer}}} \quad (4.4)$$

where w_{membrane} is the width of the membrane, and δ_{spacer} is the thickness of the spacer.

However, in the RO and UF cells described by Matsuura (1994), the flow is not uniform, since the cross-sectional area changes with the distance. In the case of the UF cell, the flow of water is radial and the effective area is not uniform because of the funnel-shape of the inner chamber (Table 4.2). In this case the mean cross-flow velocity was calculated as follows:

$$U_c = \frac{Q}{2\pi} \frac{1}{(h_{\text{gap}} - r_1 \tan \theta)} \frac{1}{(r_2 - r_1)} \ln \left(\frac{r_2}{r_1} \frac{h_{\text{gap}}}{h_{\text{gap}} + \tan \theta (r_2 - r_1)} \right) \quad (4.5)$$

where U_c is the mean cross-flow velocity, Q is the feed flowrate, r_1 is the radius of the feed conduit, r_2 is the radius of the chamber and θ is the angle that the funnel-shape walls of the chamber has with respect to the membrane and h_{gap} is the height of the gap between the membrane and the outer edge of the cone-shape chamber (equivalent to the thickness of the spacer in the case of the CF) (Table 4.2). Since this gap depend on the extent that the o-ring is compressed, cells were closed and tightened by applying the same pressure every time.

For the RO cell the flow dynamics are somewhat more complicated, since the liquid enters the cells through an orifice at the top of the cylindrical chamber and leaves at the bottom on the opposite side of the chamber. It was assumed that the cross-flow velocity may be approximated as the ratio between Q and an average area calculated as:

$$\begin{aligned} \bar{A} = h_{top} & \left[\frac{\left(-\frac{r_t \sqrt{x}}{2} + \frac{x^{3/2}}{2} \right) \sqrt{2r_t x - x^2} - r_t^2 \sqrt{2r_t x - x^2} \text{ArcTan} \left(\frac{\sqrt{2r_t - x} \sqrt{x}}{-2r_t + x} \right)}{\sqrt{x}} \right] \Bigg|_{x=x_{min t}}^{x=x_{max t}} + \\ & + h_{bottom} \left[\frac{\left(-\frac{r_b \sqrt{x}}{2} + \frac{x^{3/2}}{2} \right) \sqrt{2r_b x - x^2} - r_b^2 \sqrt{2r_b x - x^2} \text{ArcTan} \left(\frac{\sqrt{2r_b - x} \sqrt{x}}{-2r_b + x} \right)}{\sqrt{x}} \right] \Bigg|_{x=0}^{x=x_{max b}} \quad (4.6) \end{aligned}$$

where h_{top} and h_{bottom} are the heights of the top and bottom cylinders that form the chamber, with their respective radii r_t and r_b ; $x_{max t}$, $x_{min t}$, and $x_{max b}$ are the distances from the inlet end of top and bottom circumferences to the inlet and outlet orifices. Substituting the dimensions of each of the cells, shown in Table 4.2, it was determined that when RO cells were connected in series with UF cells, the flowrate was the same, but the cross-flow velocity for the UF cells was almost five times larger than that for the RO cells (0.2 m/s vs. 0.04 m/s). As it was mentioned, the cross-flow velocity for the CF cell was also 0.2 m/s.

In the case of the Reynolds number, the concept of hydraulic radius, R , was used, therefore Re , was calculated by:

$$Re = \frac{4Q}{\nu P_{wetted}} \quad (4.7)$$

where ν is the kinematic viscosity of the liquid at the operating temperature, and P_{wetted} is the wetted perimeter.

The Reynolds numbers of the three different cells were related to compare their values. Two different ratios were calculated:

$$\frac{Re_{UF}}{Re_{RO}} = \frac{(h_{total} + 2r_t)_{RO}}{[r_2 + (r_2 - r_1) / \cos \theta + h_{gap}]_{UF}} \quad (4.8)$$

$$\frac{Re_{UF}}{Re_{CF}} = \frac{1.104(w_{membrane} + \delta_{spacer})_{CF}}{[r_2 + (r_2 - r_1) / \cos \theta + h_{gap}]_{UF}} \quad (4.9)$$

For the systems tested $Re_{UF}/Re_{RO} = 1$. Although the mean cross-flow velocity was the same for UF and CF, their Re were quite different ($Re_{UF}/Re_{CF} = 1.9$). In the case of the UF and the RO cells, Re was slightly over 300 and for the CF cells it was almost 600; both being in the laminar region. It is difficult to define which hydrodynamic parameter had a greater influence on the flux reduction due to fouling, U_c or Re, since at the end of the 6-day experiment, the flux reduction for the three types of cells was very similar (statistically the same). This was probably because the membranes tend to the same steady state (permeate flux plateau). If the objective were to find the effect of the hydrodynamic parameters, the recommended course of action would be to test similar types of cells, with small variations in geometry. However, in this study the objective was to evaluate membrane test cells used in the literature.

In the case of the UF cells, they initially fouled quickly but then stabilized, so it seems that 80-h tests with UF cells would generate a good measure of fouling. As was mentioned, the system with the UF cells has the additional advantage that it includes multiple cells in series, thus it can be used to test simultaneously different membrane coupons as opposed to the larger single coupon for the CF cell. When having small coupons, the probability of encountering defects in the membrane is less than when larger membrane coupons are tested.

4.4.4 Variability

Since several UF cells and coupons were tested, a statistical analysis was performed to find out if the variability between replicates was due to the difference between UF cells

or coupons. From the results of the membrane precompaction, it was noted that the degree of compaction was different between RO and UF cells. On the other hand, when the second (UF2), third (UF3) and fourth (UF4) UF cells in series were used to test coupons from the same membrane sheet the fluxes for the individual cells did not follow a clear pattern (i.e., UF3 sometimes had higher and other times lower fluxes than UF2 or UF4). Thus, there was a difference between RO cells and UF cells and also between membrane coupons. The figures in this paper present the average performance of replicates rather than the performance of individual cells. Most of the time, each coupon seems to follow the same trend. For example, if at the beginning the flux of UF3 was higher than UF4 and UF5, the same trend was observed until the end. This implies that the coupons were different, because the ranking of the various cells in terms of flux varied from one set of tests to the next. Note that the UF units were built one after the other by one technician using the same specifications, so there should be no difference among cells. This means that the differences arose primarily due to variations in the membrane coupons.

Furthermore, variance component analysis (Box et al., 1978) was conducted in an attempt to establish if the variations in flux among replicates were due to differences among the coupons or differences among the UF cells. This type of analysis for the pure water test and fresh membranes indicated that the main source of the long-term (post 20 h) variations was differences among coupons. Similar analysis for the CORW test indicated that the differences in flux were impacted to a greater extent by differences among cells than by differences among coupons. However, the variance analysis indicated that at 95% level of confidence, for the limited number of replicates conducted using UF cells (i.e., 2 runs using 3 different coupons each time) there was no significant difference among the coupons or among the units. $F_{0.5,2,3}$ is equal to 9.55, which is much higher than $F_{0\text{unit}}$, 1.54 or $F_{0\text{coupon}}$, 0.001, in the case of fresh membranes and pure water. For CORW tests, $F_{0\text{unit}}$ was 6.68 and $F_{0\text{coupon}}$, 0.0004, which are also lower than $F_{0.5,2,3}$.

4.4.5 Batch system

In the case of the dead end cell no blank with mQ water was run. Therefore results presented in Fig. 4.10 are analogous to results in Fig. 4.7 in the case of continuous flow cells. It was clearly observed how fouling was accelerated because of the increase of the bulk concentration inside the cell with time. The stirred UF cell (Amicon) with concentrated feed followed the same curve with time. It can be seen that the same level of flux reduction for the concentrated feed in the case of the batch cell was achieved in one hour, compared with more than 10 h in the case of the continuous flow cells. Thus, the stirred UF cell reduced the time for membrane testing. However, when studying the performance of a membrane, fouling is not the only aspect to be evaluated, the level of removal of the particular solute also has to be considered. Given that the NOM removals by the batch cell were different from that of the continuous flow cells, the use of batch cells is not recommended.

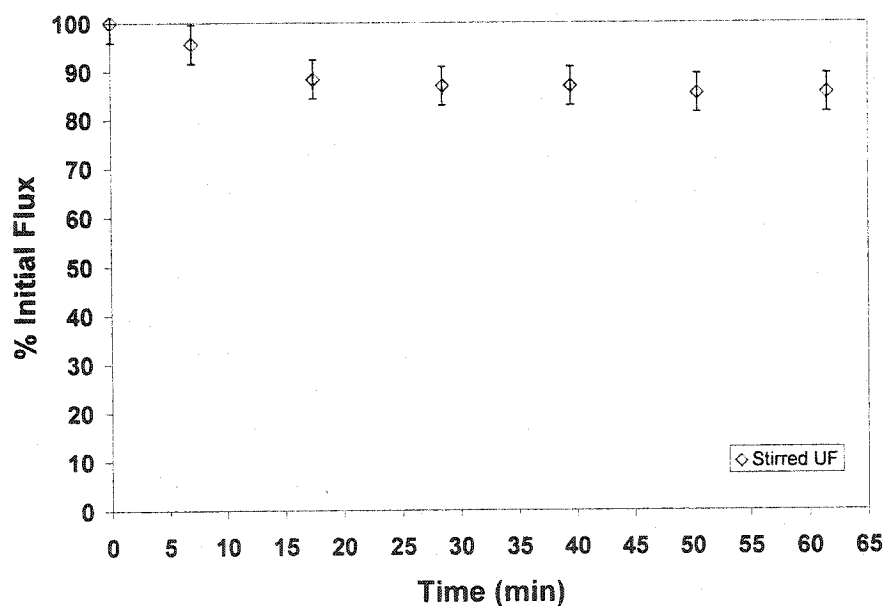


Fig. 4.10 Flux decline with CORW obtained by dead-end cell. PES HO51 membrane. Operating pressure: 345 kPa gauge (50 psig).

4.5 Conclusions

1. The six-day continuous experiments with the polyethersulfone membranes showed that membrane flux decline was primarily caused by membrane compaction. The contribution of fouling by contaminants in river water was not as significant as previously believed.
2. As various membrane materials compact to different extent, studies into the fouling characteristics of different types of membranes should incorporate precompaction and pure water testing to quantify the contribution of membrane compaction and true fouling to the overall flux decline.
3. Five-fold concentration of Ottawa River water did not significantly accelerate flux decline.
4. To achieve a reasonably thorough evaluation of a particular membrane the use of dead-end cells in batch mode to evaluate membranes is not encouraged, since this cell performed differently from continuous flow cells.
5. The six-day continuous flow tests showed that the RO, UF and CF cells yielded very similar DOC removals and flux declines. However, the coupon size required for UF cells was almost eight times smaller than that of CF cells, so in membrane development UF cells are favored.
6. Representative fouling data could be obtained within 80 h with the UF cells. For the CF cell it took longer. Further research is required to establish if such testing times are also applicable to other surface waters and other membranes.

4.6 Acknowledgements

We acknowledge Materials and Manufacturing Ontario (MMO) and Conacyt for their financial support. We also thank Dr. David McLean for his help in the statistical analysis of the data and Dr. Geeta Chowdhury for her valuable comments throughout this study.

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Notation

C_0 = initial concentration

$C_{b(t)}$ = bulk concentration at time t

C_f = feed concentration

$C_{p(t)}$ = permeate concentration at time t

h_{bottom} = bottom cylinder height (RO cell)

h_{gap} = height of the gap between the membrane and the outer edge of the cone-shape chamber (UF cell)

h_{top} = top cylinder height (RO cell)

P_{wetted} = wetted perimeter

Q = feed flowrate

R = hydraulic radius

r_1 = feed conduit radius (UF cell)

r_2 = chamber radius (UF cell)

r_b = bottom cylinder radius (RO cell)

Re = Reynolds number

r_t = top cylinder radius (RO cell)

U_c = mean cross-flow velocity

V_0 = initial volume (Stirred UF cell)

V_t = total volume permeated through the membrane at time t (Stirred UF cell)

w_{membrane} = width of the membrane (CF cell)

$x_{\text{max } b}$ = distance from the inlet end of bottom circumference to the outlet orifice (RO cell)

$x_{\text{max } t}$ = distance from the inlet end of top circumference to the outlet orifice (RO cell)

$x_{\text{min } t}$ = distance from the inlet end of top circumference to the inlet orifice (RO cell)

Greek

δ_{spacer} = thickness of the spacer (CF cell)

θ = angle between the funnel-shape walls of the chamber and the membrane (UF cell)

λ = wavelength

ν = kinematic viscosity of the liquid at the operating temperature

CHAPTER 5

EFFECTS OF MANUFACTURING CONDITIONS OF SMM-MODIFIED MEMBRANES ON FINAL CHARACTERISTICS

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5.1 Abstract

The effect of four processing variables on the final properties of ultrafiltration membranes was investigated. Flat-sheet membranes were prepared by wet phase inversion. The variables of interest were: the concentration of base polymer in the casting solution (dope solution), the solvent evaporation time, the surface modification of the membrane, and the use of the additive polyvinylpyrrolidone (PVP). The membranes were characterized by solute transport and scanning electron microscopy (SEM). No appreciable difference between the structures of surface-modified and unmodified membranes was observed by SEM. Membranes prepared with PVP had pure water permeation rates (PWP) significantly higher than membranes prepared without the PVP additive. However, the average polyethylene glycol (PEG 35 kDaltons) separation by membranes with PVP was approximately 15% lower than the tightest membranes prepared without PVP. The effect of surface modification with fluorinated additives and solvent evaporation time was observed only with high molecular weight cut-off (MWCO) membranes prepared with 12 wt % polyethersulfone (PES) casting solution.

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Key words

Membrane preparation, phase inversion, fouling, ultrafiltration, surface modifying macromolecules, mean pore size

5.2 Introduction

In the preparation of asymmetric membranes by the phase inversion technique, several different variables can be adjusted to control different membrane properties, which in turn, determine the performance of the membranes. The main factors are: the composition of the polymer solution, the solvent evaporation temperature and evaporation time, the nature and the temperature of the gelation media, among others (Matsuura, 1994).

The effects that these variables have on the membrane characteristics and at the same time on its performance have been studied for different types of systems in the literature (Chan et al., 1982; Tweddle et al., 1983; Lafrenière et al., 1987; Wood et al., 1993; Nakamae and Mohamed, 1993, etc.). Membrane surface modification is another potential way to control membrane performance. There are several techniques used for membrane surface modification, including, cross-linking, pre-adsorption of water-soluble polymers, grafting, etc. (Hamza et al., 1997; Mahmud, 1996). These techniques are complicated and require at least one additional step in the membrane preparation process (Suk et al., 2002). The addition of surface modifying macromolecules (SMMs) to polyethersulfone (PES) casting solutions can produce surface-modified membranes via a single-step casting. The main feature of an SMM is that it has a lower surface free energy than that of the base polymer, thus, it has the ability to migrate preferentially toward a polymer-air interface when the membrane is cast from a dope solution where the SMM is blended with the base polymer. In the case of hydrophobic SMMs, migration makes the surface significantly more hydrophobic. This methodology has been successfully employed by our research group to improve the performance of PES membranes for environmental applications, such as for the separation of volatile organic compounds (VOCs) from aqueous solutions via pervaporation (Pham et al., 1999; Mahmud et al., 2001; Fang,

1997; Minnery, 2000); ultrafiltration (UF) of oil/water emulsions (Hamza et al., 1997); as well as, biomedical UF 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 a longer performance than PES membranes (Suk et al., 2002). Therefore, there is a particular interest on studying SMM modified UF membranes, specifically for their potential to reduce fouling, since it is believed that fouling depends on the interactions between membrane surface and feed solution.

The possible interactions among the effect of different manufacturing variables and the surface modification of UF membranes have not been studied. The objective of this project was to study the characteristics of UF PES flat-sheet membranes resulting from changing the concentration of PES in the casting solution, the solvent evaporation time, the addition of different surface modifying macromolecules, and the additive polyvinylpyrrolidone (PVP).

5.3 Experimental methods and analysis

5.3.1 Materials

PES (Viktrex 4100P, ICI Advanced Materials, Billingham, Cleveland, England) was the base polymer used in the preparation of the membrane casting solution. Reagent grade N-methyl-2-pyrrolidone (NMP), supplied by Aldrich Chemical Company, Inc. (Milwaukee, WI), was used as the solvent. PVP with average molecular weight 10,000 Daltons, also supplied by Aldrich, was used as a nonsolvent pore-forming additive.

SMMs have an amphiphatic structure that consists of a polyurethane chain end-capped with two fluorine-based (low-polarity) polymer chains (Suk et al., 2002). The nomenclature of the three SMMs used in this study depended on the type of diol used in the synthesis of the polyurethane, they were as follows: diethylene glycol (DEG), dihydroxy diphenyl sulfone (DPS), and polypropylene diol (PPO). Therefore, the three different SMMs used were designated as DEG, DPS and SMM41 (to be consistent with previous references), respectively. Mandeep (2001) explained that each of the

components used in the synthesis of these SMMs (i.e., diisocyanate, diol, oligomeric fluoroalcohol) was carefully chosen with the objective of producing SMMs with a PES-like structure to achieve a uniform SMM distribution at the membrane surface. The diisocyanate has aromatic groups, DEG and PPO possess ether groups and DPS contains a sulfone group, as PES does. The oligomeric fluoroalcohol used in the synthesis was selected because it helped achieve the desired surface migration effect in previous studies (Pham et al., 1999; Ho et al., 2000; Mandeep, 2001).

SMMs DEG and DPS, were synthesized according to the methodology developed by Mandeep (2001), while SMM41 was synthesized according to the methodology outlined in Ho et al. (2000). Table 5.1 presents the following SMM properties: the weight-average molecular weight (M_w), the number-average molecular weight (M_n), and polydispersity (PD) determined by gel permeation chromatography (GPC) with polystyrene standards, together with their fluorine content. According to their molecular weights, the order of the three different SMMs was SMM41 > DEG > DPS, while for their fluorine content the order was DEG > DPS > SMM41. Pham et al. (1999) explained that the SMM surface migration is driven by the incompatibility of the oligomeric fluoroalcohol with the PES versus the air/polymer interface, therefore fluorine content in the SMMs determines in part the effectiveness of the surface modification, together with its chemical structure and, possibly, its molecular weight.

Table 5.1 Bulk properties of SMMs used for PES membrane surface modification

<i>SMM polymer</i>	$M_n/10^4$ ^a	$M_w/10^4$ ^b	<i>PD</i> ^c	<i>wt % F</i>
DEG ^d	1.2 (8%) ^e	1.4 (7%)	1.2 (8%)	28
DPS ^d	0.5 (20%)	0.6 (17%)	1.2 (8%)	23
SMM41	1.3 (16%)	2.0 (20%)	1.5 (12%)	11

^a M_n = number-average molecular weight,

^b M_w = weight-average molecular weight,

^c PD = polydispersity

^d Reference: Mandeep (2001)

^e Standard deviation

The probe solute for the solute transport method was either polyethylene glycol (PEG) (Sigma Chemical, St. Louis, MO), or polyethylene oxide (PEO) (Aldrich Chemical,

Milwaukee, WI). These polymers are standard probe solutes because they exhibit low membrane-solute interactions (Tam and Tremblay, 1991). The molecular weight of the different PEG fractions used ranged from 300 to 35,000 Daltons, while for PEO it was 100 or 200 kDaltons. Previous studies have shown that PEGs have narrow molecular weight distributions (determined by gel permeation chromatography) with polydispersities close to 1 (Cleveland et al. 2002). Feed solutions were prepared with PEG or PEO and ultra pure water to produce a concentration of 100 ppm total organic carbon (TOC). This ultra pure water was prepared with a Milli-Q Water System (Millipore, Bedford, MA), and was referred to as Milli-Q water.

5.3.2 Membrane preparation

During the first stage of the study, membranes were prepared with eight different casting solutions consisting of PES, SMM and NMP. From each casting solution membranes with two solvent evaporation times were cast. In the second stage of the study, PVP was added (as a pore forming additive) in two different concentrations: 6 and 18 wt %.

Table 5.2 shows the manufacturing conditions used in the preparation of membranes during the first and second stages of this study. All the components were weighed and the SMM powder was added to the NMP in 150 mL narrow-mouth glass bottles with Teflon lined caps. The SMM was dissolved, usually in less than an hour of mixing. PES and PVP were added, and the bottle was capped and sealed. Teflon tape together with electric tape, were used to provide an effective leak-proof seal. Low-concentration (low-viscosity) solutions were mixed by placing the bottles on the spinning rollers of a bottle rotator (U.S. Stoneware, East Palestine, OH). The bottles were spun for several hours, usually overnight. Very viscous solutions were mixed in an environmental incubator orbital shaker (model G24, New Brunswick Scientific Co., Inc., Edison, NJ) operating at 50°C. Usually 24 to 48 h were required to achieve the complete dissolution of the ingredients.

Table 5.2 Membrane manufacturing conditions

<i>Membrane ID</i>	<i>Solvent evap. time (min)</i>	<i>PES Conc. (wt %)</i>	<i>SMM</i>	<i>SMM Conc. (wt %)</i>	<i>PVP Conc. (wt %)</i>
Stage 1					
A1 1	0	12	No SMM	0	0
B1 1	3	12	No SMM	0	0
C1 1	0	18	No SMM	0	0
D1 1	3	18	No SMM	0	0
A2 1	0	12	DEG	1.5	0
B2 1	3	12	DEG	1.5	0
C2 1	0	18	DEG	1.5	0
D2 1	3	18	DEG	1.5	0
A3 1	0	12	DPS	1.5	0
B3 1	3	12	DPS	1.5	0
C3 1	0	18	DPS	1.5	0
D3 1	3	18	DPS	1.5	0
A4 1	0	12	SMM41	1.5	0
B4 1	3	12	SMM41	1.5	0
C4 1	0	18	SMM41	1.5	0
D4 1	3	18	SMM41	1.5	0
Stage 2					
E1 2	0	18	No SMM	0	6
F1 2	0	18	No SMM	0	18
E4 2	0	18	SMM41	1.5	6
F4 2	0	18	SMM41	1.5	18

After the solutions became homogeneous, they were filtered using Teflon PTFE 47-mm discs with pore size of 5.0 μm in a stainless steel pressure filter (Model XX4004700, Millipore, Bedford, MA) driven by nitrogen gas at pressures ranging from 69 - 276 kPa (10 - 40 psig) (depending on the viscosity of the solution). After the non-soluble impurities were removed, the filtrate was placed in sealed bottles and degassed overnight (or longer) at room temperature inside a vacuum dessicator. Solutions were then ready for casting. Dilute solutions were placed inside the refrigerator at 4°C to increase their viscosity. With each batch of casting solution it was possible to prepare several sheets of membranes.

All membranes were cast using the phase inversion technique described by Matsuura (1994). The casting was conducted at room temperature via the following steps. First, the polymer solution was poured over a smooth glass plate and spread with a metal rod with side runners to produce a 250 μm (10 mils) thick layer. The size of the casting area was approximately $28 \times 22 \text{ cm}^2$. For those membranes with solvent evaporation time, the glass plate was placed inside a 95°C oven. Three minutes was the maximum solvent evaporation time that permitted the preparation of these membrane sheets, longer times resulted in holes within them, especially for DPS-modified membranes. After the solvent evaporation period (or immediately after the membrane film was cast in the case of the membranes without solvent evaporation), the glass plate was immersed into ice-water at 4°C for at least 1 h. The hardened membranes were eventually peeled from the glass plate and after the gelation, membranes were stored at 5°C in Milli-Q water until they were tested. Every membrane sheet was inspected with a light-box to detect defects, such as thin spots and pinholes; defective membranes were discarded. Membrane coupons (51-mm diameter) were cut from the flat sheets for the filtration tests.

Some of the techniques used for membrane characterization (described in the following subsection) required that the membrane sample was dry. Therefore, after the preparation of each batch of membranes, some sheets were dried by solvent exchange. First, the membranes were sequentially submerged in four ethanol/water solutions (25, 50, 75 and 100 %w/w ethanol) to remove the water from the membrane. Soaking in each of these solutions lasted at least 6 h. Afterwards each membrane sheet was placed in between filter papers to dry at room temperature.

5.3.3 Analysis

A model JSM-6400 JEOL (Japan Electron Optics Limited, Japan) Scanning Electron Microscope (SEM) was used to observe the cross-sectional area of the dry membranes. Samples were submerged in liquid nitrogen and then they were torn using tweezers and mounted in chair-shaped sample holders for the SEM with double-sided tape; then, samples were coated under vacuum with a thin layer (60% gold and 40% palladium) in a Hummer VII sputting system (Anatech, Springfield, VA).

The chemical analysis of the membrane surface was determined using a Kratos Axis X-ray photoelectron spectrometer (Kratos, Manchester, UK). Each sample was analyzed at take-off angles of 0 and 60°, which corresponded to X-ray penetration depths of 6.3 and 3.15 nm, respectively (Suk et al., 2002). Comparing these readings was helpful in providing a measure of the migration of the SMMs to the membrane surface. When performing these analyses, several spots (randomly selected) of each sample were analyzed; in each case the results presented in this document correspond to an average of the information obtained.

5.3.4 Testing protocol

The fresh ultrafiltration membranes were placed in random order in a six-cell in-series system, which was described elsewhere (Mosqueda-Jimenez et al., 2003a). The existence of a possible cell effect or cell order effect within cells in a series system was disproved using an analysis of variance (ANOVA) test of a greco-latin square type of design. Results are reported in Appendix E.

Prior to membrane characterization by the solute transport technique, the membranes were subjected to a precompaction protocol consisting of filtering Milli-Q water through each new coupon at 620 kPa gauge (90 psig) for 52 h. The pure water permeation rate (PWP) was then determined during a period of 50 h under an operating pressure of 345 kPa gauge (50 psig). After its completion, the membranes were ready for the molecular weight cut-off (MWCO) determination. Each PEG or PEO solution, starting with those having the lower molecular weight, was circulated through the systems at a flow rate of 1.1 Lpm for 1 h. Feed and permeate samples were then collected and analyzed for TOC using a Total Carbon Analyzer (Model DC-190, Dohrman, Santa Clara, CA) with the combustion-infrared method described in standard method 5310 B (Standard Methods, 1995). The system was flushed with distilled water, and then, using Milli-Q water, the PWP was monitored for another hour between the testing with each probe solution. At the end, the PWP was measured to corroborate that it had remained constant throughout the MWCO determination process. Solute transport data were used to determine some of the morphological characteristics of the membranes, as explained in the next subsection.

5.3.5 Membrane characterization (solute transport)

Michaels (1980) found that the log-normal probability function is an accurate way to describe UF membranes sieving curves. In other words, the solute separation, $f(\%)$, of an UF membrane and the solute diameter (d_s) follow a log-normal correlation (Singh et al., 1998). PEG and PEO are polydisperse hydrophilic polymers used as probe solutes to minimize fouling (Zeman and Zydney, 1996). If the dependence of solute separation on the steric and hydrodynamic interaction between solute and pores are ignored, parameters calculated for these solutes may be considered to be the same as the parameters for the pores (Singh et al., 1998). This is not a denial of the role of these interactions, it is rather a simplification linked to the context and practical limits of this study.

Therefore, the pore size distribution of an UF membrane is expressed by the log-normal distribution:

$$\frac{df(d_p)}{dd_p} = \frac{1}{d_p \ln \sigma_p \sqrt{2\pi}} \exp \left[-\frac{1}{2} \left(\frac{\ln(d_p/\mu_p)}{\ln \sigma_p} \right)^2 \right] \quad (5.1)$$

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. $\mu_p = d_s @ f = 50\%$, and σ_p is calculated by:

$$\sigma_p = \frac{d_s @ f = 84.13\%}{d_s @ f = 50\%} \quad (5.2)$$

where d_s is the solute diameter ($d_p = d_s$). Also 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 of the solute diameter, and σ_s is the GSD of the solute diameter. Instead of determining these values using log-normal paper, library functions from Microsoft Excel for the standard normal distribution and base-10 logarithm, were used (i.e., NORMSINV and LOG10, respectively).

The Stokes radius is the radius of a hypothetical sphere that would diffuse with the same speed as the particle under study. 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):

$$a_{PEG} = 16.73 \times 10^{-10} M^{0.557} \quad (5.3a)$$

$$a_{PEO} = 10.44 \times 10^{-10} M^{0.587} \quad (5.3b)$$

Equations 5.3a and 5.3b were derived by Singh et al. (1998) from empirical expressions of PEG and PEO's intrinsic viscosities and the Stokes-Einstein equation for diffusivity.

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):

$$J_i = \frac{N_i \pi d_i^4 \Delta P}{128 \eta \delta} \quad (5.4)$$

where

J_i = solvent flux for pores with diameter d_i ($\text{m}^3/\text{m}^2\text{-s}$)

N_i = density of pores with diameter d_i (dimensionless)

ΔP = pressure difference across the pores (Pa)

η = solvent viscosity (N-s/m^2)

δ = length of the pores, considered equivalent to the thickness of the skin layer (no tortuosity) (m)

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

$$J = \sum J_i = \frac{\pi \Delta P}{128 \eta \delta} \sum N_i d_i^4 = \frac{\pi \Delta P N}{128 \eta \delta} \sum_{d_{\min}}^{d_{\max}} f_i d_i^4 \quad (5.5)$$

where

f_i = fraction of pores with diameter d_i .

Therefore,

$$N = \frac{128\eta\delta J}{\pi\Delta P \sum_{d_{\min}}^{d_{\max}} f_i d_i^4} \quad (5.6)$$

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

$$S_p(\%) = \left(\frac{\pi}{4} \sum_{d_{\min}}^{d_{\max}} N d_i^2 \right) \times 100 = \left(\frac{N\pi}{4} \sum_{d_{\min}}^{d_{\max}} f_i d_i^2 \right) \times 100 \quad (5.7)$$

5.3.6 Experimental Design

A $2 \times 2 \times 4$ multifactor design was used during the first phase of the test to evaluate the effect of the solvent evaporation time, the concentration of PES in the casting solution, together with the absence or presence of three different SMMs in the casting solution. This design allowed the study of the interplay of the independent variables on each of the response variables with fewer experimental runs than a one-factor-at-a-time experiment would require (Devore and Farnum, 1999). The response variables included both morphological characteristics (i.e., mean pore size, geometric standard deviation, and MWCO) and performance characteristics (i.e., PWP, and solute separation).

It is worth noting that the “repeats” in the multifactor design, which allowed us to measure the experimental error, corresponded to a complete replicate of the experimental conditions of each test (Devore and Farnum, 1999). This means that each coupon tested came from a different membrane sheet and it was randomly located in one of the six test cells. Statistical calculations were performed using STATGRAPHICS Plus V. 7.0 (Statistical Graphics Corporation, Manugistics, Inc., Rockville MD).

5.4 Results and discussion

5.4.1 Morphological characteristics

5.4.1.1 Sieving curves

Figure 5.1 shows the sieving curves (also known as polydisperse solute spectrum (Zeman and Zydney, 1996)) of the sixteen membranes prepared without PVP during the first stage of this study. As Michaels (1980) indicated, in order to describe the sieving characteristics of an UF membrane, two parameters are necessary, the mean pore size (referred to in Michaels' study as "mean" Einstein-Stokes radius or ESR) and the GSD. Sieving curves were generated with mean pore sizes and GSDs from solute transport data of two to four different membrane coupons. It is worth noting that the GSD used in the generation of sieving curves does not refer to the scatter of the data among different coupons, but the scatter of the pore size distribution and defined as the deviation from the mean pore size.

Figure 5.1 shows that for both modified and unmodified membranes, the increase of solvent evaporation time decreased the mean pore size (pore diameter when solute separation is 50%). This effect was more important at lower PES concentrations. An increase in the PES concentration also decreased the mean pore size, and this effect was more important than the solvent evaporation time. When studying the effect of manufacturing conditions using experiments designed to test one-factor-at-a-time, Chan et al. (1982) also observed the general decrease of mean pore size when the polysulfone concentration in the casting solution was increased from 12 to 20%. When solvent evaporation time was increased during the preparation of aromatic polyamidohydrazide membranes, Chan et al. (1982) observed a decrease in the number of large pores with the consequent decrease in mean pore size.

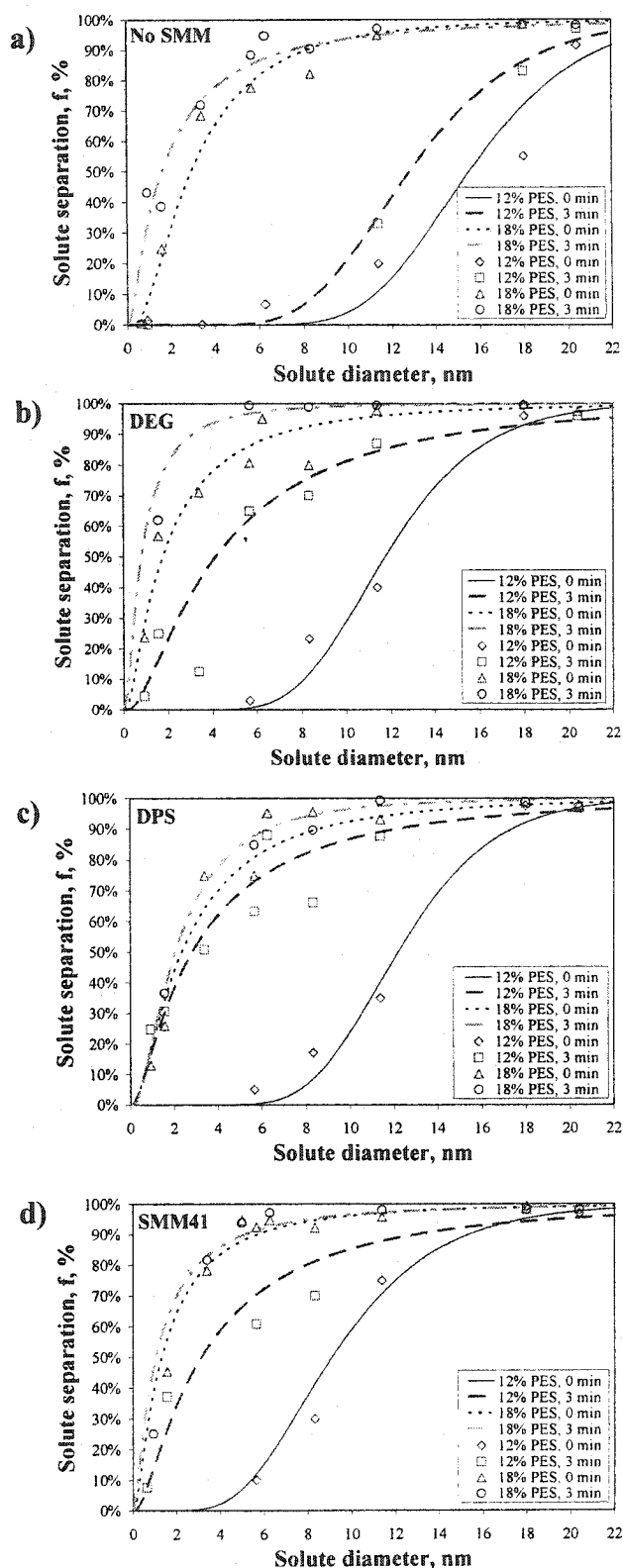


Fig. 5.1 Sieving curves for membranes prepared under several manufacturing conditions, with different SMMs: a) No SMM, b) DEG, c) DPS, d) SMM41

The probability density function plots in Figures 5.2a-5.2d gave an indication of the pore size distribution for the different membranes. It is observed that unmodified membranes prepared with 12 wt % PES had some pores with diameter larger than 22 nm. The most probable size of the pores (mode, maximum in the probability density function curves) was smaller for the surface-modified membranes than for their unmodified counterparts. The same trend was observed for the mean pore sizes in Figures 5.1a-5.1d. It is believed that this effect was due to the surface active SMM molecules, which promoted the formation of smaller pores. It is worth noting that because of the assumptions (mentioned in Section 5.3.5) made to generate the model, the pore size distributions in Figures 5.2a-5.2d represents just an approximation of the actual data, especially below 2 nm, where the conditions are not purely steric. However, these approximations are helpful in the study of the effect of the manufacturing conditions.

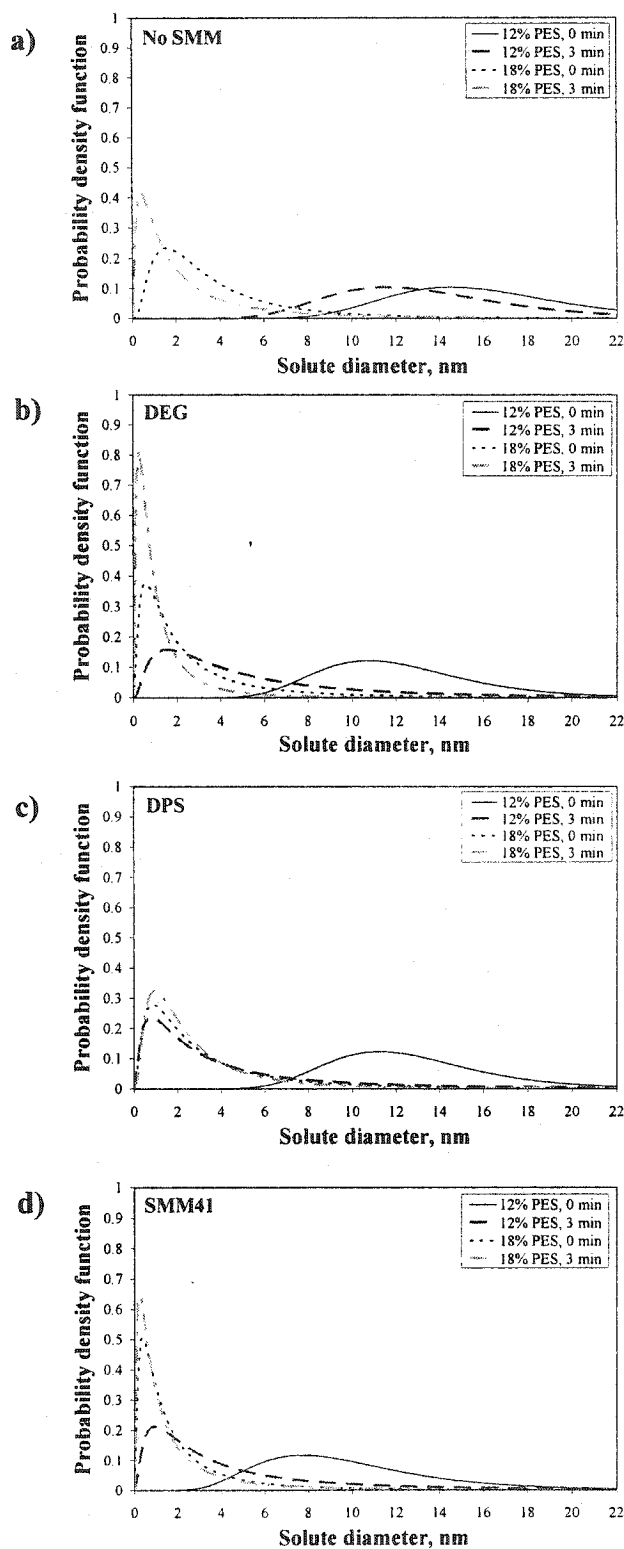


Fig. 5.2 Pore size distribution curves for membranes prepared under several manufacturing conditions, with different SMMs: a) No SMM, b) DEG, c) DPS, d) SMM41

Results of the ANOVA tests are presented in Table 5.3. The null hypothesis (H_0) was that the effect of any particular independent variable on each of the response variables does not exist. P-values in Table 5.3 indicate the probability of obtaining a test statistic value that contradicts the null hypothesis (Devore and Farnum, 1999). In other words, a small P-value indicates that it is unlikely that the independent variable has no effect i.e., a small P-value means that the independent variable has an effect. The null hypothesis was rejected if $P\text{-value} \leq 0.05$ ($\alpha = 0.05$ or 5%). It is worth noting that the design was not a 2^k design (factorial design at two levels), therefore, it did not automatically yield a set of linear models. In this case a separate regression would be required.

Results in Table 5.3 indicate that at a significance level of $\alpha = 0.05$, pore size was significantly affected by all three independent variables, together with two two-factor interactions: evaporation time $\times$ PES conc., and PES conc. $\times$ SMM. According to Devore and Farnum (1999), in view of the presence of statistically significant interaction effects, results were interpreted by examining the interaction plots and not the main effect plots. From the evaporation time $\times$ PES conc. plot (Fig. 5.3a) it is observed that at 18 wt % PES for both solvent evaporation times, the membrane pore size was significantly smaller. Moreover, the effect of the solvent evaporation time was only significant when the casting solution is prepared with 12 wt % PES. On the other hand, from the PES $\times$ SMM plot (Fig. 5.3b) it was confirmed that membranes prepared with 18 wt % PES gave consistently smaller pore sizes ($d \approx 2$ nm). The effect of surface modification is significant only at a 12 wt % PES concentration. It is worth noting that main effects and interaction plots were generated by averaging all response values in which the factor level (or factor-level combination) was present, versus that factor level (Devore and Farnum, 1999).

Table 5.3 P-values of the independent variables obtained from the analysis of variance (ANOVA) for morphological and performance parameters ($\alpha = 0.05$)

<i>Source of variation</i>	<i>Mean pore size</i>	<i>GSD^a</i>	<i>MWCO^b</i>	<i>PWP^c</i>	<i>Solute separation</i>
MAIN EFFECTS					
A: Evaporation time	0.0001 ^d	0.0249	0.0073	0.1861	0.0000
B: PES conc.	0.0000	0.0050	0.0000	0.0006	0.0000
C: SMM	0.0024	0.2262	0.0744	0.0776	0.0010
INTERACTIONS					
AB	0.0009	0.1389	0.0718	0.1339	0.0000
AC	0.5495	0.9977	0.9104	0.2816	0.0511
BC	0.0144	0.5951	0.1873	0.5215	0.0012
ABC	0.3481	0.2670	0.9169	0.4438	0.1196

^a GSD = Geometric standard deviation of the pore diameter

^b MWCO = Molecular weight cut-off

^c PWP = Pure water permeation rate

^d If P-value ≤ 0.05 the effect is statistically significant

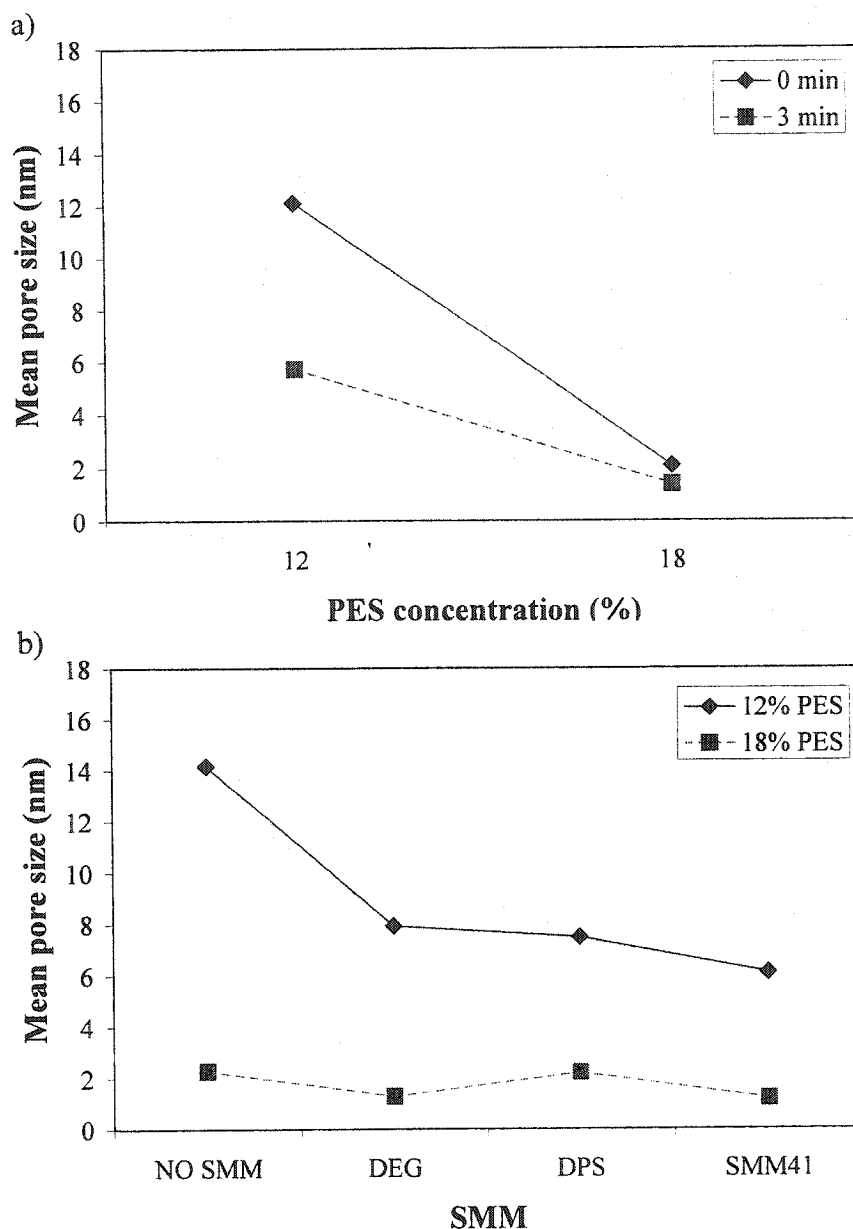


Fig. 5.3 Two-factor interaction plots for mean pore size: a) Time × PES; b) PES × SMM

According to Michaels (1980), the GSD about the mean pore diameter is a measure of the “sharpness” of the rejection spectrum of the membrane (Fig. 5.1). However, the mean pore size of the membranes prepared under different manufacturing conditions varied over a wide range (from 1 nm to more than 15 nm) (Figures 5.1a-5.1d), making it difficult to compare the dispersion of the curves. Among the membranes with the same mean pore size, and different GSD, comparison of the dispersion is straightforward, i.e.,

curves of the same family (same mean pore size) would share the same middle point, and for a smaller GSD one should observe a larger slope in the curve. From the ANOVA test, it was established that solvent evaporation time and PES concentration resulted in significant increases in the GSD of the pore size (Table 5.3, Figures 5.4a and 5.4b), i.e., membranes prepared with longer solvent evaporation time and higher PES concentration had more disperse pore size distributions. Figure 5.4c shows that surface-modified membranes had statistically the same GSD. The Y-bars in the main effect plots represent the results of multiple range tests (multiple comparisons procedure) performed for each independent variable via the Least Significance Difference technique (LSD) at a 5% significance level (Montgomery, 1991).

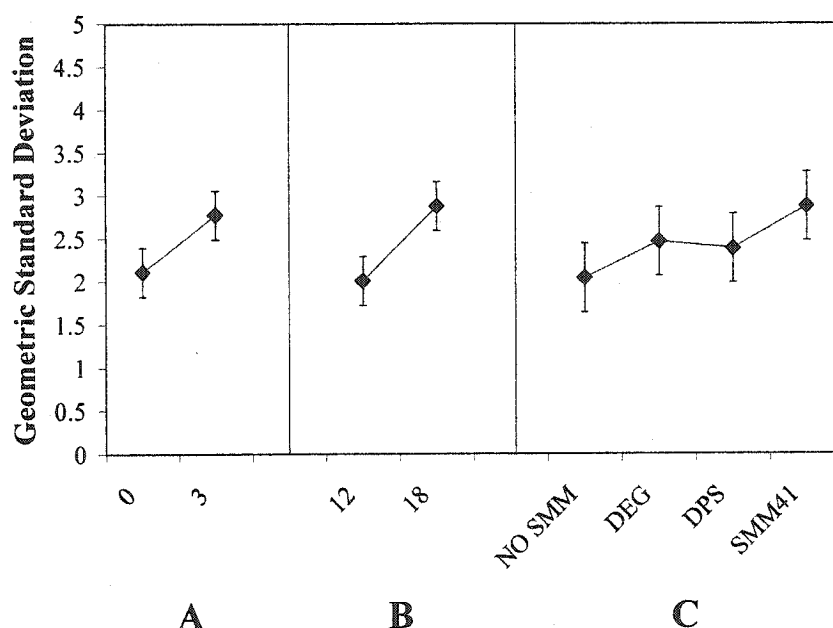


Fig. 5.4 Main effects of independent variables on GSD of the pore size distribution.
A = Solvent evaporation time (min), B = PES concentration in the casting solution (wt %), C = SMM

5.4.1.2 MWCO

By definition, a MWCO is the molecular weight at which 90% of the solutes are rejected by the membrane; therefore, it was calculated from the sieving curves as the solute diameter corresponding to 90% solute separation. Figures 5.5a and 5.5b show that MWCO decreased when solvent evaporation time or PES concentration in the casting

solution increased. The MWCO of modified membranes was lower than that of the unmodified membranes (Fig. 5.5c). So the general trends for MWCO are the same as for mean pore size i.e., MWCO decreased either with the increase of solvent evaporation time, or the increase of PES concentration in the casting solution, or by surface modification of the membrane. The ANOVA test confirmed these results (Table 5.3).

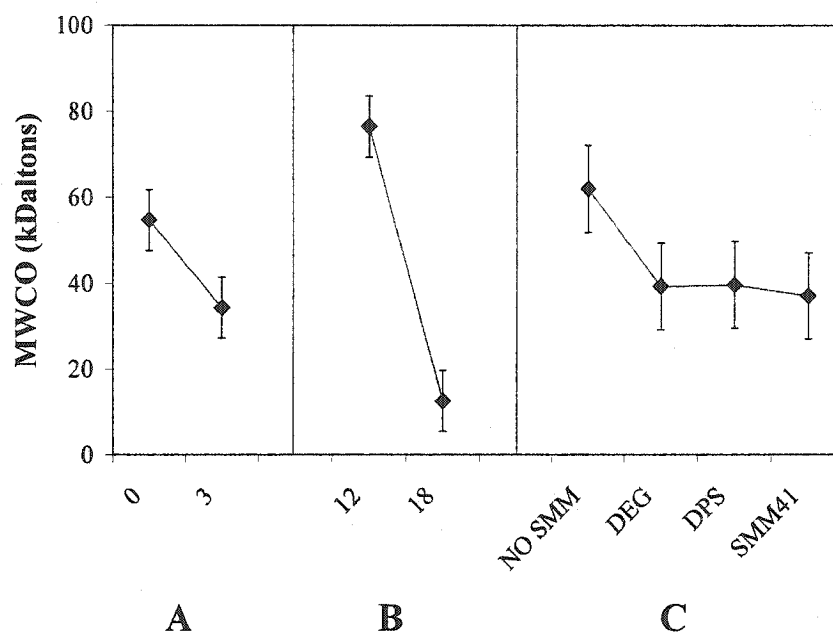


Fig. 5.5 Main effects of independent variables on molecular weight cut-off. A = Solvent evaporation time (min), B = PES concentration in the casting solution (wt %), C = SMM

5.4.1.3 Pore density and porosity

The pore density (N) and the surface porosity (S_p) were computed via equations 5.6 and 5.7, respectively, with the sieving data generated from mean pore sizes and GSDs (obtained from two to four different membrane coupons, as explained in the sieving curves section). A single set of values for N and S_p were calculated for each kind of membrane; hence, the ANOVA test could not be performed, since the lack of replicated values for N and S_p means that no estimate of experimental error was available (Devore and Farnum, 1999). Pore density results are presented in Fig. 5.6. Membrane surface modification increased the amount of pores in comparison with the unmodified membranes (except in the case of the DPS-modified membranes prepared with 18 wt %

PES). As it was explained earlier, due to the surface-active character of the SMMs the size of the pores decreased and the number of pores increased, therefore porosity changed slightly upon surface modification. When DPS was used in the surface modification of 18 wt % PES membranes, the number of pores did not increase as in the case of the other SMMs. It is possible that this effect was related to the reduced solubility of the DPS in the casting solution. The order of the SMM solubilities was $\text{SMM41} > \text{DEG} > \text{DPS}$ (visually evaluated). The casting solutions prepared with DPS and 18 wt % PES were unstable and they became cloudy with time after they were completely mixed (indicating phase separation or formation of suspended insoluble matter (Tweddle et al., 1983)).

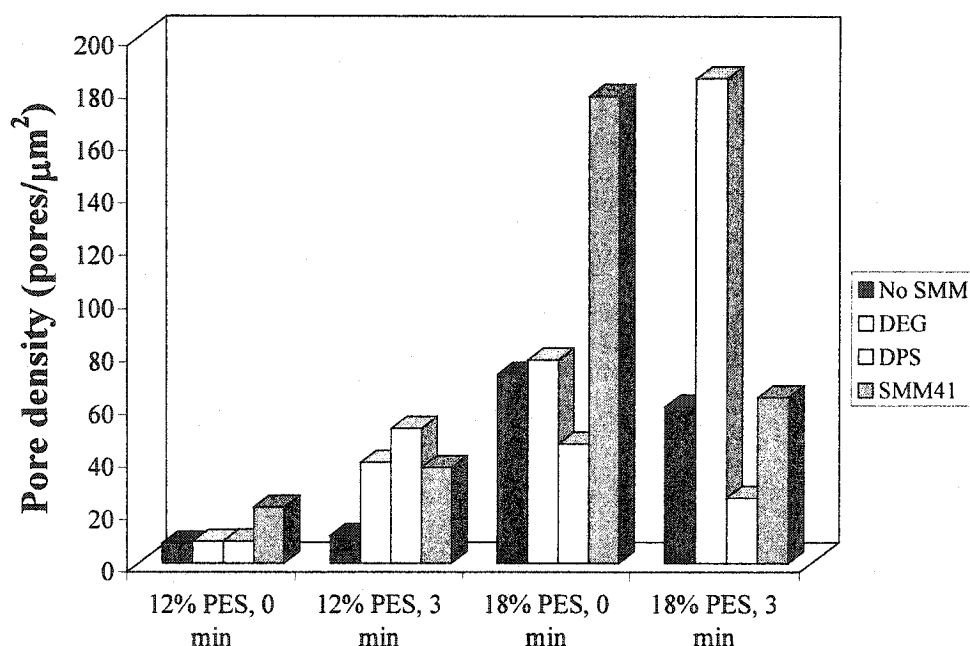


Fig. 5.6 Pore density for membranes prepared under several manufacturing conditions, with different SMMs: No SMM, DEG, DPS, SMM41

No clear trend was observed for pore density when increasing solvent evaporation time, however in general, an increase of PES concentration in the casting solution caused an increase of pore density. Porosity was similar for all membranes, except for the very tight membranes prepared with 18 wt % PES and 3-minute solvent evaporation time (Fig. 5.7). Porosity generally decreased with increasing solvent evaporation time. For membranes with no solvent evaporation time, in most cases porosity remained constant when PES

was increased from 12 to 18 wt %. On the other hand, for membranes prepared with 3-minute solvent evaporation time the porosity decreased, when PES concentration in the casting solution was increased. No clear effect of SMM on porosity was observed, i.e., sometimes porosity increased upon surface modification, but sometimes it decreased.

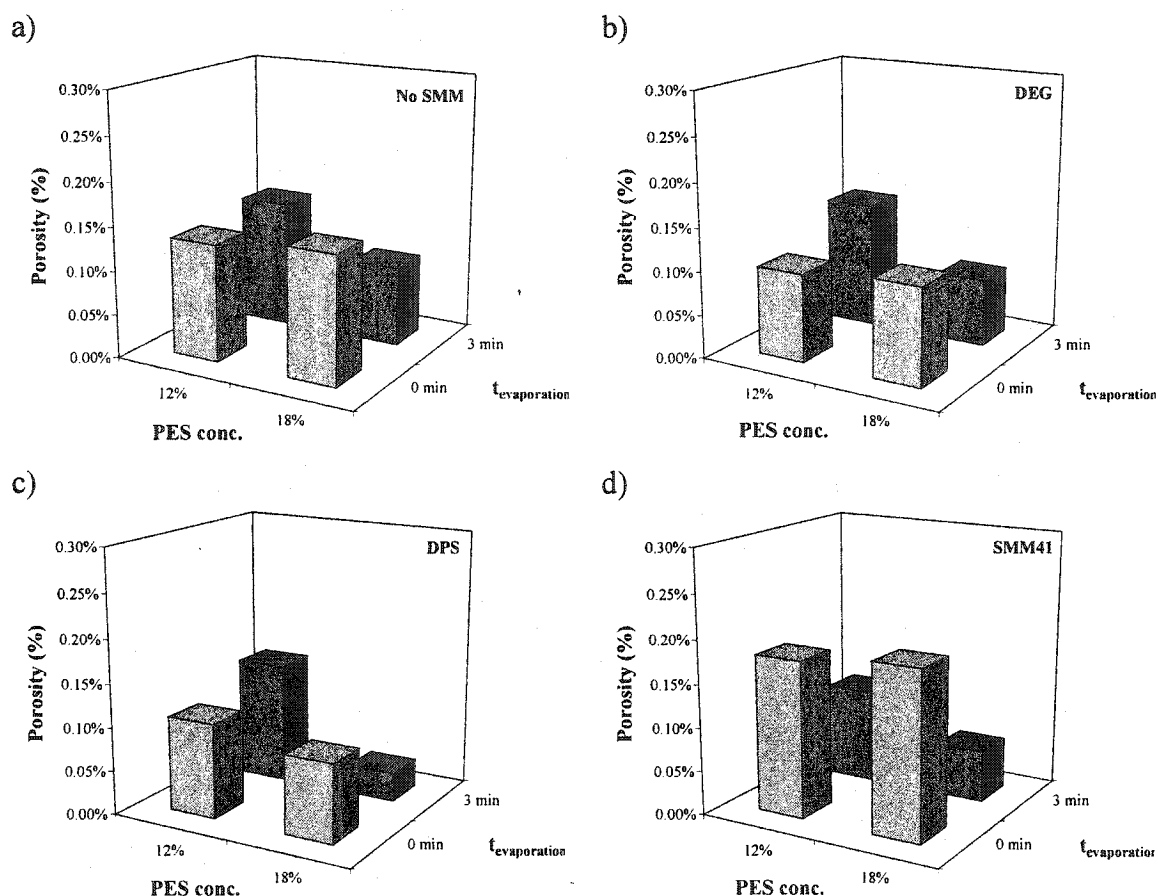


Fig. 5.7 Porosity for membranes prepared under several manufacturing conditions, with different SMMs: a) No SMM, b) DEG, c) DPS, d) SMM41

5.4.1.4 SMM Migration

SMM migration to the surface was corroborated through measurements of fluorine content with XPS, at two different depths. The amount of fluorine increased with the proximity to the surface. Figure 5.8 represents the ratio of fluorine concentration at a depth of 3.15 nm with respect to the concentration at 6.3 nm. It demonstrates the SMM migration since ratios were always higher than 100%. Although the experimental variation was high, a general trend is observed, migration increased with an increase of solvent evaporation time, with a decrease of PES concentration, and with the use of

SMM41. Because the % F in each of the SMMs was different, these results might mislead the comparison of the migration with different SMMs. The levels of migration observed in this study differed from the results obtained by Mandeep (2001). SMMs analyzed correspond to different batches; however, it is believed that the disagreement was mainly due to the significantly longer time allowed for migration by Mandeep (2001). Hence, it was demonstrated that the kinetics of migration played a very important role in the results of both studies, as determined by Suk et al. (2002).

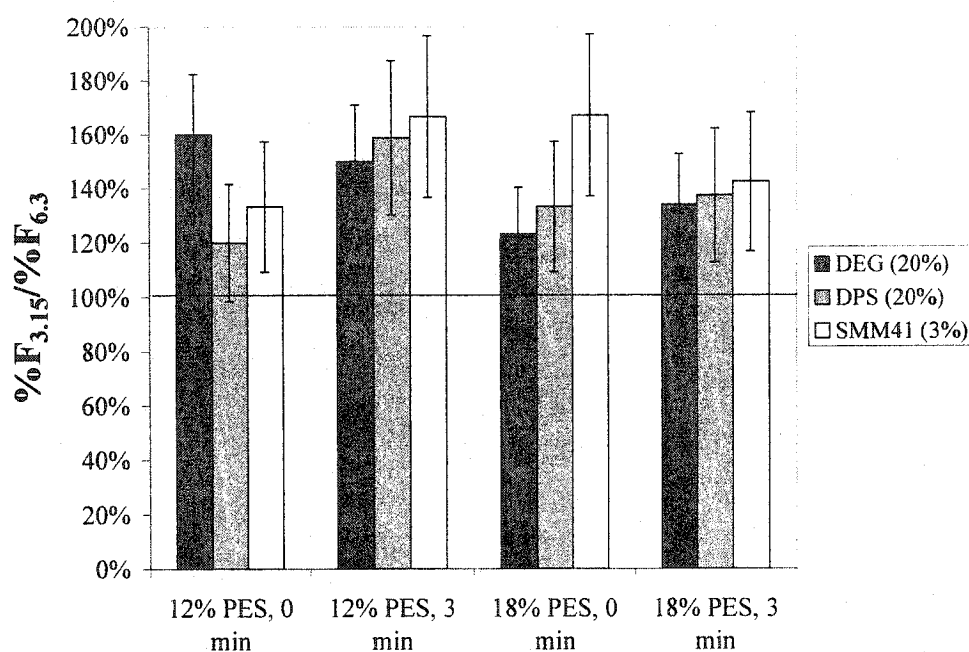


Fig. 5.8 SMM migration to the surface. Ratio of fluorine concentration at two different depths. Numbers in brackets represent the fluorine content in each SMM

5.4.2 Membrane performance parameters

5.4.2.1 Solute separation

The probe solute was PEG with a nominal molecular weight of 35,000 Daltons. Solute separation, as pore size, was affected by all three independent variables, together with two two-factor interactions: time $\times$ PES conc. and PES conc. $\times$ SMM (Table 5.3). From the time $\times$ PES conc. plot, in Fig. 5.9a, it is observed that the increase of solute separation with solvent evaporation time was very evident with 12 wt % PES-membranes. Furthermore, when PES concentration was increased to 18 wt % PES, membranes

prepared with no solvent evaporation time or 3-minute solvent evaporation time, increased significantly the solute separation, reaching a maximum solute separation (while membrane pore size is minimum, Fig. 5.3a) of this experiment. The effect of solvent evaporation time was significant only when the PES concentration in the casting solution was 12 wt %. On the other hand, from the PES conc. $\times$ SMM plot, in Fig. 5.9b, it was concluded that no matter which SMM was used (even with No SMM), casting solutions with 18 wt % PES give membranes with higher solute separation (these membranes had smaller pore size, according to Fig. 5.3b). Solute separation was significantly improved by surface modification only in the case of membranes with 12 wt % PES (average results are presented in Fig. 5.9b).

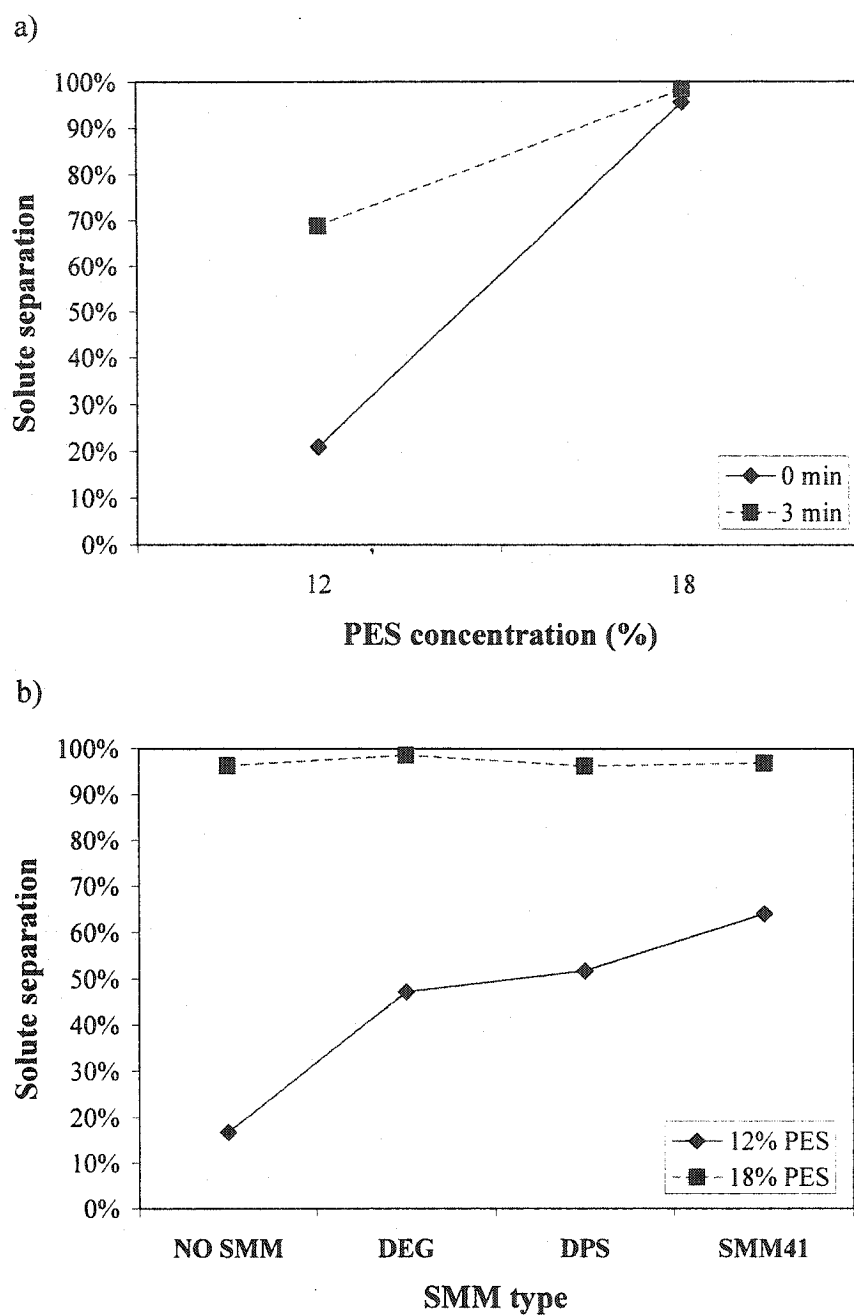


Fig. 5.9 Two-factor interaction plots for solute separation (PEG 35 kDaltons): a) Time $\times$ PES; b) PES $\times$ SMM

5.4.2.2 PWP

UF membrane permeability is conceptually related to its pores. Changes of PWP with solvent evaporation time, PES concentration, and surface modification basically followed the same trends as porosity (Fig. 5.7). In general, PWP decreased by increasing solvent

evaporation time, and/or increasing PES concentration. These observations are in accordance with the effects indicated by Kesting (1985). Several authors have observed the same kind of effects when testing different base polymers (Borneman et al. (1997); Tweddle et al. (1983)). Mulder (1991) explained that the increase of polymer concentration in the casting solution implies a higher volume fraction of polymer, leading to a lower porosity, and consequently, a decrease in flux. Mohamed (1997) indicated that longer evaporation times result in less residual solvent, decreasing the cell size (Kesting, 1985), which causes a membrane with denser structure, with smaller porosity, and with lower permeability.

From the results of the ANOVA test in Table 5.3, it can be observed that only PES concentration had a significant effect on PWP, i.e., the lower the PES concentration in the casting solution the membrane had a higher PWP (Fig. 5.10b). However, membranes with high PWP showed a low solute separation. SMM41-modified membranes and unmodified membranes had higher PWP (Fig. 5.10c) than membranes prepared with other SMMs.

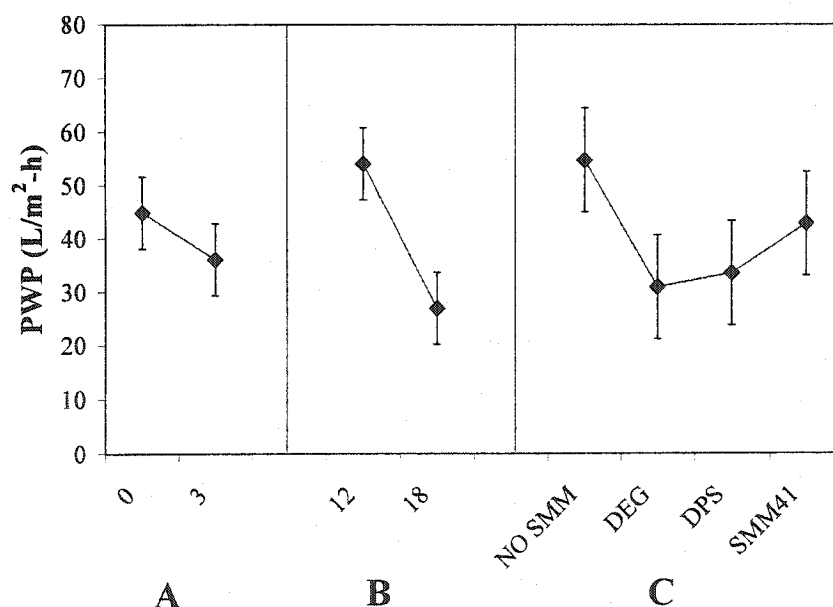


Fig. 5.10 Main effects of independent variables on PWP. A = Solvent evaporation time (min), B = PES concentration in the casting solution (wt %), C = SMM

5.4.2.3 Membranes with PVP

In Fig. 5.11, results for the morphological and functional parameters of the membranes prepared during the second stage of experiments with PVP-containing membranes, are compared with their counterpart membranes from the first stage. Note that only SMM41 was used during the second stage (i.e., impact of PVP) because of its superior miscibility and higher PWP in stage 1-experiments. Adding PVP to the casting solution significantly increased the MWCO, however the differences between the membranes prepared with 6 wt % PVP and those prepared with 18 wt % were not statistically significant (Fig. 5.11a). In the case of the unmodified membranes (without SMM), pore density remained almost constant with PVP addition, while for the SMM41-modified membranes the number of pores decreased (Fig. 5.11b) when increasing PVP concentration. A statistically significant increase on PWP with PVP was detected (Fig. 5.11d). This increase of PWP was explained by the increase of porosity observed in Fig. 5.11c, meaning that even though the number of pores remained constant or decreased with PVP in the casting solution, the total area of the pores increased, because the size of the pores increased. In turn, this increase on the pore size caused a decline of the solute separation as observed in Fig. 5.11e. Several authors have studied the effect of PVP on the PWP and have found a maximum PWP at different PVP/PES ratios. When using different PVP/PES ratios at different levels of PES, Lafrenière et al. (1987) found a maximum on the permeation rate, when PVP/PES was 1.0 at three different PES concentrations (i.e., 15, 20 and 25%). On the other hand, Jacobs et al. (1992) found the maximum at PVP/PES ratio of 1:4.5 and Torrestiana-Sanchez et al. (1999) at PVP/PES ratio of 1:4. It is believed that differences in ratios with a maximum PWP are due to variations in other manufacturing variables, e.g., solvent evaporation time, gelation temperature, etc. In this study, a further point would have been necessary to identify the real maximum, since the PWPs at PVP/PES ratios of 1:3 to 1:1 were statistically the same (at a 95% level of confidence).

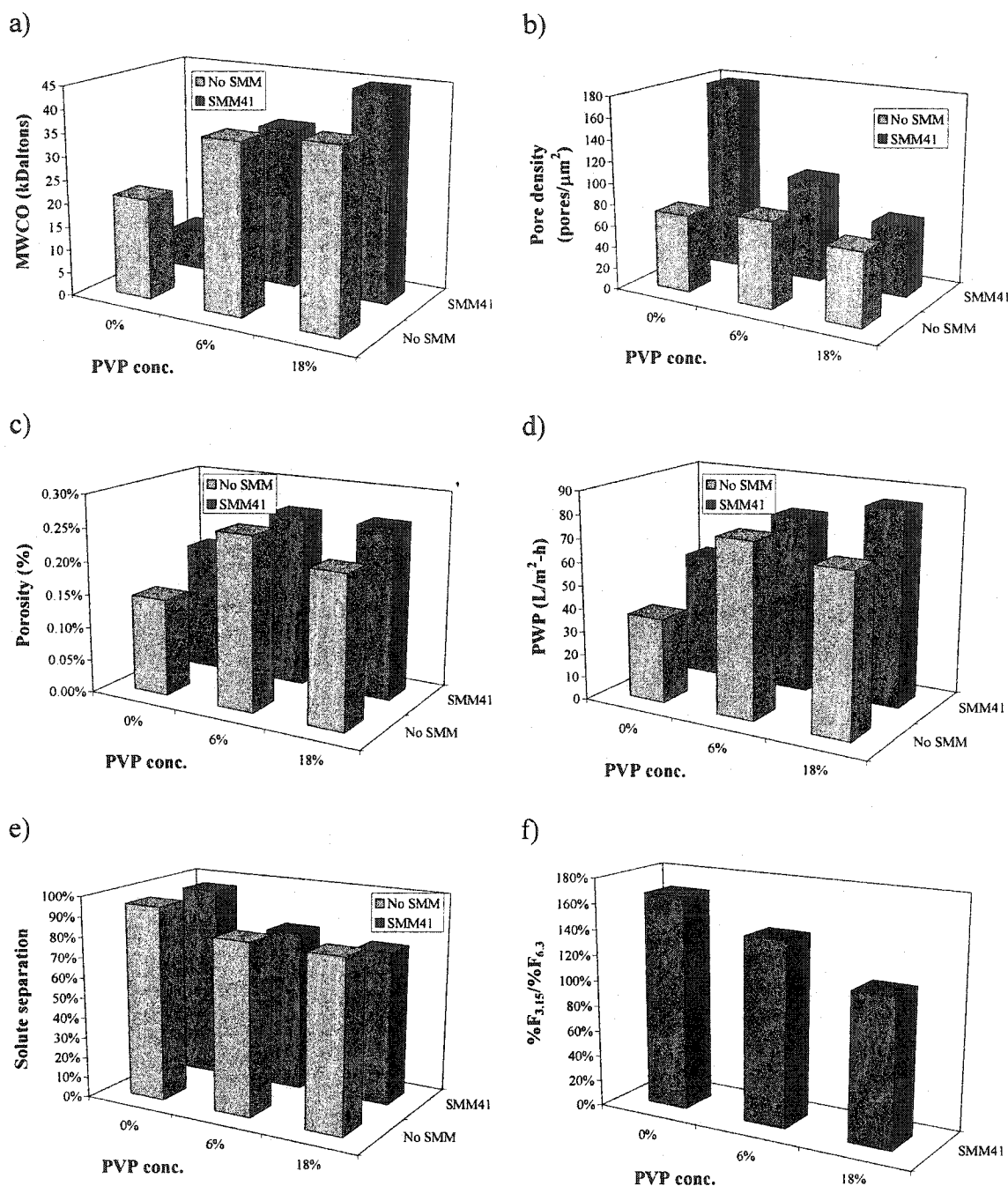


Fig. 5.11 Comparison between characteristics of the membranes prepared during the second stage, with those prepared on the first stage

Figure 5.11f shows a reduced SMM migration (expressed as the ratio of fluorine concentration at a depth of 3.15 nm with respect to the concentration at 6.3 nm), observed when the amount of PVP was increased in the casting solution. This is believed to be due

to the consequent increase of viscosity, although for the validation of the latter additional studies will be necessary.

5.4.3 Relationship between morphology and performance parameters

The relationship between PWP versus surface porosity and solution separation versus mean pore size is presented in Figures 5.12 and 5.13, respectively. Results for the membranes prepared with PVP and without solvent evaporation time are presented in these figures as the full diamonds. These PVP membranes proved to follow the same trend as the membranes with no PVP with or without solvent evaporation time. However, the PVP membranes tended to be among the better performing membranes in terms of PWP. On the other hand, Fig. 5.13 shows that membranes with and without SMM, and with or without PVP follow the same trend indicating that the interaction forces between solute and membrane material are not significantly different. Solute separations for membranes with PVP were in the range between 73 and 84%, while tighter membranes prepared without PVP achieved higher solute separations.

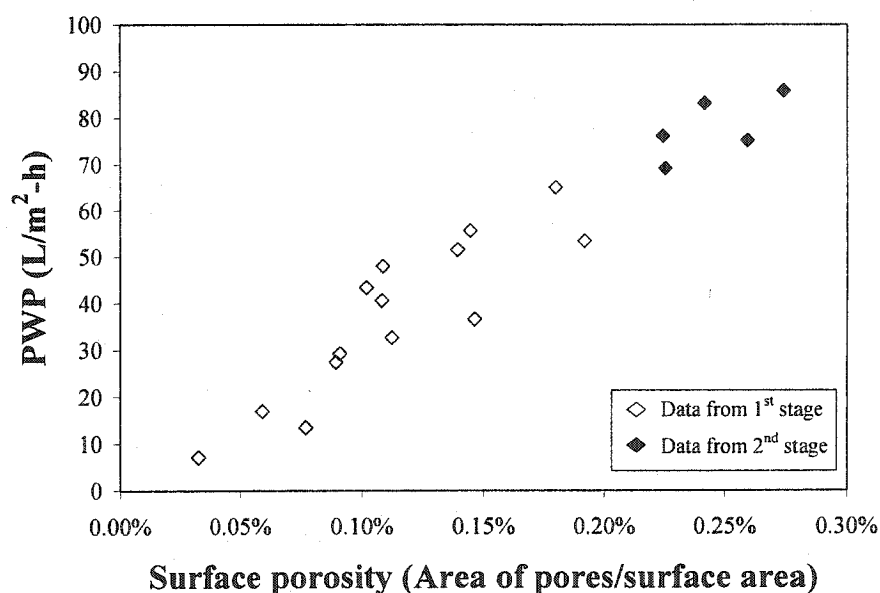


Fig. 5.12 Pure water permeation (PWP) for membranes prepared without (open symbols) and with (closed symbols) PVP

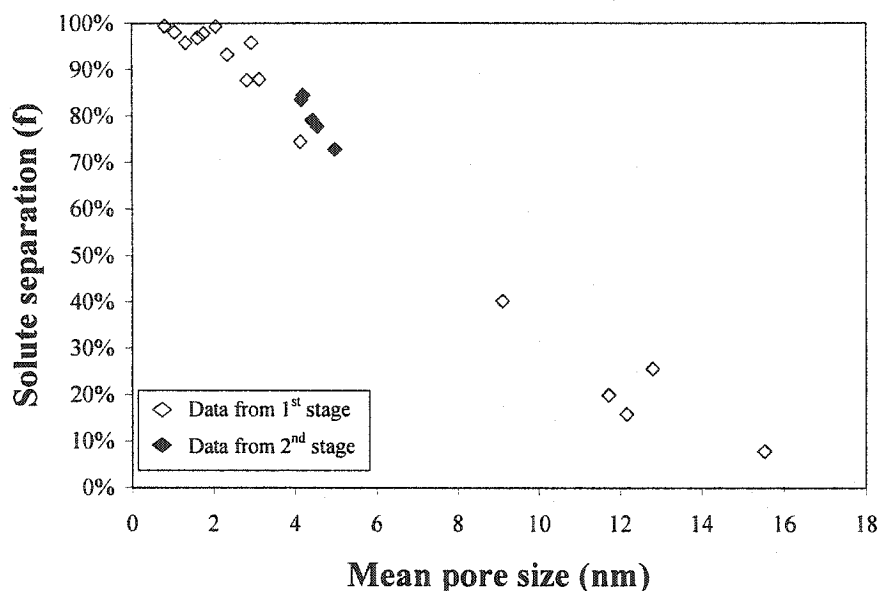


Fig. 5.13 Solute separation (PEG 35 kDaltons) for membranes prepared without (open symbols) and with (closed symbols) PVP

The cross-sectional area of some of the membranes prepared during the first stage are shown in the SEM-micrographs of Fig. 5.14. (See Appendix I for more details). General structures were very similar, consisting of a bottom layer of fully developed macropores, an intermediate layer with a finger-like structure, and a skin layer on top. The size and amount of macropores decreased with solvent evaporation time and with PES concentration in the casting solution. Morphologies of the unmodified (without SMM) and modified membranes were very similar, except in the case of the tighter membranes prepared by surface modification with 18 wt % PES and 3-minute solvent evaporation time (Fig. 5.14h), where macrovoids were almost totally eliminated. SEM-micrographs of PVP membranes are presented in Fig. 5.15. There were no appreciable morphological variations between the membranes without PVP (Figures 5.15a and 5.15b) and the membranes with low PVP content (Figures 5.15c and 5.15d). However, the membranes with high PVP content (i.e., PVP/PES = 1:1) (Figures 5.15e and 5.15f) showed a relatively suppressed macropore structure at the bottom of the cross section. In addition, they had a much thicker sponge-like layer immediately below the skin layer that was much less dense than the no- and low-PVP membranes (Figures 5.16a-5.16f). A larger finger-like type of structure was observed when the presence of macrovoids was suppressed. It was not possible to conclude if these structural differences had an effect on

PWP and MWCO, since membranes with low and high PVP content (PVP/PES ratios 1:3 and 1:1, respectively) had statistically the same PWP and MWCO. Again, no appreciable difference was observed between the surface-modified membranes and the membranes without SMM.

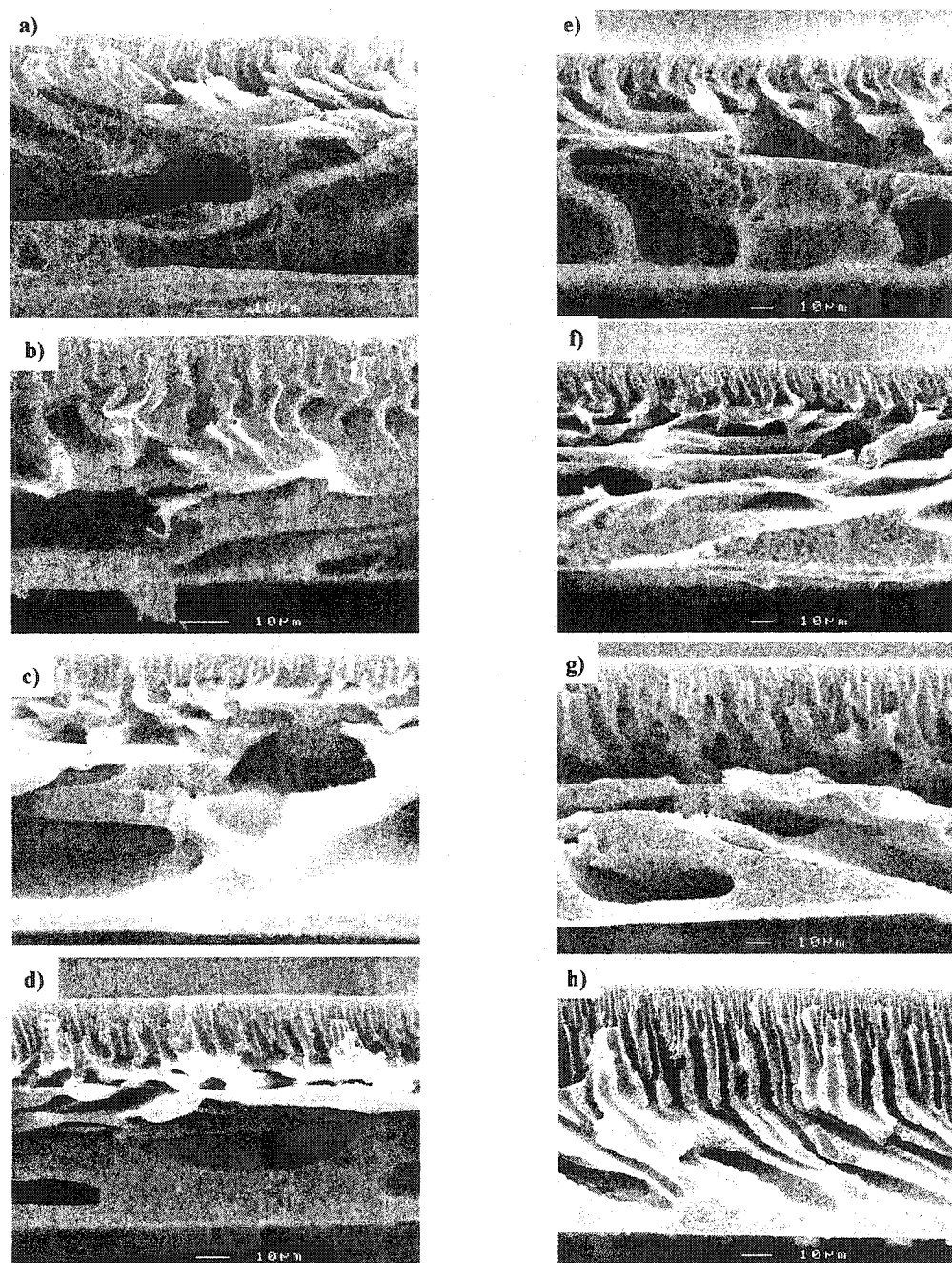


Fig. 5.14 SEM cross-section of the UF membranes prepared without SMM a) 12% PES, 0 min evaporation time, b) 12%, 3 min, c) 18%, 0 min, d) 18%, 3 min. Membranes with SMM41 and e) 12% PES, 0 min, f) 12%, 3 min, g) 18%, 0 min, h) 18%, 3 min

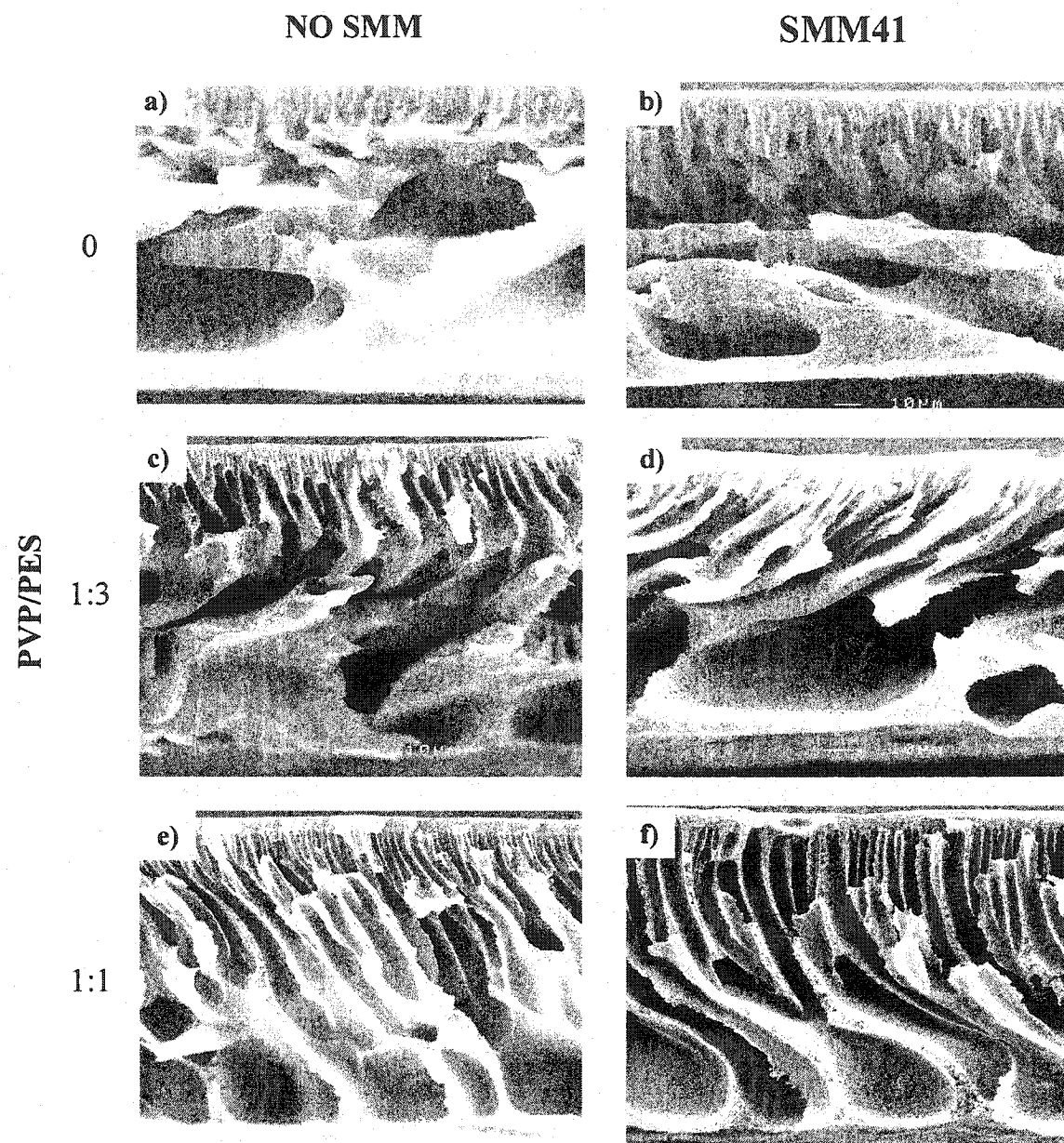


Fig. 5.15 SEM cross-section of the UF membranes prepared without PVP, with and without SMM41, a) and b) respectively; PVP/PES ratio 1:3, with and without SMM41, c) and d) respectively; PVP/PES ratio 1:1, with and without SMM41, e) and f) respectively

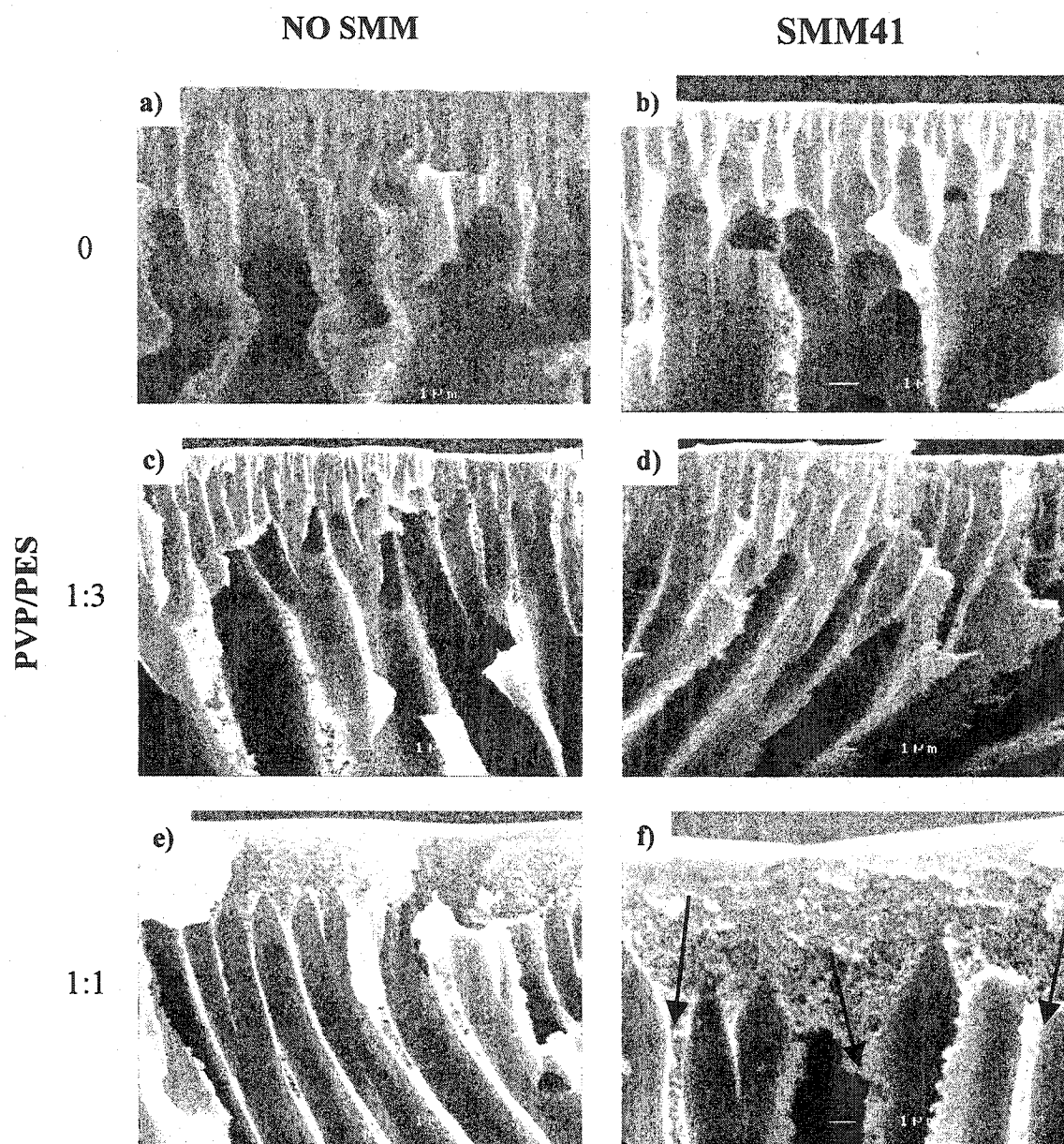


Fig. 5.16 Magnified SEM cross-section of the top layer of UF membranes without PVP, with and without SMM41, a) and b) respectively; PVP/PES ratio 1:3, with and without SMM41, c) and d) respectively; PVP/PES ratio 1:1, with and without SMM41, e) and f) respectively

Recently, Han and Nam (2002) explained a similar phenomenon that they observed when using polysulfone (PS) and PVP dissolved in NMP as membrane casting solution. As a nonsolvent additive, PVP produces two opposite effects. It reduces the miscibility of the casting solution with water (used as nonsolvent during the phase inversion), which causes the thermodynamic enhancement of the phase separation. However, at the same time, it

increases the viscosity of the solution (rheological factor), which causes kinetic hindrance against phase separation. Depending on the PVP content, the thermodynamic or the rheological factors will have a more important impact on the morphology and performance of the membrane. Han and Nam (2002) found that when using polysulfone and PVP concentrations of 15 and 5%, respectively, the thermodynamic property controlled the demixing process enhancing the phase separation of the solution and increasing PWP. When PVP was further increased, the rheological factor was more important than the thermodynamic, causing a delay of the solution demixing and decreasing the PWP. Based on these results, Han and Nam (2002) found the maximum on PWP at a PVP/PS ratio of 1:3. Kesting (1985) identified macrovoids (with different shapes, such as tear dropped, spherical, ellipsoidal, or fingerlike) as weak spots within the gel matrix. He suggested that macrovoids should always be avoided whenever possible; and when they are located near the high-pressure surface, they represent areas of potential rupture. Furthermore macrovoids make membranes more susceptible to compaction upon pressure application (Persson et al., 1995). Kesting (1985) also stated that normally, fingerlike cavities have skinned interior surfaces, which makes them useless dead space with no permeation. The actual permeation pathways are the very narrow porous structure underneath the skinned fingerlike cavities (Fig. 5.16f). Addition of PVP to the casting solution at a certain ratio would consequently help to reduce the presence of macrovoids. In this study, a PVP/PES ratio of 1:1 reduced the presence of macrovoids in the support layer, but it also produced the formation of a thick porous sublayer immediately below the skin layer.

5.5 Conclusions

1. The mean pore size and MWCO of the membranes were decreased either by increasing the PES concentration in the casting solution or by increasing the solvent evaporation time. However, the effect of the PES concentration was more important than that of the evaporation time. MWCO of the surface modified membranes was smaller than that of their unmodified counterparts.

2. The PEG separation was inversely proportional to the membrane mean pore size. Therefore, both parameters were affected by the same manufacturing variables. Membranes with 18 wt % PES in the casting solution achieved a maximum solute separation, which was independent of the solvent evaporation time.
3. There was clear evidence that the fluorine-containing SMMs migrated to the surface of the membrane. The character of the SMMs as surface active agents decreased the size of the pores, but increased the number of pores per unit area. PWP of the SMM41-modified membranes during the first stage was statistically the same as that of the unmodified membrane (without SMM). In membranes prepared with PVP, surface modification did not have a statistical effect on any of the response variables.
4. In general, the additive PVP increased the MWCO and PWP of the membranes. However, at the same time, the average solute separation decreased around 15%.

5.6 Acknowledgements

We acknowledge Materials and Manufacturing Ontario (MMO), Natural Sciences and Engineering Research Council of Canada (NSERC) and CONACyT (Mexico) for their financial support.

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Notation

A = solvent evaporation time (factor with two levels: 0, 3 min)

a = Stokes radius

B = PES concentration in the casting solution (factor with two levels: 12, 18%)

C = SMM (factor with four levels: No SMM, DEG, DPS, SMM41)

d_s = solute diameter

$f(\%)$ = solute separation of an ultrafiltration membrane

f_i = fraction of pores with diameter d_i .

GSD = geometric standard deviation

J = total flux

J_i = solvent flux

M = molecular weight

N = pore density (number of pores per unit area)

N_i = density of pore with diameter d_i

P-value, associated with a calculated F ratio = the area under the F distribution to the right of the calculated F ratio (Devore and Farnum, 1999).

PWP = pure water permeation rate.

S_p = surface porosity (ratio of the area of pores to the total membrane surface area)

ΔP = pressure difference across the pores

α = significance level related to the probability of rejecting a true hypothesis

δ = length of the pores, considered equivalent to the thickness of the skin layer (no tortuosity)

η = solvent viscosity

μ_p = geometric mean pore size

μ_s = geometric mean diameter

σ_p = geometric standard deviation about the mean pore size

σ_s = geometric standard deviation about the mean diameter

CHAPTER 6

EFFECTS OF MANUFACTURING CONDITIONS OF SMM-MODIFIED MEMBRANES: ON ULTRAFILTRATION PERFORMANCE

D. B. Mosqueda-Jimenez¹, R. M. Narbaitz², T. Matsuura³

6.1 Abstract

The treatment of a surface water was studied using different experimental ultrafiltration (UF) SMM-modified polyethersulfone (PES) membranes. They were prepared adjusting three membrane-manufacturing variables: addition of three surface modifying macromolecules (SMMs), the solvent evaporation time, and the PES concentration in the casting solution. Membrane performance was evaluated in terms of TOC removal, the amount of natural organic matter (NOM) deposited on top of the membrane after filtration, the permeate flux, and the flux reduction. In order to define the manufacturing conditions resulting in the “best membrane”, in addition to the performance results, other considerations such as membrane strength and SMM compatibility were necessary. SMM41 proved to have a positive effect on the treatment of this particular surface water. A trade-off between TOC removal and permeate flux, and a logical connection between membrane characteristics and performance were observed. Membranes with small molecular weight cut-off (MWCO) (and pore size) had high TOC removals and low permeate fluxes, consequently, flux reduction was small.

Key words

Ultrafiltration, surface water, surface modification, fouling, TOC removal,

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6.2 Introduction

Membranes represent an alternative technology for drinking water treatment whose application has lately increased exponentially, since it has become economically competitive with conventional water treatment (Schäfer, 2001). Numerous studies have demonstrated that nanofiltration (NF) membranes can successfully remove natural organic matter (NOM) (Tan and Sudak, 1992; Fu et al., 1994; etc.), while the more porous microfiltration (MF) and ultrafiltration (UF) membranes can only remove between 5 and 30% of the NOM in water (USEPA, 1999). In addition to imparting color to water and reacting with chemical disinfectants to form toxic disinfection by-products (DBPs), NOM can cause other problems at water treatment plants. NOM significantly reduces the toxic compound adsorption capacity of activated carbon beds and exerts an additional demand for chlorine and other oxidants (Amirtharajah and O'Melia, 1990). NOM also causes severe reductions of permeate flux with time in membrane processes, a phenomenon referred to as fouling. The modification of the membrane surface is an attractive approach in the reduction of membrane fouling. Carroll et al. (2002) mentioned two different ways to modify the surface of polyethersulfone (PES) membranes: physical coating with hydrophilic surfactants and chemical graft-polymerisation of hydrophilic monomers. In addition to disadvantages associated with these techniques (such as, reduction of rejection and water permeability, (Carroll et al., 2002)), the preparation of these membranes requires additional membrane manufacturing steps.

The use of tailor-made surface modifying macromolecules (SMMs) compatible with PES allows the surface modification of PES membranes in a single-step casting procedure. Membranes prepared with hydrophobic SMMs have proven to be less susceptible to fouling in oil/water emulsions separation (Hamza et al., 1997), and to enhance the mechanical strength of PES membranes (Suk et al., 2002b). These SMMs, with a PES-like structure and hydrophobic end groups, were specifically designed and synthesized to achieve a uniform SMM distribution at the membrane surface and give membranes a more hydrophobic surface.

The aim of this work was to study the effect that three different hydrophobic additives (i.e., SMMs) and the manufacturing conditions (employed during the phase-inversion casting procedure) had on the treatment of a surface water. The performance of the modified-UF membranes is compared with their unmodified counterparts in terms of TOC removal, the amount of NOM deposited on top of the membrane after filtration, the final permeate flux, and the flux reduction.

6.3 Experimental methods and analysis

6.3.1 Materials

PES (Victrex 4100P, ICI Advanced Materials, Billingham, Cleveland, England) 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 SMMs employed in the surface modification were referred to as DEG, DPS, and SMM41. The chemical structure of these SMMs only differs from each other in the type of polyol used in their synthesis; however each one of them has a similar functional group to those of the base polymer, PES. Diethylene glycol and polypropylene diol (PPO) used for the preparation of SMMs DEG and SMM41, respectively, possess an ether group, while dihydroxy diphenyl sulfone, used in manufacturing SMM DPS, contains a sulfone group. Moreover, as PES has aromatic groups in its chemical structure, the diisocyanate used in the SMM synthesis also contains them. DEG and DPS, were synthesized according to the method developed by Mandeep (2001), while SMM41 was synthesized according to the method outlined in Ho et al. (2000). The three SMMs were tested to determine if any of them improved the performance of UF membranes in terms of fouling reduction. 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 June 6, 2000, and concentrated five-fold to accelerate the fouling evaluations (Mosqueda-

Jimenez et al., 2003a). The concentration was accomplished via a portable reverse osmosis system (RealSoft, Norcross, GA), which included a pre-filter and a composite membrane (FT30, Filmtec Membranes, Midland, MI). The concentrated Ottawa River water is referred to as CORW.

6.3.2 Membrane preparation

Flat-sheet membranes were cast using the phase inversion technique described by Matsuura (1994) with PES, SMM, and NMP as ingredients of the casting solutions. The concentration of SMM in the polymer solution was kept constant for all modified membranes at 1.5 wt %, the concentration of PES was either 12 or 18 wt %, and the remaining percentage was NMP. PES concentration levels were chosen based on the solubility of the least soluble SMM, i.e., 18 wt % was the maximum PES concentration that produced a clear solution with DPS. Filtered homogeneous solutions were degassed and then cast on smooth glass plates (250- μ m (10 mils) thickness). In the preparation of half of the membranes no solvent evaporation time was allowed, for the other half the glass plate was placed inside a 95°C oven for a 3-minute evaporation period. A summary of the manufacturing variables evaluated in this study is presented in Table 6.1. After the solvent evaporation period (or immediately after the membrane film was cast, in the case of the membranes without solvent evaporation time), the glass plate was immersed into ice-water at 4°C for at least 1 h. The hardened membranes were eventually peeled from the glass plate and after the gelation period membranes were stored in ultra pure water until they were used. Each 22 $\times$ 28 cm membrane sheet produced one or two defect-free 51-mm diameter coupons.

Table 6.1 Values of the key membrane manufacturing variables evaluated in this study

<i>Membrane ID</i>	<i>Solvent evaporation time (min)</i>	<i>PES Concentration (wt %)</i>	<i>Additive</i>
A1	0	12	No Additive
B1	3	12	No Additive
C1	0	18	No Additive
D1	3	18	No Additive
A2	0	12	DEG
B2	3	12	DEG
C2	0	18	DEG
D2	3	18	DEG
A3	0	12	DPS
B3	3	12	DPS
C3	0	18	DPS
D3	3	18	DPS
A4	0	12	SMM41
B4	3	12	SMM41
C4	0	18	SMM41
D4	3	18	SMM41

6.3.3 Analysis

Physicochemical characteristics of the test water were determined using standard methods (Standard Methods, 1995). TOC 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, ultra pure water was used as a blank. UV absorbance was used as TOC surrogate since they are linearly related (see Appendix N).

Contact angles were determined using the sessile drop technique with a 20- μ L droplet of distilled water and a standard goniometer apparatus (Ramé-Hart, model 100, Mountain

Lakes, NJ). The values of the advancing and receding angles reported were the average of at least 10 measurements.

The apparent molecular weight distribution (AMWD) of the organic matter within the ORW was determined by UF fractionation using a 50-mL batch stirred UF cell (model 8050, Amicon Corp., Danvers, MA), and regenerated cellulose membranes (Millipore, Bedford MA) with four different nominal molecular weight cut-offs (MWCO): 5,000, 10,000, 30,000, and 300,000 Daltons. The fractionation was conducted following the procedure outlined in Amy et al. (1987).

6.3.4 Testing protocol

The 51-mm diameter membrane coupons were placed in random order in a six-cell in-series system (Fig. 6.1). 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., 2003a). The existence of a possible cell effect or cell order effect within the cells in-series was disproved using an analysis of variance (ANOVA) test of a greco-latin square design, as the effects of these variables were not statistically significant (See Appendix E). The UF cells were operated within a recirculation system consisting of a feed reservoir, a high pressure diaphragm pump (Hydra-Cell, Wanner Engineering, Inc.; Minneapolis MN), 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 feed concentration constant. 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); 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 recirculation to the feed reservoir. The temperature of the water in the refrigeration unit ranged between 10 and 15°C, depending on the season and the time of the day. 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.

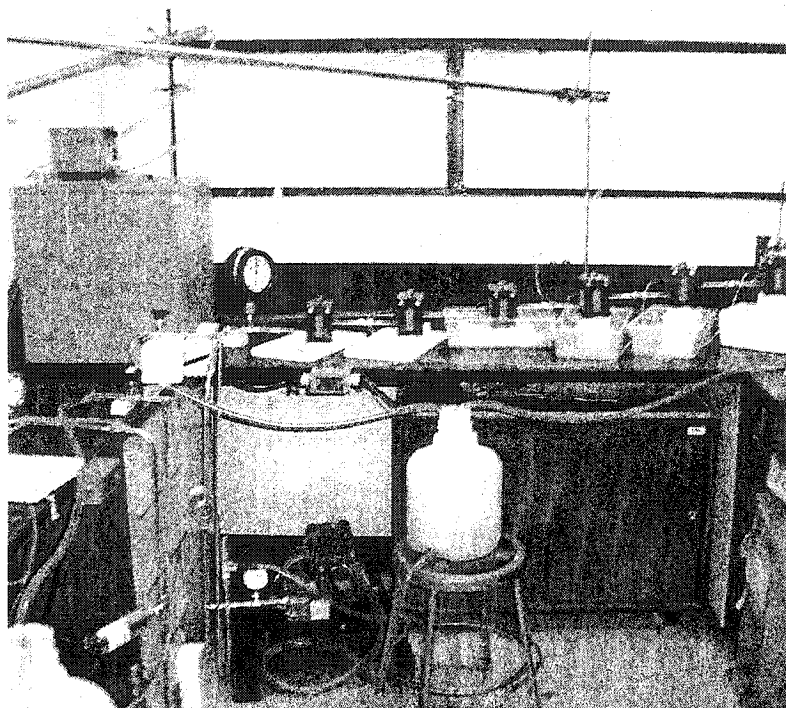


Fig. 6.1 Experimental set-up

Figure 6.2 shows the flow chart of the membrane test protocol. Operating conditions were determined through preliminary tests trying to reach stable fluxes (less than 1% change per hour) in as short a time as possible (See Appendix D). Prior to each run, the membranes were subjected to a precompaction step consisting of filtration of ultra pure water through each new coupon at 620 kPa (90 psig) for 52 h. Next, the pure water permeation rate (PWP) was determined during a period of 50 h under a 345 kPa (50 psig) operating pressure using ultra pure water. This was considered the second stage of the test. Then, the UF membranes were characterized based on solute transport data of 5 solutions prepared with polyethylene glycol (PEG) (Sigma Chemical, St. Louis, MO), or polyethylene oxide (PEO) (Aldrich Chemical, Milwaukee, WI) with molecular weights in the range of 300 to 200,000 Daltons. MWCO was calculated based on separation data of these probe solutions (Mosqueda-Jimenez et al., 2003b). After completion of the membrane characterization, the membranes were ready for the fourth phase of the test,

which involved filtration of CORW. The permeation rate (PR) of CORW was measured at a feed flow rate of 1.1 Lpm and an operating pressure of 345 kPa (50 psig) during six days of continuous operation. The permeation rates were measured at different intervals, and feed and permeate samples were collected to assess the TOC removal. The amount of NOM accumulated on top of the individual membranes at the end of the six-day test (referred to as NOM deposition) was measured using the technique described by Hong and Elimelech (1997). In a second test, the same protocol was repeated with a second coupon of each of the membranes prepared under different manufacturing conditions, but during the fourth stage CORW was substituted by ultra pure water as the feed solution. This last test quantified the fraction of the flux decrease that can be attributed to further membrane compaction (Mosqueda-Jimenez et al., 2003a).

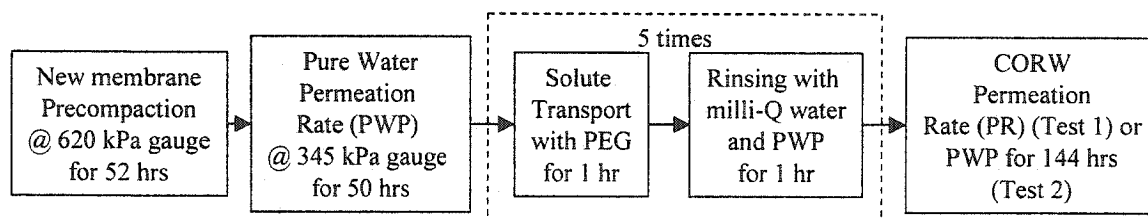


Fig. 6.2 Membrane test protocol

While this long multi-step testing protocol and its 50 h 90 psig precompaction stage may be considered unrealistic and harsh, it was developed to obtain long-term stable fluxes for PES membranes. Because of the intensive precompaction it is not reasonable to compare the PWP's from this study with those in the literature, as they are going to be lower.

6.3.5 Experimental Design

A $2 \times 2 \times 4$ multifactor design was used to evaluate the effect of the solvent evaporation time (0 or 3 min), the concentration of PES in the casting solution (12 or 18 wt %), and the absence or presence of three different SMMs in the casting solution (No Additive, DEG, DPS or SMM41). This design allowed the study of the interplay of the independent variables in each of the response variables with less experimental runs than a one-factor-at-a-time experiment would require (Devore and Farnum, 1999). The performance of the new membranes was evaluated in terms of (response variables): the percentage of TOC

removed, the amount of NOM deposited on the surface of the membrane, the permeate flux at the end of the six-day test, and the normalized flux reduction. Statistical calculations were performed using STATGRAPHICS Plus V. 7.0 (Statistical Graphics Corporation, Manugistics, Inc., Rockville MD).

6.4 Results and discussion

The characteristics of the test water (CORW) are presented in Table 6.2. In a previous study (Mosqueda-Jimenez et al., 2003a), it was found that the concentration process performed to obtain CORW not only increased the TOC concentration, but also increased the concentration of mono and divalent ions, and in turn, increased the alkalinity and hardness. According to Fig. 6.3, the apparent molecular weight distribution of the organic matter within ORW (Mosqueda-Jimenez et al., 2003a) was as follows. Close to 30% of the NOM was smaller than 5,000 Daltons; almost 60% of TOC of the NOM was in the molecular weight range of 10,000 to 30,000 Daltons, while less than 7% was higher than 30,000 Daltons.

Table 6.2 Ottawa River water quality characteristics

<i>Parameter</i>	<i>ORW</i>	<i>CORW</i>
TOC concentration (mg/L)	7	28
SUVA ($\text{m}^{-1}\text{mg}^{-1}\text{L}$)	3.4	3.9
Colour (cu)	30	180
pH	7.6	8.2
Alkalinity (mg/L as CaCO_3)	26	120
Turbidity (NTU)	0.8	0.3
Total hardness (mg/L as CaCO_3)	30	153
Calcium hardness (mg/L as CaCO_3)	22	122

ORW = Ottawa River water; CORW = Concentrated Ottawa River water

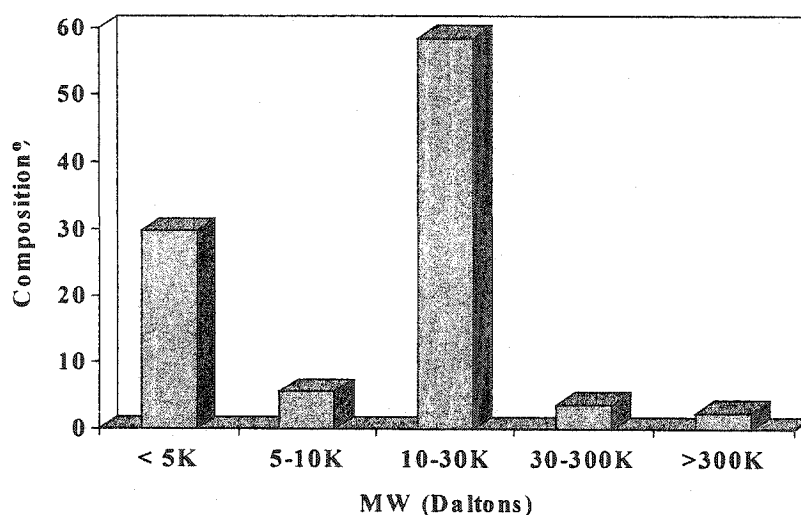


Fig. 6.3 AMWD of organic matter in ORW (Mosqueda-Jimenez et al., 2003b)

6.4.1 MWCO and PWP

MWCOs of the membranes determined by solute transport (PEG) are presented in Fig. 6.4. MWCO decreased either with an increase in solvent evaporation time, or with an increase in PES concentration in the casting solution, or by surface modification of the membrane (Mosqueda-Jimenez et al., 2003b). At the same time, Fig. 6.5 shows that in general, PWP decreased with increasing solvent evaporation time, and/or increasing PES concentration (Mosqueda-Jimenez et al., 2003b). Based on the results of multiple comparison tests (Least Significant Difference method (LSD), as explained by Montgomery, 1991), surface modification with DEG and DPS decreased PWP; however at a 5% level of significance, SMM41-modified membranes had statistically the same PWP as the unmodified membranes.

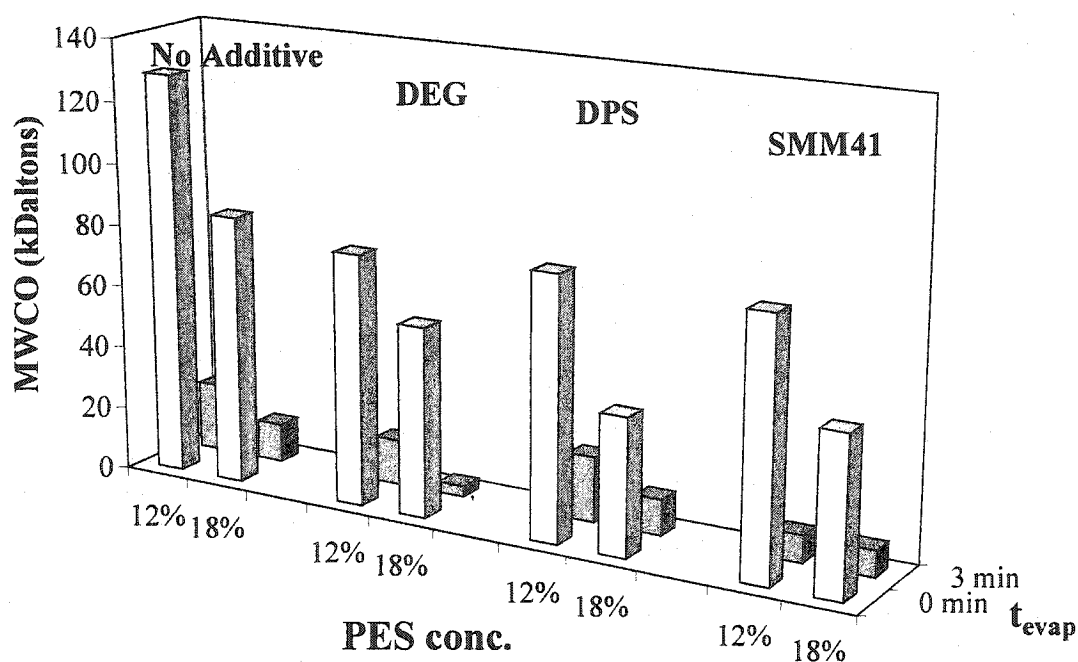


Fig. 6.4 MWCO of membranes prepared under different manufacturing conditions

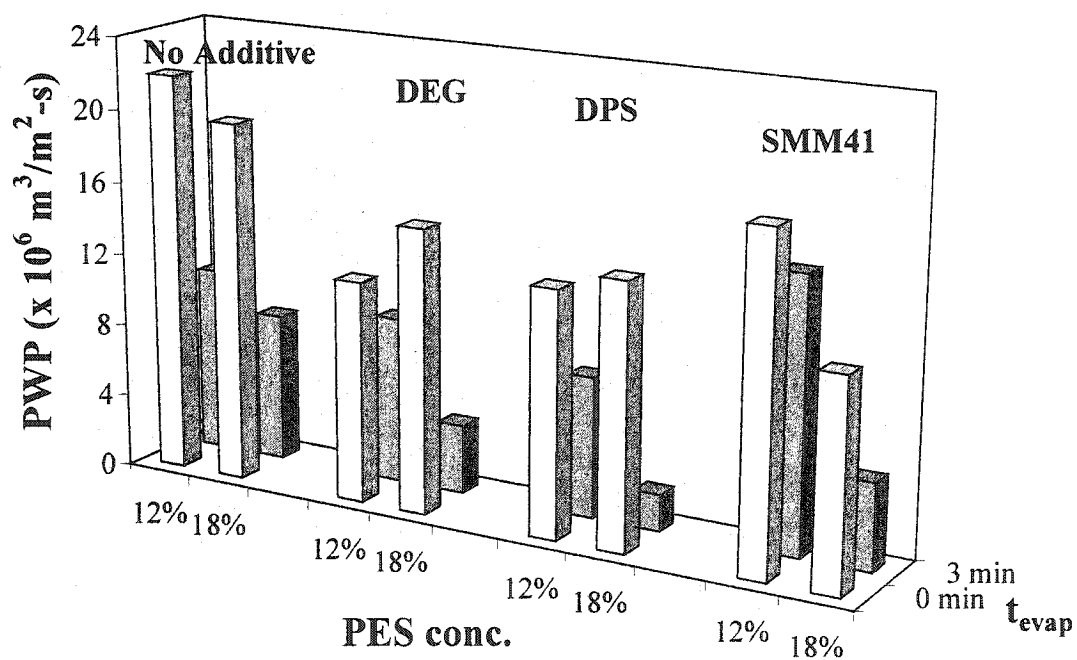


Fig. 6.5 PWP of membranes prepared under different conditions

6.4.2 TOC removal

TOC removal was calculated by the following equation:

$$TOC \text{ removal} = 100 \left(1 - \frac{C_{p(t)}}{C_f} \right) \quad (6.1)$$

where $C_{p(t)}$ is the permeate concentration at time t and C_f is the feed concentration (mass/volume). The TOC removal was evaluated during the fourth phase of the test, after completion of the precompaction, the 50-h PWP determination, and membrane characterization with solute transport data.

During the 6-day test, TOC removal changed with time, increasing up to 10% during the first 24 h, then, a steady value was reached. The steady value reached for each of the membranes prepared under different conditions is presented in Fig. 6.6. TOC removals ranged between 59 to 77%. Jacangelo et al. (1994) obtained less than 14% TOC removal in the ultrafiltration of Ottawa River water, and 83% when using a 400-600 Dalton MWCO NF membrane. The experimental membranes are tight UF membranes; therefore, fluxwise their performance was in the lower end of the UF range, close to that of the NF membranes. It is believed that the precompaction step used during the test protocol may have modified the structure of the membranes making them more similar to each other than they were right after casting. In general, when the solvent evaporation time was increased to 3 minutes, TOC removals increased slightly, except in the case of the DPS-modified membranes. On the other hand, a very slight increase was observed when PES concentration in the casting solution was increased from 12 to 18 wt %.

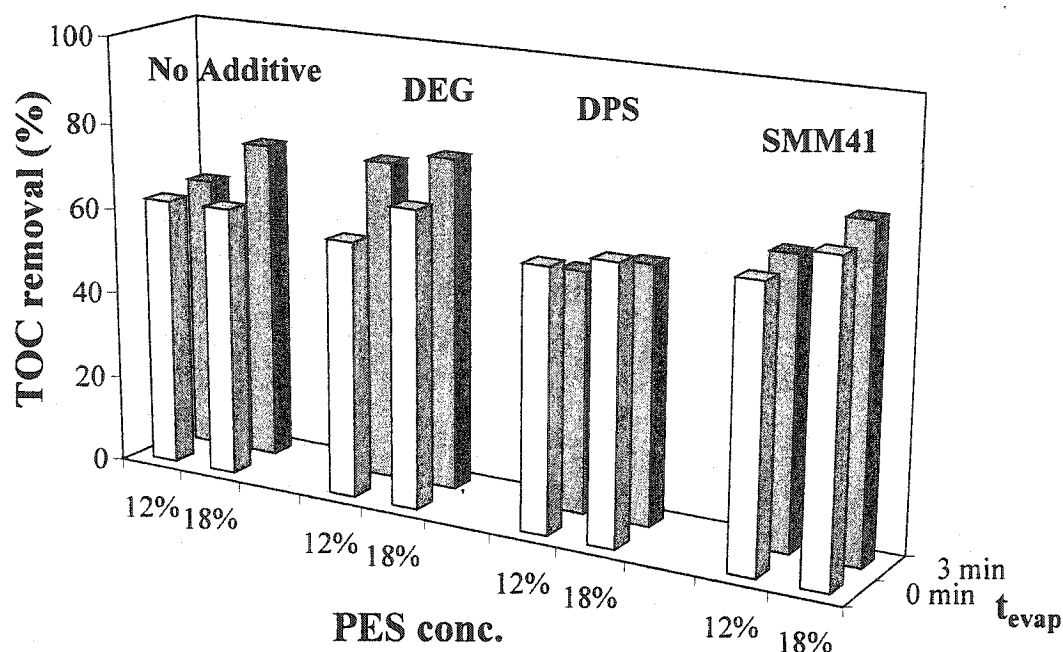


Fig. 6.6 TOC removal of membranes prepared under different manufacturing conditions

Given the AMWD of the organic matter in the ORW (Fig. 6.3), and assuming the sieving mechanisms controls NOM separation, membranes with MWCO around 10 kDaltons would achieve NOM removals in the range of 59 to 64%. However, the MWCO of the membranes with these removals was between 40 and 130 kDaltons, whilst membranes with higher removals (66 to 77%) had smaller MWCOs. The membrane with the smallest MWCO (3 kDaltons) had the greatest removal (77%). Although there was an inverse relationship between MWCO and TOC removals, a large decrease in MWCO corresponded to a very small increase in TOC removal.

When the removal of a hydrophilic solute, PEG with nominal molecular weight of 35,000 Daltons, was tested for the same membranes in a previous study (Mosqueda-Jimenez et al., 2003a), the performance was quite different from that of the NOM. When the PES concentration in the casting solution was 12 wt %, surface modification and an increase of solvent evaporation time caused a statistically significant increase of PEG (35 kDaltons) separation (from 20 to 70%, approximately).

The lack of such drastic effects in the case of TOC removal (in river water treatment) is very likely attributed to fouling. While PEG is a standard probe solute used to characterize membranes because of its very low-fouling characteristics (Zeman and Zydney, 1996), NOM is widely known as a membrane foulant either by surface adsorption or by adsorption in the bulk of the membrane (Anselme and Jacobs, 1996). It seems that membranes prepared with 12 wt % PES became more fouled than those prepared with 18 wt % PES, and that NOM removal was controlled by a foulant cake, therefore improving TOC removal in comparison to the removal of the low-fouling PEG. Moreover, as Anselme and Jacobs (1996) indicated, retention by the sieving mechanism is probabilistic, since it not only depends on the membrane pore-size distribution, and on the solute size distribution in the feed (NOM), but also on the probability that species that may pass through pores of a given size encounter such pores. Another potential explanation is that, besides sieving effects, other effects such as physicochemical interactions (electrostatic exclusion, hydrophobicity/aromaticity interaction) were taking place, contributing to a higher TOC removal.

Results of the ANOVA test are presented in Table 6.3. As explained in Chapter 5, the null hypothesis (H_0) (the effect of any particular independent variable on each of the response variables does not exist) was rejected if $P\text{-value} \leq 0.05$ ($\alpha = 0.05$ or 5%). So, for the P-values in Table 6.3 to be statistically significant they should be ≤ 0.05 . Therefore, only the solvent evaporation time and the surface modification had a significant effect on the TOC removal. No significant interactions were detected between the different factors (i.e., solvent evaporation time, PES concentration, or SMM) on the TOC removal. This means that the magnitude of a factor's effect on the response variable did not depend on the particular level of any other factor in the experiment (Devore and Farnum, 1999). Thus, results were interpreted through the examination of the main effect plots (Devore and Farnum, 1999), as presented in Fig. 6.7. The Y-bars in the main effect plots represent the results of multiple range tests (multiple comparisons procedure) performed for each independent variable via the LSD technique at a 5% significance level (Montgomery, 1991). A statistically higher TOC removal was achieved with a 3-minute solvent evaporation time. Furthermore, using 12 or 18 wt % PES in the casting solution produced membranes with statistically the same TOC removal. The TOC removals that DPS-

modified membranes achieved were statistically lower than those achieved by unmodified membranes, or by DEG and SMM41-modified membranes.

Table 6.3 P-values of the independent variables obtained from the analysis of variance (ANOVA) for the performance variables

<i>Source of variation</i>	<i>TOC Removal</i>	<i>NOM deposition</i>	<i>Final flux</i>	<i>Normalized flux reduction</i>
MAIN EFFECTS				
A: Evaporation time	0.0271 ^a	0.0176	0.0355	0.3791
B: PES conc.	0.0533	0.0009	0.1133	0.2531
C: SMM	0.0453	0.0755	0.0679	0.7707
INTERACTIONS				
AB	0.5322	0.3021	0.0625	0.6401
AC	0.5115	0.2952	0.0631	0.8462
BC	0.0836	0.1337	0.0127	0.9459
ABC	0.2530	0.1742	0.4115	0.9080

^a If P-value ≤ 0.05 the effect is statistically significant

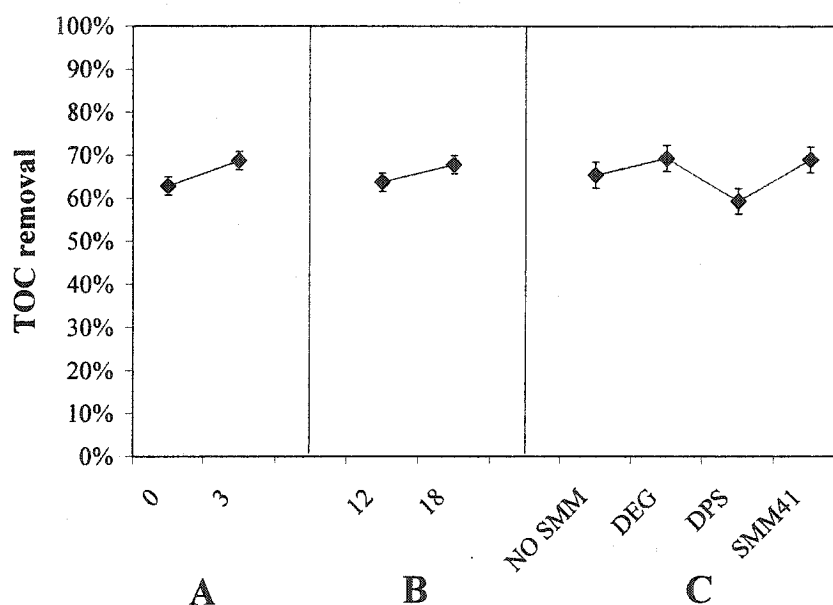


Fig. 6.7 Main effects of independent variables on TOC removal. A = Solvent evaporation time (min), B = PES concentration in the casting solution (wt %), C = SMM

6.4.3 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 6.8 shows a drastic decrease in the amount of NOM deposited when solvent evaporation time was increased from 0 to 3 minutes. Moreover, increasing the PES concentration in the casting solution from 12 to 18 wt %, also caused a decrease in NOM deposition (large amounts of NOM deposited were suspected for membranes prepared with 12 wt % PES, since they achieved large TOC removals having high MWCOs). Except for one case, surface modification reduced NOM deposition.

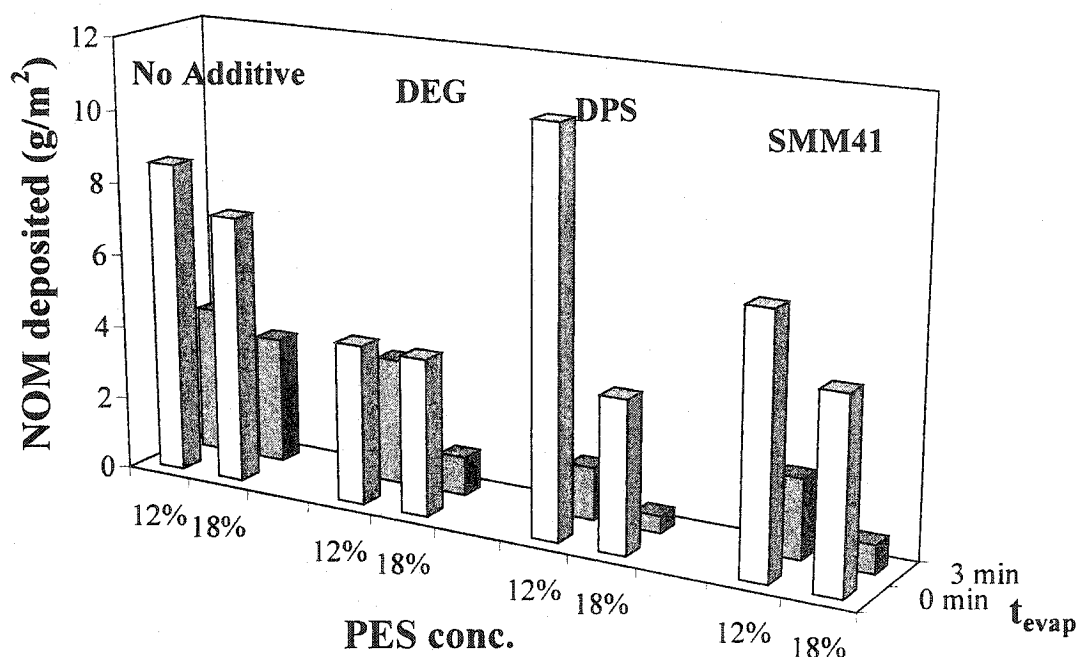


Fig. 6.8 NOM deposition of membranes prepared under different manufacturing conditions

Results of the ANOVA test are presented in Table 6.3. PES concentration in the casting solution and solvent evaporation time proved to have statistically significant effects on NOM deposition at a significance level of 5%. The measurements of NOM deposition were subject to large errors; this is reflected in the Y bars of the main effects plots in Fig. 6.9. It is evident from Figures 6.9a and 6.9b that the PES concentration had a greater

impact on NOM deposition than the effect of the solvent evaporation time. According to the ANOVA, SMM modification was significant at a higher significance level, 7.6%, giving a reasonable indication of the effect of SMM, thus, it was decided to perform multiple comparison tests among the 4 different levels, i.e., No Additive, DEG, DPS, and SMM41. Results of these tests are indicated by the Y bars in Fig. 6.9. DEG- and SMM41-modified membranes demonstrated to improve membrane characteristics when they reduced the NOM deposition compared with the unmodified membranes. Miscibility of the casting solutions was visually evaluated. The order of the miscibility for the different SMMs was SMM41 > DEG > DPS. Migration of SMM41 and DEG (the two most miscible SMMs) to the membrane surface proved, through XPS measurements (see Chapter 5 or Mosqueda-Jimenez et al., 2003b), to be greater than the migration of DPS. As mentioned earlier, although the mean NOM deposition of the DPS-modified membranes was smaller than that of the unmodified membranes, statistically the decrease was not significant at a 5% level of significance. It was believed that this marginal effect of SMMs on the reduction in NOM deposition was in part due to the increase of hydrophobicity with surface modification.

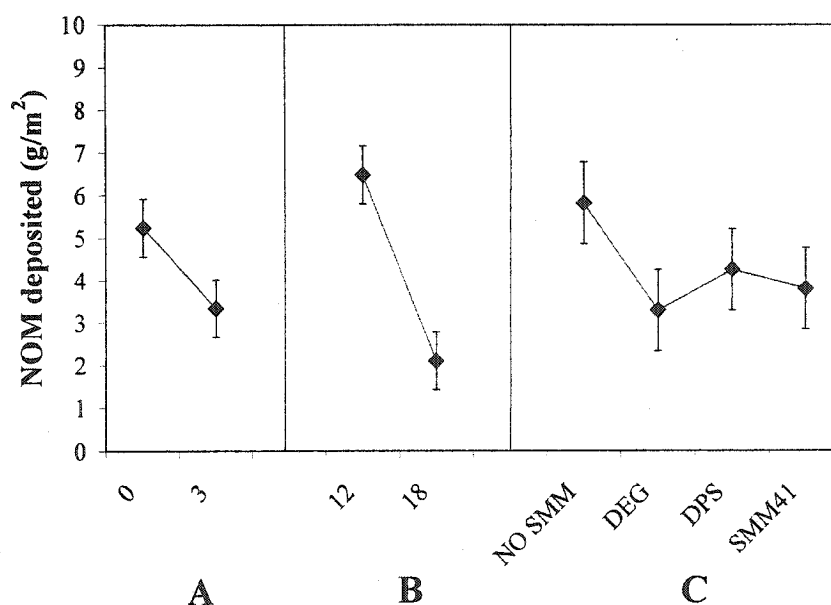


Fig. 6.9 Main effects of independent variables on NOM deposition. A = Solvent evaporation time (min), B = PES concentration in the casting solution (wt %), C = SMM

In order to confirm this hypothesis contact angles were measured. Figure 6.10 shows the advancing contact angles for the different types of membranes. As in previous studies (Suk et al., 2002a and Suk et al., 2002b) no difference in contact angles between membranes with and without SMM was observed when evaporation time was 0 min. In addition, only in 1 out of 6 cases, the increase of solvent evaporation time from 0 to 3 min caused a significant increase in the contact angle. This is not surprising since Suk et al. (2002b) had shown that evaporation times longer than 3 min were necessary in order to obtain a sufficient migration of the SMM to the surface that causes a significant increase in the contact angle. It is worth noting that previous studies (Ho et al., 2000; Mandeep, 2001) that showed SMM-modified membranes with contact angles similar to those of Teflon used significantly longer evaporation times during their manufacturing process. To ensure a complete coating of the SMMs on the PES membranes, attempts were made to prepare SMM-PES composite membranes. Results are presented in Appendix M.

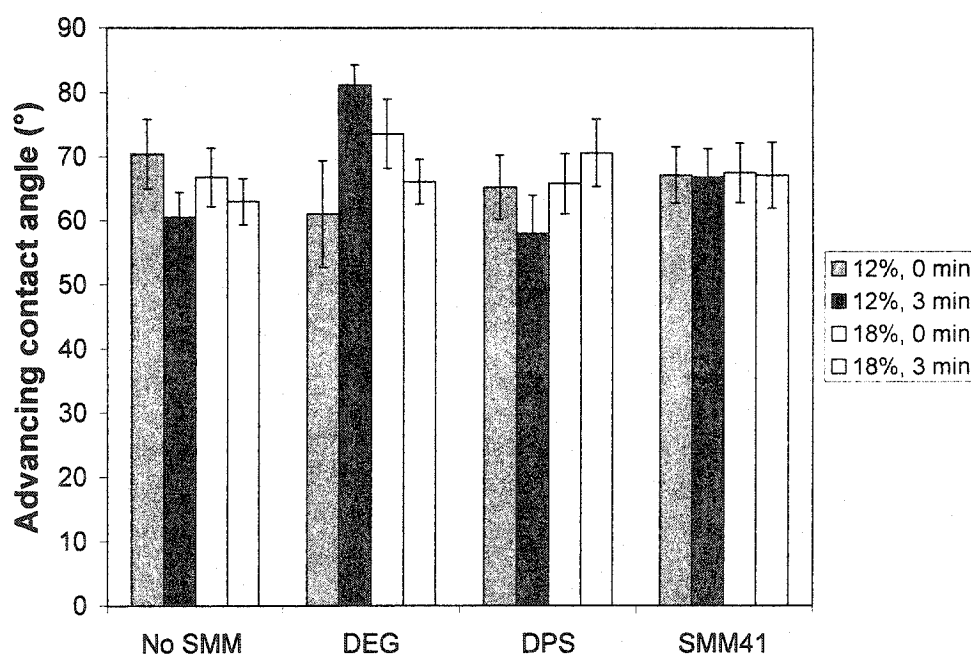


Fig. 6.10 Advancing contact angles of membranes prepared under different conditions

Given these results for the contact angles, it seems that the main cause of the reduction of NOM deposited was the modification of the pore size distribution observed in Fig. 6.4 and the consequent reduction in PWP (Fig. 6.5). As shown in Section 6.4.1, membranes with high PES concentration, long evaporation times, and/or membranes with SMM, in general, had lower MWCOs with lower PWPs. This modification of the pore size distribution also impacted the river water permeation rate as, in most cases, the initial permeation rate was the same as the PWP at the end of the PWP determination stage (Fig. 6.11).

6.4.4 Permeate flux

The membrane permeate flux was monitored throughout the entire experiment. The typical behaviour of the permeate flux with time is shown in Fig. 6.11. For each membrane, a drastic reduction of permeate flux was observed during the precompaction step. It is worth noting that in full-scale operation and field evaluations membranes are not subjected to precompaction. In addition, only some laboratory evaluations include precompaction, and these only last one hour or less. In this study, precompaction was included in the test protocol in order to minimize the effect of membrane compaction when fouling with CORW was studied. Unfortunately, in addition to making permeate fluxes more stable and reducing further compaction, it is believed that this long precompaction step caused excessive deformation of the membrane structure. Therefore, permeation rates of these membranes were low for UF membranes. Also, minute amounts of solute present in Milli-Q water during this long precompaction might have caused some fouling. On the other hand, the precompaction yielded a significant benefit throughout the second stage of the test, when PWP was determined, fluxes changed only slightly. During the final stage, two runs were conducted, using different coupons of the same membrane material. The first runs used CORW, which resulted in a continuous flux decrease; while the second runs with ultra pure water resulted in only a very slight decrease in flux (i.e., the empty diamonds in Fig. 6.11).

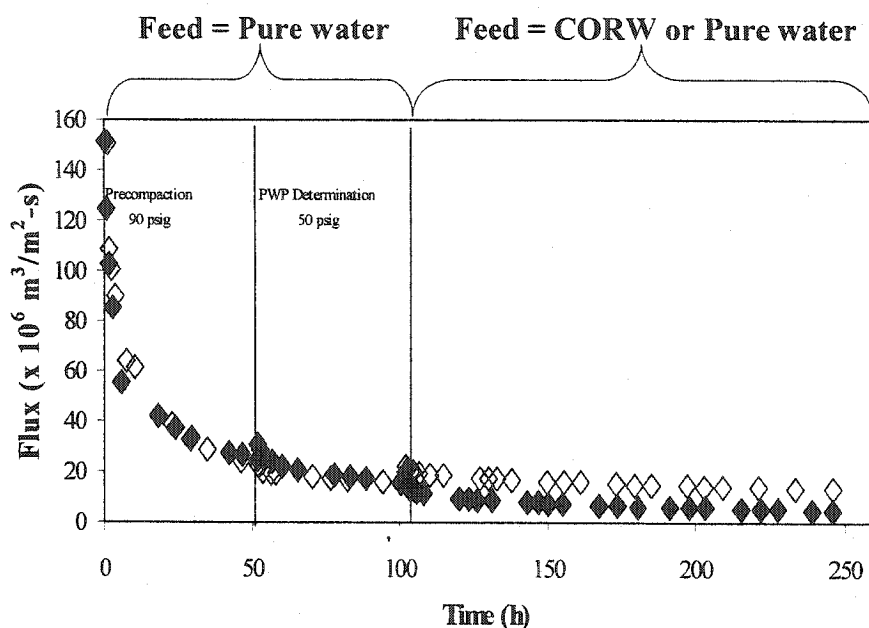


Fig. 6.11 Change of permeate flux along the experiment. ♦ = 1st run, ◇ = 2nd run

In Fig. 6.12, permeate flux is plotted against throughput in order to observe the decrease in the flux caused by the amount of CORW that passes through the membranes during the fourth stage of the first tests. Membranes with shorter lines represent those membranes with lower water productivity, since the last point of every curve corresponds to the total amount of treated water produced during the same time span. The rate of flux reduction was much higher at the beginning, and then it became stable. DPS-modified membranes prepared with 18 wt % PES had very low permeate fluxes, which remained almost constant for the entire experiment (Figures 6.11c and 6.11d). Although there was one exception for every manufacturing condition, in general, the final fluxes were statistically the same, despite the differences in the initial fluxes (Figures 6.11a, 6.11b, 6.11c and 11d).

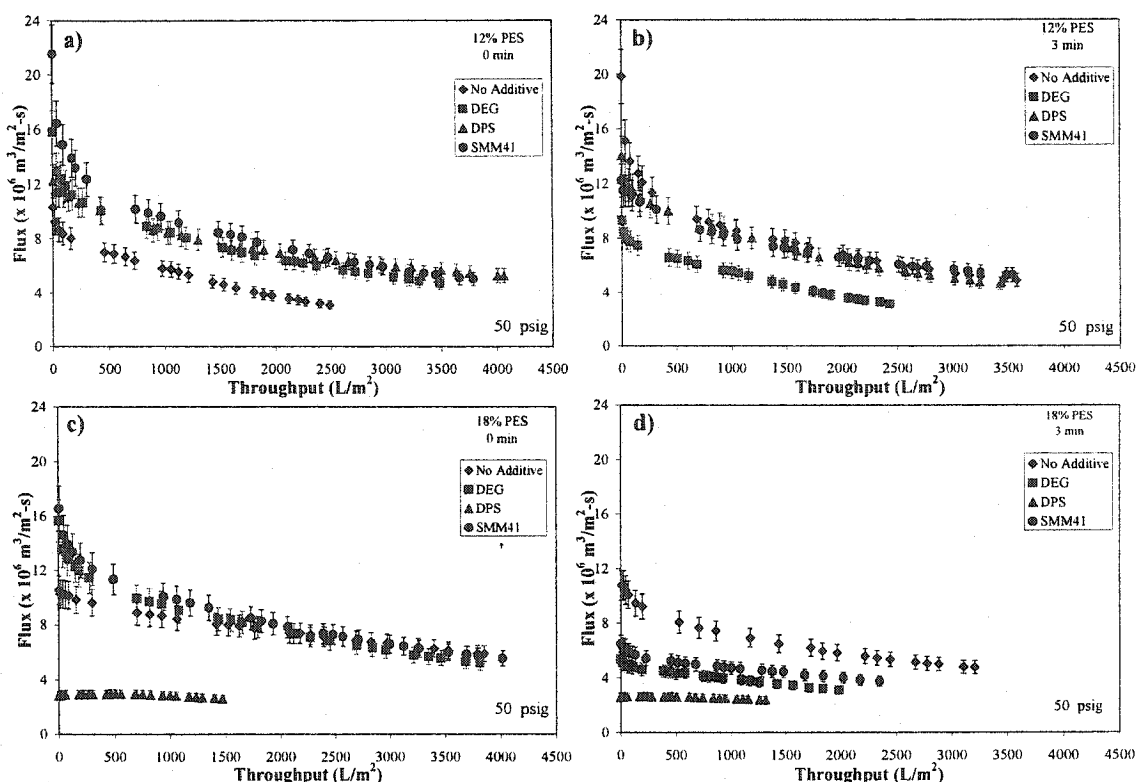


Fig. 6.12 Change of permeate flux as a function of the amount of water filtered for membranes prepared under different manufacturing conditions:

a) 12 wt % PES, 0 min evaporation time, b) 12 wt % PES, 3 min evaporation time, c) 18 wt % PES, 0 min evaporation time, d) 18 wt % PES, 3 min evaporation time

The ANOVA test of those final fluxes (Table 6.3) showed that, at a significance level of $\alpha = 0.05$, only the solvent evaporation time and the two-factor interaction PES concentration $\times$ SMM statistically affected the final flux. Membranes prepared without evaporation time had statistically higher final permeation rate than the membranes prepared with 3-minute solvent evaporation time (Fig. 6.13a). According to the interaction plot (Fig. 6.14), final permeate fluxes of SMM41-modified membranes were consistently among the highest, in comparison with membranes prepared with no additive or the other SMMs. The latter conclusion, drawn from the interaction plot, agrees with the main effects plot in Fig. 6.13c. Besides having a high final flux the SMM41-modified membranes, together with the unmodified membranes, had the highest PWP (Fig. 6.5). With the exception of SMM41-modified membranes, that had high final flux with low NOM deposition, main effect plots for NOM deposited (Fig. 6.9) and final flux (Fig.

6.13) seemed to be directly related. Therefore, as explained before, membranes with high permeate flux had higher NOM depositions. This increase in NOM deposition with increasing permeate flux was observed in previous studies (Hong and Elimelech, 1997; Mosqueda-Jimenez et al., 2002).

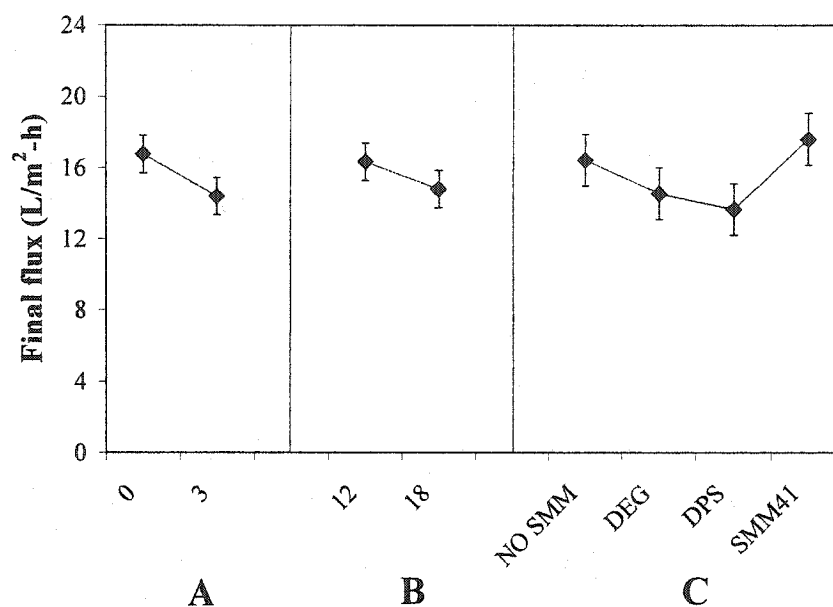


Fig. 6.13 Main effects of independent variables on final permeate flux. A = Solvent evaporation time (min), B = PES concentration in the casting solution (wt %), C = SMM

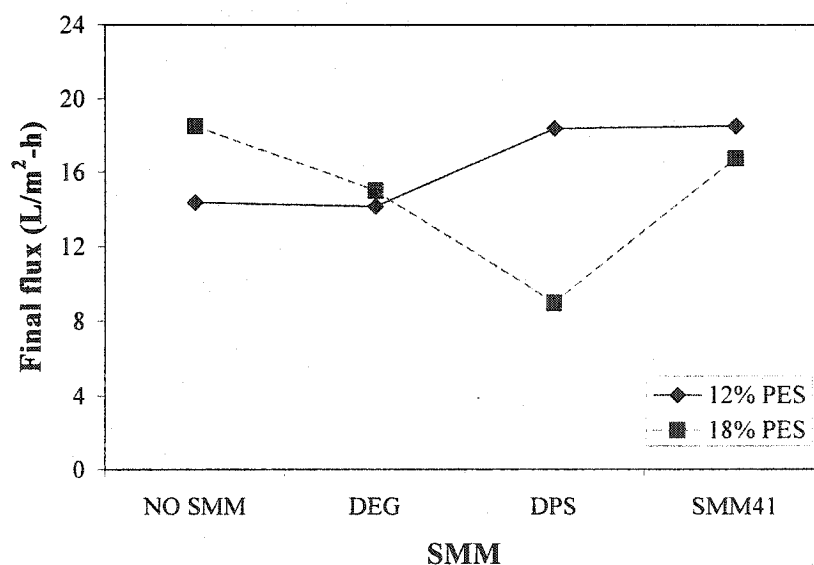


Fig. 6.14 PES concentration in the casting solution – SMM (BC) interaction for final permeate flux

As mentioned above, because of the long precompaction at high operating pressures, the observed fluxes were somewhat lower than those reported in the literature for other UF membranes. However, two other membranes were evaluated with CORW and similar testing conditions. One of these membranes (PES HO51, Osmonics, Minnetonka, MN) had an average terminal flux 26% lower than SMM41-modified membrane prepared with 18 wt % PES and 0 min solvent evaporation time. While a commercial regenerated cellulose membrane (YM3 by Millipore, Bedford, MA) had an average terminal flux 33% higher than the same SMM41-modified membrane, and a 35% lower TOC removal. Thus, the 18 wt % PES and 0 min membrane modified with SMM41, had comparable flux to commercially available membranes (See Appendix A).

6.4.5 Flux reduction

Membrane fouling was experimentally measured through the determination of the normalized flux reduction, which is calculated according to Equation 6.2.

$$\text{Normalized flux reduction}_{(t)} (\%) = 100 \left(1 - \frac{PR_{(t)}}{PWP} \right)_{CORW} \quad (6.2)$$

where $PR_{(t)}$ is the permeate flux (product rate) of CORW at time t of the fourth stage of the test, and PWP has dimensions = volume/time/area, measured during the second stage of the test. The effect of the manufacturing conditions on the normalized flux reduction at the end of the 6-day experiment (Fig. 6.15) was similar to, but of smaller magnitude than, the NOM deposition (Fig. 6.8). The ANOVA test results in Table 6.3 did not show any statistical effect of the manufacturing conditions on the normalized flux reduction at a significance level of $\alpha = 0.05$. This was mainly due to the relatively high experimental error observed for the repeats. It is worth noting that in all cases, the membrane coupons used for the repeats came from different membrane sheets (prepared under identical manufacturing conditions) and they were randomly located in one of the six test cells. Even when none of the effects were statistically significant, the data suggest lower flux reductions in the case of the membranes with SMM prepared with 18 wt % PES and 3-minute evaporation time. These results point to a correlation between permeate flux and flux reduction i.e., membranes with high permeate flux had higher flux reductions (as in

the case of NOM deposition). However, SMM41-modified membranes seemed to be an exception, with high final fluxes and relatively low flux reductions.

The effect of further membrane compaction (after the precompaction protocol) on the normalized flux reduction was eliminated when pure water was used as feed (see Chapter 4 or Mosqueda-Jimenez et al., 2003a). The modified flux reduction was calculated via Equation 6.3.

$$\text{Modified flux reduction}_{(f)} (\%) = \left(\frac{PR_{(f)}}{PWP} \right)_{\text{CORW}} \times 100 - \left(\frac{PWP_{(f)}}{PWP} \right) \times 100 \quad (6.3)$$

where $PR_{(f)}$ and $PWP_{(f)}$ are the product rate and permeability of the pure water at the end of the fourth stage of the test, respectively. The flux reduction with ultra pure water (second term on the right-hand side of equation 6.3) was in the order of 20% for membranes prepared with 12 wt % PES, and around 10% for those prepared with 18 wt % PES (see flux reduction plots in Appendix G).

In general, the modified flux reduction followed the same trend as the normalized flux reduction with CORW (Fig. 6.15). Membranes with low PES content had modified flux reductions around 40 and 50%, while the reduction in the higher-PES content membranes was close to 30 to 40%.

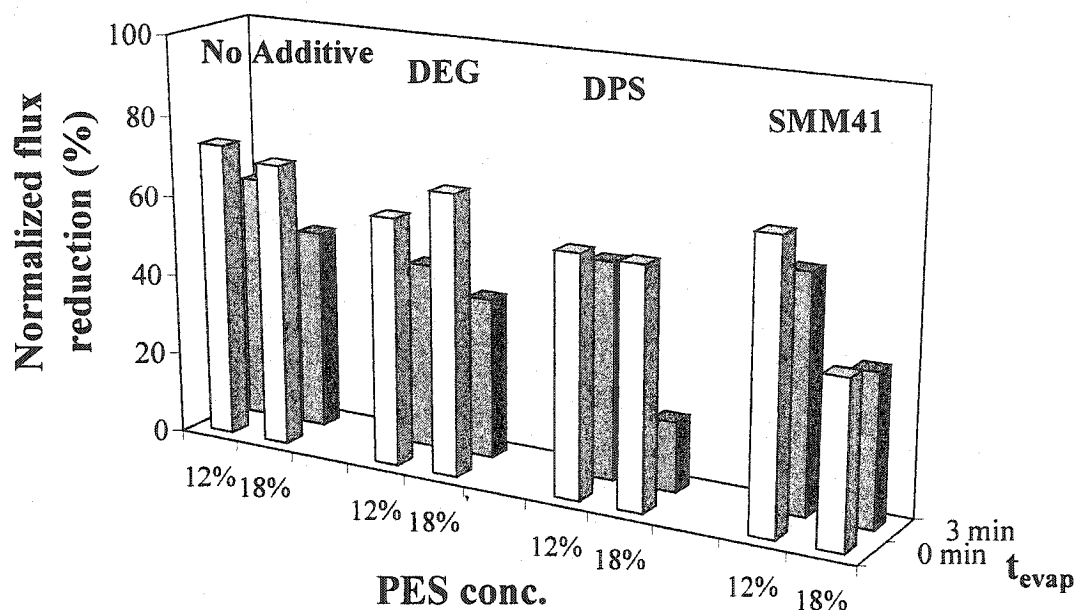


Fig. 6.15 Normalized flux reduction of membranes prepared under different manufacturing conditions

Changes in manufacturing conditions resulted in improvements in terms of some performance variables, but were detrimental in terms of others. Moreover, in addition to the manufacturing conditions in this study, there are other considerations that are important:

- Membranes prepared with low PES content were fragile (some membranes lost integrity in the middle of the test, ca. 1 out of 9 membranes tested), making their manipulation harder, so they would be riskier for water treatment applications.
- DPS was not as miscible in the casting solution as the other two SMMs, limiting the solvent evaporation period used in the membrane preparation.

In summary, PES concentration in the casting solution did not affect statistically the TOC removal (Fig. 6.7b) or the final flux (Fig. 6.13b), however membranes prepared with 18 wt % PES had significantly lower NOM deposition (Fig. 6.9b) and superior strength (more likely to keep their integrity during the test). Results of additional experiments

with membranes prepared with 21 wt % PES in the casting solution are presented in Appendix J. The performance of the membranes with 21 wt % PES was statistically the same to that of the membranes with 18 wt % PES. The use of SMM41 maximized the permeate flux, from the beginning to the end of the membrane process. Furthermore, SMM41-modified membranes achieved high TOC removal (Fig. 6.7c) and low NOM deposition (Fig. 6.9c). This small effect of the SMM on the membrane performance was not due to an increase of surface hydrophobicity, but to a structural modification of the pores. The evaporation time of 3 minutes slightly increased the TOC removal (Fig. 6.7a), and at the same time, reduced the NOM deposition (Fig. 6.9a); however, it decreased the permeate flux (Fig. 6.13a). These trends were corroborated with results of prediction equations, presented in Appendix F. It is worth noting that the complexity of the membrane manufacturing process also increases when a solvent evaporation period is required. Because there is a compromise between performance variables, in order to select the best level of evaporation time, it is necessary to decide, if an increase of TOC removal is worth the reduction in water productivity for the application in question.

In general, there was a logical connection between membrane characteristics and performance. Membranes with small MWCO (and pore size) had high TOC removal and lower permeate flux (either with ultra pure water, or with CORW as feed solution), and since less amount of water went through the membranes, the amount of NOM deposited on the membrane surface (as indicator of membrane fouling) was smaller. The same type of trend was observed by Amy et al. (2001) and Liikanen et al. (2003): low permeate fluxes resulted in high TOC removals and less fouling.

6.5 Conclusions

1. Although the addition of SMM to the casting solution did not cause the expected increase of surface hydrophobicity, it caused a modification of the pore size distribution. In turn, this modification provoked a change on membrane performance.

2. Since these membranes were tight UF membranes, NOM removals were exceptionally good. Under the same operating conditions, membranes prepared with SMM had permeate fluxes within the range of commercial membranes.
3. The use of 18 wt % PES and SMM41 in the casting solution proved to be the most suitable combination of manufacturing conditions in order to maximize the TOC removal and final flux. The presence or absence of solvent evaporation period in the manufacturing process depends on the main objective of the membrane treatment: higher TOC removal or flux.
4. Membrane fouling by NOM seemed to reduce the effect that the membrane MWCO has on the TOC removal, therefore the TOC removal achieved by the membranes with high MWCO was exceptionally good, compared with that expected by UF membranes from the literature.

6.6 Acknowledgements

We acknowledge Materials and Manufacturing Ontario (MMO), Natural Sciences and Engineering Research Council of Canada (NSERC) and CONACyT (Mexico) for their financial support.

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Notation

A = solvent evaporation time (factor with two levels: 0, 3 min)

B = PES concentration in the casting solution (factor with two levels: 12, 18 wt %)

C = SMM (factor with four levels: No Additive, DEG, DPS, SMM41)

$C_{p(t)}$ = permeate concentration at time t.

C_f = feed concentration.

$PR_{(f)}$ = final permeate flux (product rate).

$PR_{(t)}$ = permeate flux (product rate) at time t.

P-value, associated with a calculated F ratio = the area under the F distribution to the right of the calculated F ratio (Devore and Farnum, 1999).

PWP = pure water permeation rate.

$PWP_{(f)}$ = final pure water permeation rate.

α = significance level related to the probability of rejecting a true hypothesis

CHAPTER 7

IMPACT OF POLYVINYLPIRROLIDONE AND NOM FRACTION ON TREATMENT OF SURFACE WATER

D. B. Mosqueda-Jimenez¹, R. M. Narbaitz², T. Matsuura³

7.1 Abstract

New polyethersulfone (PES) based membranes for ultrafiltration (UF) were developed by blending a surface modifying macromolecule (SMM) in the casting solution, in an attempt to minimize the impact of fouling. Fouling was evaluated using concentrated Ottawa River water (CORW), either unfractionated or fractionated via UF. These membranes also included some polyvinylpyrrolidone (PVP), a pore forming additive.

A statistical analysis was conducted to evaluate the impact of some variables on the treatment of the surface water. The independent variables included PVP/PES ratio in the casting solution, with and without SMM, and the nature of the feed CORW (low molecular weight fraction (LMW), unfractionated, high molecular weight fraction (HMW)). The performance variables studied were TOC removal, the amount of natural organic matter (NOM) deposited on top of the membrane after filtration, the flux reduction, and the final permeate flux. The most important variable was the feed water. Filtration of LMW had a higher final flux, less fouling, but slightly lower TOC removal. The SMM did not significantly impact the membrane performance.

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Key words

Membrane processes, surface waters, organic matter, fouling, organic carbon

7.2 Introduction

The removal of natural organic matter (NOM) from water is a critical issue since chemical disinfection of these compounds produces a number of potentially harmful disinfection by-products (DBPs) (Rook, 1977). Pilot studies and full-scale operation (Taylor et al., 1987; Thorsen, 1999) have demonstrated that nanofiltration membranes may achieve NOM removals greater than 90%. The possibility of replacing them by ultrafiltration (UF) membranes seems very attractive because UF membranes are likely to require less pretreatment, to have higher water production rates and lower operating pressures. However, published results of pilot studies with UF membranes have generally shown NOM removals of less than 50%, when they are not combined with some kind of pretreatment (Taylor et al., 1987; Jacangelo et al., 1994).

Another obstacle that hinders more widespread application of low-pressure membrane processes is the decline of the permeate flux with time, generally known as membrane fouling (Song, 1998). The term fouling includes all the phenomena responsible for permeate flux reduction with time, except those linked to membrane compaction and mechanical characteristics modification (Anselme and Jacobs, 1996). In several studies of drinking water treatment, NOM has been reported to be a major membrane foulant (Braghetta et al., 1997; Cho et al., 2000). Fouling increases the costs and complexity of membrane filtration operations (Song, 1998), and may also affect the quality of the product water (Tracey, 1996). There are several approaches used to reduce membrane fouling, for example: feed pretreatment, or adjustment of the operating conditions, especially cross-flow velocity, together with pressure and temperature (Cheryan, 1986), and cleaning of the membrane system with acid or alkaline solutions (Hamza et al., 1997). It is believed that fouling by NOM is caused by the affinity between NOM and the polymer that constitutes the membrane. Then, another way to reduce fouling may be by

modifying the surface of the membrane. According to Zeman and Zydney (1996), almost 50% of all microfiltration and UF membranes marketed by 1996 were surface-modified. The additives used and procedures followed in commercial membrane manufacture are, however, industrial secrets.

Surface modification employing tailor-made surface modifying macromolecules (SMMs) is an approach that has been used during the last decade in an attempt to improve polyethersulfone (PES) membranes for environmental applications. The surface characteristics of the membranes are altered by the addition of these SMMs. The SMM additives were specially developed to be hydrophobic (via their fluorinated groups) and to be compatible with PES so that they can be simply blended into the polymer casting solution (Pham et al., 1999). The SMMs migrate to the membrane surface during a single-step casting process and the surface of the membrane becomes more hydrophobic while keeping its bulk properties essentially the same as that of an unmodified membrane. The surface-modified membranes have demonstrated to have a somewhat better performance in the separation of volatile organic compounds (VOCs, such as chloroform) from aqueous solutions via pervaporation (Pham et al., 1999); UF of oil/water emulsions (Hamza et al., 1997), and biomedical UF 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 performance for a much longer period than PES membranes (Suk et al., 2002). Because of the characteristics associated with the fluorinated-based compounds used in the SMM synthesis, such as surface lubrication and low surface free energy, the PES/SMM membranes are expected to exhibit low adhesive energy and consequently have more fouling resistant characteristics. DiGiano et al. (2001) followed a similar approach in the quest for better membrane materials. Several studies (Cabasso et al., 1976; Lafrenière et al., 1987; Torrestiana-Sanchez et al., 1999; among others) have demonstrated that the use of polymeric additives, such as polyvinylpyrrolidone (PVP) and polyethylene glycol (PEG), has improved the performance of PES membranes by increasing the productivity.

The aim of this work was to investigate the effects of the surface modification via the addition of SMM to the casting solution (with and without PVP), and the nature of the

feed water on the performance of UF membranes and the extent of fouling. Membrane performance in the treatment of a surface water was evaluated in terms of TOC removal, the amount of NOM deposited on top of the membrane after filtration, the flux reduction, and the permeate flux at the end of the test.

7.3 Experimental methods and analysis

7.3.1 Materials

PES (Victrex 4100P) supplied by ICI Advanced Materials (Billingham, Cleveland, England) was the base polymer used in the preparation of the membrane casting solution. Reagent grade N-methyl-2-pyrrolidone (NMP), supplied by Aldrich Chemical Company, Inc. (Milwaukee, WI), was used as the solvent. Polyvinylpyrrolidone (PVP) powder with average molecular weight 10,000 Daltons, also supplied by Aldrich, was used as a nonsolvent pore-forming additive. The SMM, referred to as SMM41, was synthesized according to the methodology outlined by Ho et al. (2000). SMM41 has an amphiphatic structure that consists of a polyurethane chain end-capped with two fluorine-based (low-polarity) polymer chains (Suk et al., 2002). NaOH was supplied by BDH Chemicals (Toronto).

Reagent-grade water was prepared with a Milli-Q Water System by Millipore (Bedford, MA), using mixed bed ion exchange resins, synthetic activated carbon, organic scavengers and membranes. This ultrapure water is referred to as Milli-Q water.

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 June 6, 2000, and concentrated five-fold to accelerate the fouling evaluations (Mosqueda-Jimenez et al., 2003a). The concentration was accomplished via a portable Reverse Osmosis System by RealSoft (Norcross, GA), which included a prefilter and a FT30 composite membrane (Filmtec Membranes, Midland, MI). The concentrated Ottawa River water is referred to as CORW. Although it is expected that NOM would be the main type of foulant, no attempt was made to differentiate between the various river water

components that may cause fouling (i.e., biological, inorganic, or colloidal). For some tests two different fractions of the CORW, obtained using a YM3 membrane (Millipore, Bedford, MA), were used. According to the manufacturer, the nominal molecular weight limit of this membrane is 3,000 Daltons. The permeate that passed through the YM3 membranes contained the low-molecular-weight-fraction of the NOM and is referred to as LMW; while the retentate contained the high-molecular-weight-fraction of the NOM and is referred to as HMW. One week of continuous test at 345 kPa (50 psig) was required to collect a sufficient amount of the two different fractions for the test. Initially, it was believed that membrane surface modification would have a stronger effect on the interaction between smaller NOM molecules and the membranes. The YM3 membrane was selected for the fractionation because of manufacturer's claim that regenerated cellulose is non-ionic, very hydrophilic in nature and exhibits little tendency to adsorb organic macromolecules (Nilson and DiGiano, 1996). In addition, Clark and Jucker (1993) found that the performance of this membrane was only weakly affected by changes in pH and ionic strength of the feed solution.

7.3.2 Membrane preparation

The membranes were cast using the phase inversion technique described by Matsuura (1994). Four different ingredients were used to prepare the casting solution: PES, PVP, SMM41, and NMP. The concentration of PES in the casting solution was kept constant for all membranes at 18 wt %. PVP was used in three different concentrations 0, 6, and 18 wt %. The PVP/PES ratios in the casting solution were, therefore, 0, 1:3, and 1:1, respectively. For the modified membranes, 1.5 wt % of SMM41 was added to the casting solution. All concentrations were weight-based percentages. Details on membrane preparation are presented in Section 5.3.2. Membranes were cut from flat sheets into 20 cm²-coupons.

7.3.3 Analysis

The general physicochemical characteristics of the test waters were determined using standard methods (Standard Methods, 1995). TOC concentrations (feed and permeate) were measured using a Dohrman Total Carbon Analyzer (Model DC-180, Santa Clara,

CA) and UV absorbances were measured at $\lambda = 254$ nm using a Beckman DU-40 Spectrophotometer (Beckman Instruments Inc., Irvine, CA) with a 1-cm quartz cell. UV absorbance was used as TOC surrogate since they are linearly related (see Appendix N). The apparent molecular weight distribution (AMWD) of the organic matter within the 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 different nominal molecular weight cut-offs (MWCO): 5,000, 10,000, 30,000, and 300,000 Daltons. The UF fractionation technique followed is detailed by different authors: Amy et al. (1987), and Logan and Jiang (1990), among others.

A model JSM-6400 JEOL (Japan Electron Optics Limited, Japan) scanning electron microscope (SEM) was used to observe the cross-sectional area of the membranes. An atomic force microscope (AFM) (Nanoscope III from Digital Instruments) operated in the tapping mode was used to get the topological information of the membrane surface measuring roughness. The chemical analysis of the membrane surface was done by using a Kratos Axis X-ray photoelectron spectrometer (Kratos, Manchester, UK). Contact angles were determined using the sessile drop technique with a 20- μ L droplet of distilled water and a standard goniometer apparatus (Ramé-Hart, model 100, Mountain Lakes, NJ). The values of the advancing and receding angles reported were the average of at least 10 measurements.

7.3.4 Testing protocol

The performance evaluation of the membranes was made using unfractionated CORW, HMW, and LMW. The UF membranes were placed in random order in a six-cell in-series 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., 2003a). The system recirculated the permeate back to the feed reservoir to maintain a constant feed concentration. The existence of a possible cell effect or cell order effect within the cells in-series was discarded using an analysis of variance (ANOVA) test of a greco-latin

square type of design, because statistically no significant effect was observed. Details are reported in Appendix E.

Prior to each run, the membranes were subjected to a precompaction protocol filtering Milli-Q water through each new coupon at 620 kPa gauge (90 psig) for 52 h. Next, the pure water permeation rate (PWP) was determined during a period of 50 h under a 345 kPa gauge (50 psig) operating pressure using Milli-Q water. This was considered the second stage of the test. Then, the UF membranes were characterized based on solute transport data of probe solutes (polyethylene glycols (PEG) and polyethylene oxides (PEO) with different molecular weights) (Singh, 1998). After the completion of membrane characterization, the membranes were ready for the fourth phase of the test, which involved filtration of CORW or one of its fractions, depending on the type of experiment. The permeation rates of CORW and its fractions were measured at a feed flow rate of 1.1 Lpm and an operating pressure of 345 kPa gauge (50 psig) during six days of continuous operation. The permeation rates were measured at different intervals and feed and permeate samples were collected to assess the TOC removal.

The amount of NOM accumulated on top of the individual membranes at the end of the six-day 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 the temperature was lowered to room temperature in a desiccator, the beakers were weighed. Membrane coupons were removed very carefully from the test cells and placed in the beakers. Then, the NOM was dissolved using 25 mL of 0.1 M NaOH solution within the preconditioned beakers. After the NOM was completely removed, the membrane coupons were withdrawn and all the beakers were baked in an air-circulated oven at 105°C for 24 h, together with at least two blanks (consisting of 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.

7.3.5 Experimental Design

A multifactor design $3 \times 2 \times 3$ was used to evaluate the effect of the concentration of PVP (0, 6 or 18%) and SMM in the casting solution (SMM41 or No SMM), together with the fraction of the NOM used as test water (Unfractionated CORW, LMW, or HMW). This design allowed the study of the interplay of the independent variables in each of the response variables with less experimental runs than a one-factor-at-a-time experiment would require (Devore and Farnum, 1999). The response variables, which determine the performance characteristics of every membrane tested, were the level of TOC removal achieved by the membrane, the amount of NOM deposited on the surface of the membrane, the normalized flux reduction, and the permeate flux at the end of the six-day test.

It is worth noting that the “repeats” in the multifactor design, which allowed us to measure the experimental error, corresponded to a complete replicate of the experimental conditions of each test (Devore and Farnum, 1999). This means that each coupon tested came from a different membrane sheet and it was randomly located in one of the six test cells. Statistical calculations were performed using STATGRAPHICS Plus V. 7.0 (Statistical Graphics Corporation, Manugistics, Inc., Rockville MD).

7.4 Results and discussion

7.4.1 Feed water

The water quality characteristics of the three different feed waters used in this study are presented in Table 7.1. According to the AMWD of the organic matter within ORW as determined by Mosqueda-Jimenez et al. (2003a) using UF fractionation, close to 30% of the NOM was smaller than 5,000 Daltons, almost 60% of TOC of the NOMs was in the molecular weight range from 10,000 to 30,000 Daltons, while 6.2% was higher than 30,000 Daltons (Fig. 7.1). For the LMW and HMW fractions, TOC concentration decreased and increased by nearly 50%, respectively, compared with the value of CORW. Because the MWCO of this membrane is 3,000 Daltons, the size of the NOM in

the LMW should be less than 3,000 Daltons, and the size of most of the NOM in the HMW should be greater than 3,000 Daltons. The specific UV absorbance (SUVA) is commonly considered a measure of the relative aromatic content. Therefore LMW had less aromatics than the CORW and HMW. The colour measurements demonstrated that the brownish colour is associated with the larger NOM molecules.

Table 7.1. Ottawa River water quality characteristics.

<i>Parameter</i>	<i>ORW</i>	<i>CORW</i>	<i>LMW</i>	<i>HMW</i>
TOC concentration (mg/L)	7	28	15	45
SUVA ($\text{m}^{-1}\text{mg}^{-1}\text{L}$)	3.4	3.9	2.6	3.9
Colour (cu)	30	180	8	500
pH	7.6	8.2	7.6	7.6
Alkalinity (mg/L as CaCO_3)	26	120	117	128
Turbidity (NTU)	0.8	0.3	0.1	0.51
Total hardness (mg/L as CaCO_3)	30	153	141	171
Calcium hardness (mg/L as CaCO_3)	22	122	122	122

ORW = Ottawa River water; CORW = Concentrated Ottawa River water; LMW = CORW with MW < 3,000 Daltons; and HMW = CORW with MW > 3,000 Daltons

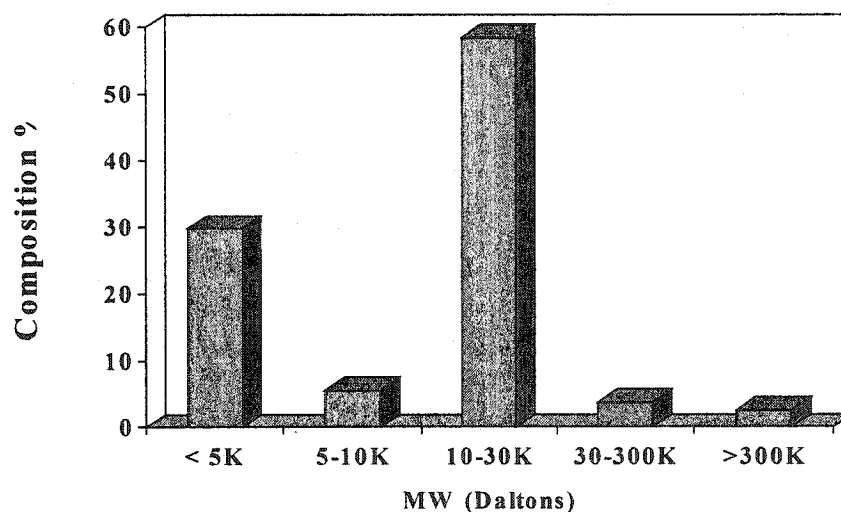


Fig. 7.1 AMWD of organic matter in ORW

In a previous study (Mosqueda-Jimenez et al., 2003a), it was found that the concentration process performed to obtain CORW not only modified the molecular weight distribution of the organic matter, but also increased the concentration of mono and divalent ions in the concentrate. On the other hand, the YM3 membrane used in the NOM fractionation

was a tight ultrafiltration membrane, with almost no rejection of inorganic ions, thus, the alkalinity and hardness changed only very slightly.

7.4.2 Membrane characteristics

The membrane characteristics are given in Chapter 5, and a brief summary is presented in Table 7.2. The numbers in parenthesis represent the range of variation of these parameters. It is believed that the wide intervals were due to the inherent variability of membrane manual casting (Hester and Mayes, 2002). The ANOVA performed on the data in Table 7.2 indicated that the PVP/PES ratio in the casting solution had a significant effect ($P\text{-value} \leq \alpha$, as explained later) on the molecular weight cut-off and pure water permeation rate. The only significant difference was between the molecular weight cut-off of the membranes without PVP and that of the membranes with 1:1 PVP/PES ratio. The pure water permeation rate of the membrane without PVP was statistically smaller than the pure water permeation rate of the membranes with PVP. Other researchers have observed the same type of behaviour, using different polymer concentrations (Lafrenière et al., 1987; Torrestiana-Sanchez et al., 1999). In the case of the solute separation, the test solute used was PEG with molecular weight of 35 kDaltons. The average PEG separation was higher for the membranes without PVP (96%), which is consistent with the MWCO information. The standard deviations of separations of membranes with PVP were very high. Therefore, statistically neither the PVP/PES nor the use of SMM made a difference in the solute separation.

Table 7.2 Membrane Characteristics.

PES/PVP	<i>MWCO (kDaltons)</i>		<i>Solute separation (%)^a</i>		<i>PWP^b (L/m²-h)</i>	
	No SMM	SMM41	No SMM	SMM41	No SMM	SMM41
18/0%	21 (3-40) ^c	9 (6-11)	96 (92-99)	96 (92-99)	37 (30-43)	53 (37-70)
18/6%	36 (18-55)	34 (7-62)	84 (73-95)	79 (52-100)	75 (63-87)	77 (56-96)
18/18%	38 (25-51)	45 (20-70)	84 (73-94)	75 (57-94)	69 (62-76)	82 (73-91)

^a Solute: PEG with nominal molecular weight of 35 kDaltons

^b Pure water permeation rate

^c The variation of the data is given in parenthesis.

SMM migration was corroborated through measurements of the amount of fluorine at different depths (d_1 and d_2 , where $d_1 < d_2$). In the three SMM-modified membranes, the closer to the surface, the greater the amount of fluorine. The Fluorine _{d_1} /Fluorine _{d_2} ratio was 1.45, 1.43 and 1.14 for modified membranes with 0, 6, and 18% PVP, respectively. Thus, the migration rate was inversely proportional to the viscosity of the casting solution, since viscosity increased with PVP concentration. Based on the ANOVA of the six different membranes, as it was mentioned in the previous paragraph, the use of SMM41 did not make any statistical difference in the MWCO, PWP and PEG_{35K} separation. Since modified and unmodified membranes were definitively different with respect to their fluorine content (unmodified membranes do not have any fluorine), the fluorine content of the membrane surface did not have a significant effect on MWCO, PWP and PEG_{35K} separation.

SEM pictures of the cross section of the SMM-modified membranes are presented in Fig. 7.2. They show an asymmetric structure and at the bottom of the cross section, fully developed macropores with walls of sponge-like structure. Such a structure is typical of the membranes prepared with PVP in the casting solution (Han and Nam, 2002). There was no significant morphology variation between the membrane without PVP and the membrane with low PVP content (Figures 7.2a and 7.2b). However, the membranes with high PVP content showed a reduced size of macropores at the bottom of the cross section (Fig. 7.2c). Figure 7.2f shows that the intermediate layer, between the top skin layer and the porous sublayer, had a sponge-like structure. This layer was very thick and much less dense compared to the no- and low-PVP membranes (Figures 7.2d and 7.2e). A more finger-like type of structure was observed when the presence of macrovoids was suppressed (Fig. 7.2c). No appreciable difference was observed between the cross section of the membranes with SMM and that of the membranes without SMM (see Appendix I).

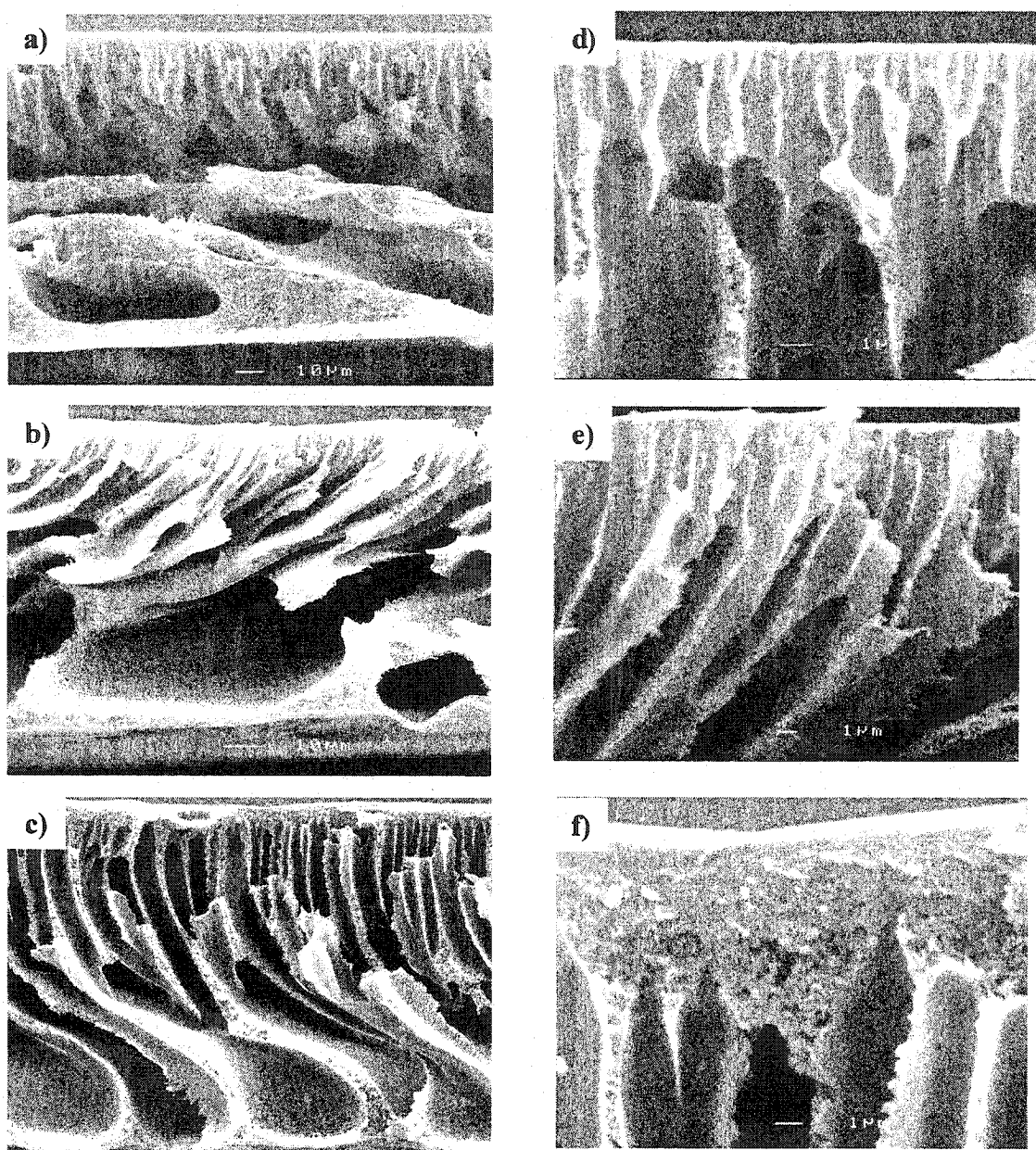


Fig. 7.2 SEM cross-section of the surface modified UF membranes. Casting solution a) and d) without PVP, b) and e) 6% PVP, c) and f) 18% PVP.

7.4.3 TOC removal

TOC removal using the different feed solutions, was calculated by the following equation:

$$TOC \text{ removal} = 100 \left(1 - \frac{C_{p(t)}}{C_f} \right) \quad (7.1)$$

where $C_{p(t)}$ is the permeate concentration at time t and C_f is the feed concentration (mass/volume). Removal by UV analysis was defined by an equation similar to Eq. (7.1), $C_{p(t)}$ and C_f are however UV absorbance of the permeate at time t , and UV absorbance of the feed, respectively. The TOC removal was evaluated during the fourth phase of the test, after the completion of the precompaction and the 50-h PWP determinations. For the unfractionated water and the HMW, the TOC removals were very similar for all the membranes with or without PVP (representative results are presented in Figures 7.3a and 7.3b) and with or without SMM. For the LMW runs, the membranes without PVP in the casting solution had somewhat different removals. At the beginning of the fourth phase of the test, TOC removal changed faster with time. In the case of the unfractionated water and the HMW, the TOC removal reached a plateau in 15 to 25 h, after the initial rapid increase. On the other hand, for the LMW, after the initial rapid increase, TOC removal kept increasing very slowly with time, and even by the end of the test it had not reached a constant value. Maybe this was because the removal mechanism was related to pore adsorption and cake formation, and it may take more than 144 h to reach a steady-state. For all membranes the highest removal was achieved with HMW and it was close to 70%. The removal of TOC from unfractionated water was around 65%, while for LMW it was between 40 and 50%. The standard deviation of the removals with different coupons was less than 5% in most cases. The value of the removals reached at the plateau for the six different membranes with different feed solutions are summarized in Table 7.3, and are analyzed in the next section. The uniformity of the TOC removal was rather surprising given the MWCO information (Table 7.2). According to the AMWD of CORW (Fig. 7.1), lower TOC removals would have been expected for the membranes with PVP. This might be related to fouling, since cake formation controls TOC removal. Removals based on UV analysis are given in parenthesis (Table 7.3). Comparing Fig. 7.3a with Fig. 7.3c, Fig. 7.3b with Fig. 7.3d, and Table 7.3, it is clear that UV absorbance removals were always higher than TOC removals, therefore, it can be concluded that

aromatic components are easier to remove by these UF membranes. Additional TOC removal graphs are presented in Appendix K.

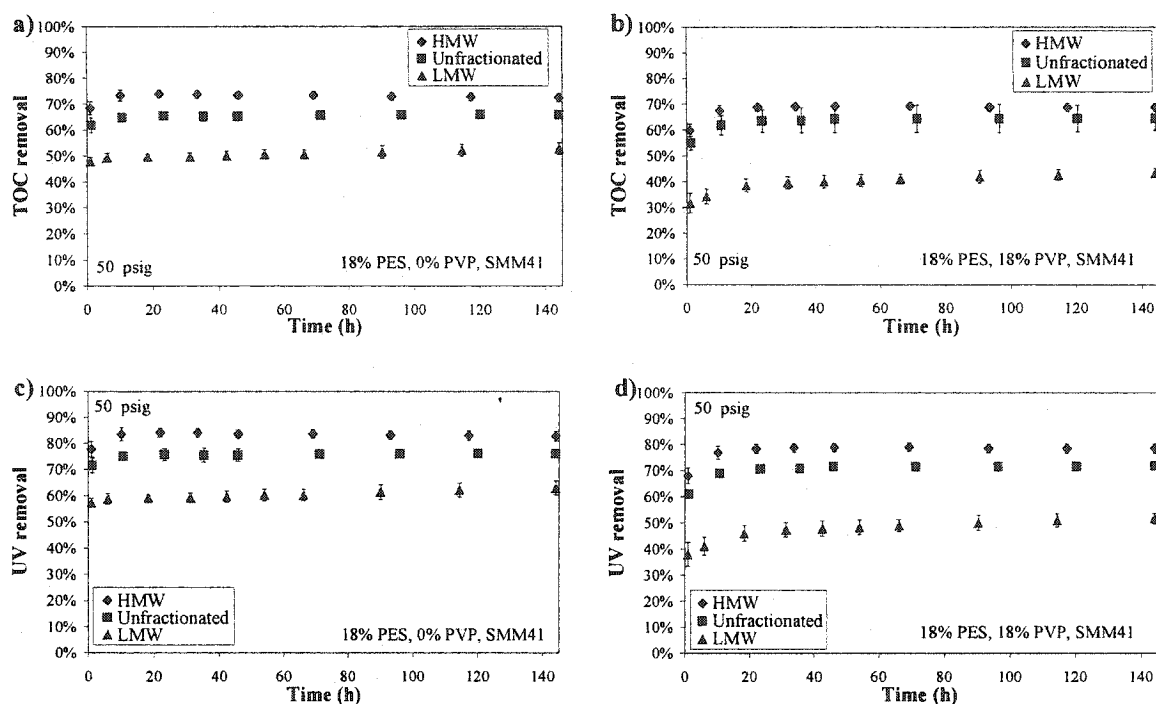


Fig. 7.3 Removals of NOM based on TOC and UV analysis. Operating pressure 345 kPa (50 psig). SMM41-modified membranes with a) and c) 18% PES, 0% PVP; b) and d) 18% PES, 18% PVP in the casting solution

Table 7.3 Average TOC and UV removal data for LMW, unfractionated and HMW feed waters with different membranes

PES/PVP	<i>LMW</i>		<i>Unfractionated</i>		<i>HMW</i>	
	No SMM	SMM41	No SMM	SMM41	No SMM	SMM41
18/0%	31% (46%) ^a	51% (61%)	63% (72%)	66% (76%)	71% (80%)	69% (83%)
18/6%	49% (58%)	46% (55%)	66% (74%)	67% (75%)	71% (81%)	70% (79%)
18/18%	43% (51%)	42% (49%)	65% (71%)	64% (71%)	72% (82%)	69% (79%)

^a Removals based on UV analysis are given in parenthesis.

7.4.3.1 ANOVA test for TOC removal

The null hypothesis for the ANOVA tests performed in this study was that the effect of any particular independent variable (i.e., PVP/PES ratio, the absence or presence of SMM in the casting solution, or NOM fraction) on each of the response variables (i.e., TOC removal, NOM deposition, normalized flux reduction, or final flux) did not exist, and the alternative hypothesis was that the effect was present. According to Devore and Farnum (1999), ANOVA tests are upper-tailed test, therefore, only large values of the F ratio lead to rejecting the null hypothesis (H_0), i.e., reject H_0 if $P\text{-value} \leq \alpha$. Commonly used values of α range from 1 to 10% (0.01 to 0.1). In this study, the value of α used for the statistical tests was 0.05 (5%). For the P-values in Table 7.4 to be statistically significant they should be ≤ 0.05 .

Table 7.4 P-values of the independent variables obtained from the analysis of variance (ANOVA) for the performance variables

<i>Source of variation</i>	<i>TOC Removal</i>	<i>NOM deposition</i>	<i>Normalized flux reduction</i>	<i>Final flux</i>
MAIN EFFECTS				
A:PVP/PES	0.2958 ^a	0.0437	0.0855	0.0722
B:SMM	0.3704	0.3522	0.6548	0.1355
C:Nature of feed water	0.0000	0.0000	0.0010	0.0000
INTERACTIONS				
AB	0.1046	0.3640	0.9721	0.1302
AC	0.7284	0.2489	0.4987	0.0616
BC	0.2339	0.1813	0.9921	0.0935
ABC	0.1098	0.0649	0.9726	0.1583

^a If $P\text{-value} \leq 0.05$ the effect is statistically significant

Among individual independent variables, the most important (and statistically significant) effect on all the response variables was the NOM fraction of the feed water. In general, no significant interactions were detected between the different factors (i.e., PES/PVP ratio, the absence or presence of SMM in the casting solution, or the NOM fraction) on any of the performance responses. In other words, the magnitude of a factor's effect on the response variable did not depend on the particular level of any other factor in the experiment (Devore and Farnum, 1999). Because interactions were not significant, results were interpreted through the examination of the main effect plots (Devore and Farnum,

1999). These results are typical of most factorial experiments, where over the range of factor levels studied, only a few factors and fewer interactions are significant. Even when Table 7.4 shows which factors were statistically significant, main effects plots were necessary to interpret how the significant independent variables affect the performance. Main effect plots (Figures 7.4, 7.5, 7.7, 7.8) were generated by averaging all response values in which the factor level is present, versus that factor level. The Y-bars represent the results of multiple range tests (multiple comparisons procedure) performed via the Least Significance Difference technique (LSD) at a 5% significance level (Montgomery, 1991).

The results of TOC removal for the different membrane coupons were very reproducible; standard deviations were less than 5% in all cases. However the effect of the different independent variables was also very small, and the only statistically significant effect was that of the fraction of NOM used in the feed solution ($P\text{-value}_{\text{fraction}} = 0.000$) (Table 7.4). It should be noted that the different NOM fractions had different TOC concentrations. Therefore, the design of the experiment did not allow us to separate the effects of TOC concentration and NOM fraction. However, Mosqueda-Jimenez et al. (2003a) found that under the same operating conditions the TOC removal experienced only a slight decrease when CORW was used as compared with ORW. Although the reason for this decrease was unknown, it was attributed to the higher concentration of mono and divalent ions in CORW, since the ORW was concentrated using an RO membrane (Nilson and DiGiano, 1996). Because the membrane used for fractionation in this study was an UF membrane (YM3), it is expected that the inorganic ions concentrations in both fractions remained almost constant. Therefore the main contribution when feed water was changed between tests from unfractionated, HMW, and LMW would be the size of the NOM molecules.

By comparison of the three levels of molecular size used in the solution, it was determined that the removal of the three fractions (HMW, unfractionated, and LMW) was statistically different. Therefore, it can be said that the larger the size of the NOM molecules in the feed solution, the better the TOC removal (Fig. 7.4c). The impact of the interactions was not statistically significant, nor was the impact of PVP/PES ratio (Fig. 7.4a) and the presence of SMM in the casting solution (Fig. 7.4b).

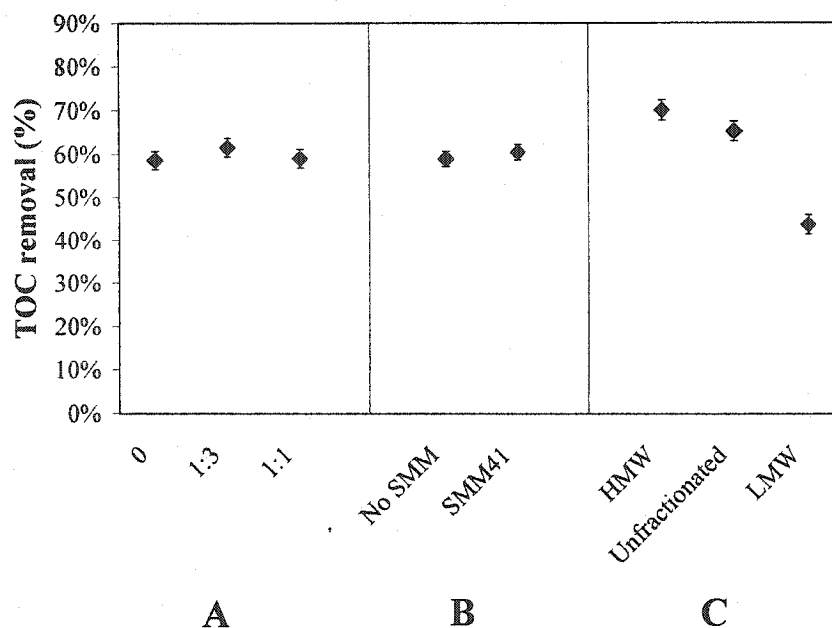


Fig. 7.4 Main effects of independent variables on TOC removal. A = PVP/PES ratio in the casting solution, B = Without and with SMM, C = Nature of feed water

Although the various membrane modifications tested did not significantly change the TOC removal, it should be noted that levels of TOC removal were very good, given that they were UF membranes. With a 100 kDalton-cellulosic membrane Jacangelo et al. (1994) removed less than 14 % TOC from Ottawa River water. The precompaction used before the MWCO determination caused a reduction of the membrane pore size; therefore, in this study UF membranes were tighter (probably with lower permeation rates than that of 100 kDalton-membrane used by Jacangelo et al. (1994)); their average MWCO was between 21 and 45 kDaltons (Table 7.2).

7.4.4 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. The measurement of NOM deposition was subjected to a large error, which is reflected in the error bars of Fig. 7.5. Simple observation revealed that the amount of NOM deposited in the case of the LMW was smaller than that deposited when unfractionated and HMW were the feed solutions. The colour of the cakes corresponded to the colour of the feed water, being very dark for HMW and light for LMW.

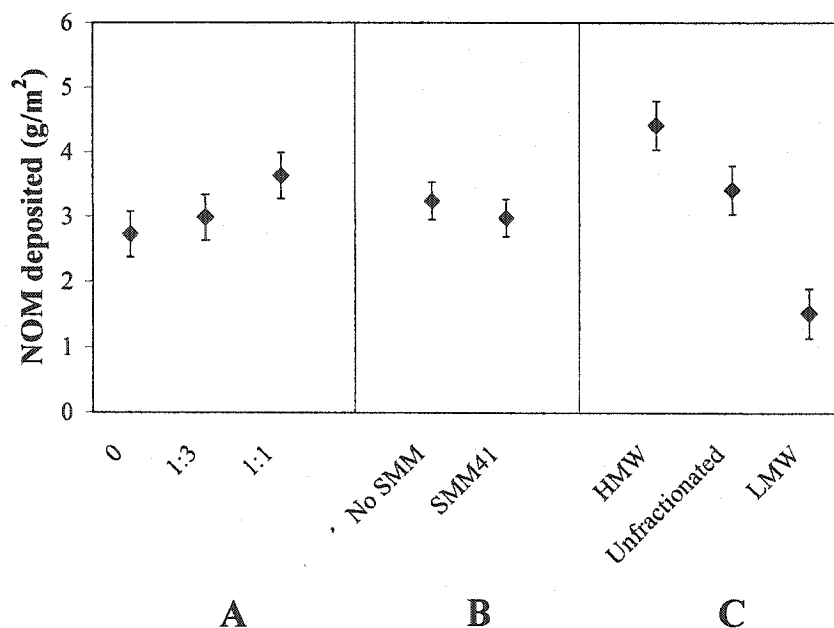


Fig. 7.5 Main effects of independent variables on the NOM deposition . A = PVP/PES ratio in the casting solution, B = Without and with SMM, C = Nature of feed water

It was found that the size of the NOM molecules and the PVP/PES ratio in the casting solution had a statistically significant effect on the amount of NOM deposited; P-values were 0.000 and 0.044, respectively (Table 7.4). Several authors have explained how the physical structure of NOM macromolecules in solution depends on the characteristics of the environment. According to Braghetta et al. (1998) the polyelectrolyte solution theory of Ghosh and Schnitzer establishes two hypothetical extreme macromolecular configurations for NOM. The first configuration is of flexible linear macromolecules, which occurs at very low ionic strength (salt content), in the absence of divalent cations (Hong and Elimelech, 1997), at low humic substances concentration, and at pH ranging between 6.5 and 9.5 (Aoustin et al., 2001). Under these circumstances intramolecular charge repulsion is high. The second configuration is that of a rigid, compact and spherocolloidal structure, which occurs at high ionic strength, in the presence of divalent cations, at low pH, and at high solution concentration. Under these circumstances intramolecular electrostatic repulsion decreases because the charge (functional) groups are neutralized (Ruohomäki et al., 1999). Depending on the particular environmental conditions, the NOM molecular configurations will be in between these extremes. In this

study the three feed waters had very similar concentrations of mono and divalent ions, and similar pH, because the fractionation was done with an UF membrane. The only difference was the NOM concentration in the solution; therefore the molecular configuration of the NOM in the three solutions is expected to be similar. Hence, the difference in the final amount of NOM deposited seems to be a function of the size of the molecules.

The amount of NOM deposited could also have been affected by the membrane characteristics. As the PVP/PES ratio in the casting solution determines the membrane structure and in turn, the permeation rate (Table 7.2), it will likely affect the magnitude of NOM deposition. Figure 7.5a shows that NOM deposition was statistically different between the membranes without PVP and the membranes with high PVP concentration, however the differences among the other pairings were not statistically significant. Most probably this effect was due to the increase of permeation rate when PVP was added to the casting solution as shown in Table 7.2. The more permeate passes through the membrane, the greater the chances of NOM being deposited on top of the membrane. Therefore, according to Fig. 7.5a, either a membrane without PVP or a membrane with low PVP should be used to achieve a goal of low NOM deposition. In addition, feed water with NOM of smaller molecular sizes also had lower NOM deposition (Fig. 7.5c). Neither the surface modification, nor any interactions have a statistically significant effect (Table 7.4); therefore, choosing either level (No SMM or SMM41) should give practically the same amount of NOM deposition (Fig. 7.5b).

7.4.5 Membrane fouling (Normalized flux reduction)

According to Nilson and DiGiano (1996), and Ramesh Babu and Gaikar (2001), the most consistent way to determine flux reduction requires normalization of the permeate flux data to the PWP baseline flux, obtained just prior to each test. Therefore,

$$\text{Normalized permeate flux}_{(t)} (\%) = 100 \left(\frac{PR_{(t)}}{PWP} \right) \quad (7.2)$$

where $PR_{(t)}$ is the permeate flux (product rate) at time t of the fourth stage of the test, and PWP has dimensions = volume/time-area, measured during the second stage of the test.

The normalized flux reduction was taken in this study as a measure of membrane fouling. Figure 7.6 shows both normalized flux reduction and absolute permeate fluxes. It is observed that the rate of flux reduction with time was faster at the beginning of the six-day tests, and then it reached a nearly constant rate of flux reduction. However the fluxes had not stabilized to a constant value even after 144 h. In both Fig. 7.6a and Fig. 7.6b, the order of flux reduction is LMW < Unfractionated < HMW; although, in the case of the membranes with PVP, the permeate flux reduction for unfractionated water was very similar to that of the HMW (Fig. 7.6b). Vrijenhoek et al. (2001) found a nearly perfect correlation between flux decline (caused by colloidal particles) and membrane surface roughness when studying four commercial NF and RO membranes with very different topographies (average roughness was between 10.1 and 52 nm). The difference between the highest and smallest flux decline was 255%, while in this study this difference was less than 33%. The experimental membranes had very similar values for average roughness R_a (measured using an AFM), ranging between 1.4 and 3.8 nm, so the experimental membranes were significantly smoother than the membranes tested by Vrijenhoek et al. (2001). When normalized flux reduction in this study was correlated with the average roughness no strong relationship between them was found. For more details, please refer to Appendix H.

Figures 7.6c and 7.6d show that the reproducibility among coupons was always smaller at the beginning of the test; however, initial fluxes for the same type of membrane were statistically the same, allowing the comparison using different feed solutions. In Fig. 7.6d it is observed that even when the initial flux of the membrane tested with LMW was the highest, at the end the flux reduction was smaller than that caused by the unfractionated and the LMW. This shows the importance of the effect that the size of NOM used in the feed solution has on the flux reduction. Additional normalized permeate fluxes are shown in Appendix K.

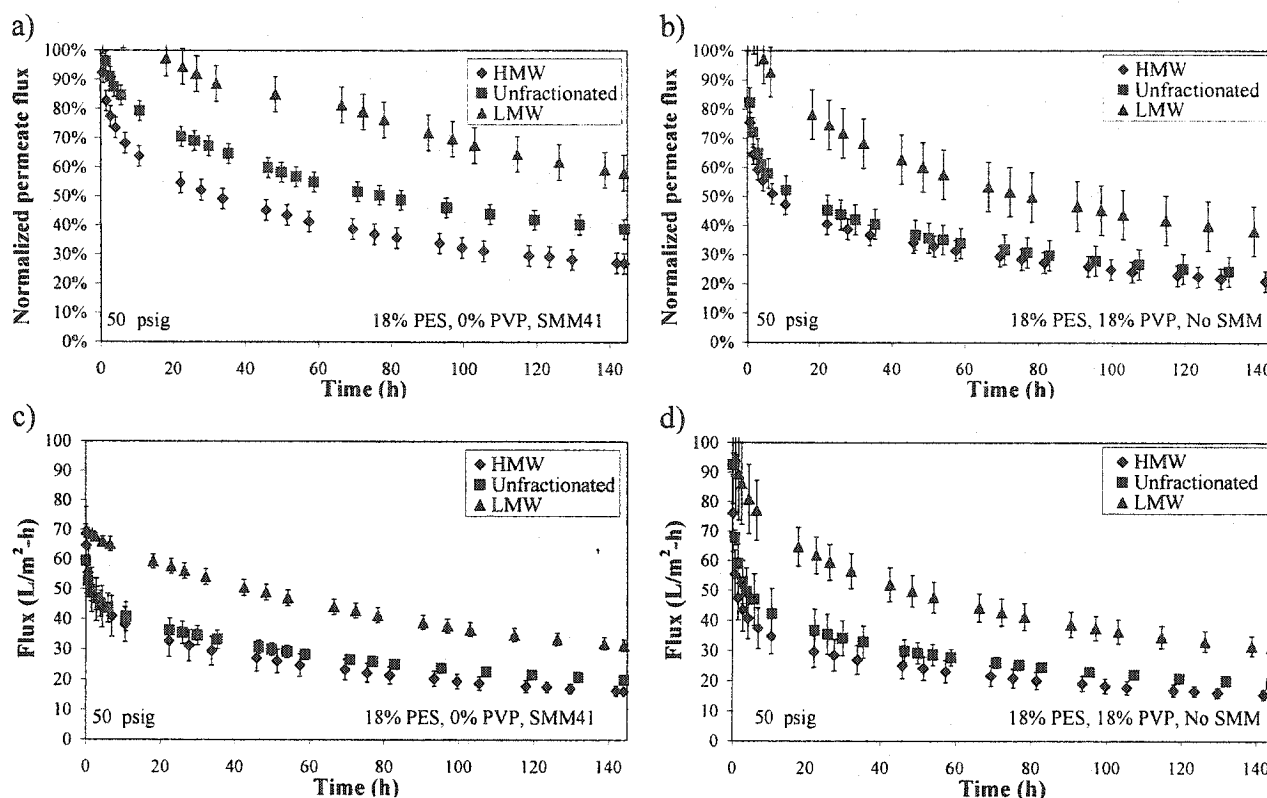


Fig. 7.6 Permeate flux and change of the normalized permeate flux with time along the 6-day test. Operating pressure 345 kPa (50 psig). a) and c) Modified membranes with 18% PES, 0% PVP, b) and d) Unmodified membranes with 18% PES and 18% PVP in the casting solution

7.4.5.1 ANOVA test for membrane fouling

The standard deviations of the 144-h flux reductions for membranes prepared under identical manufacturing conditions were less than 10%. The ANOVA test in Table 7.4 indicates that the only statistically significant effect was that of the fraction of NOM ($P\text{-value}_{\text{fraction}} = 0.001$). Even when the design of experiments did not allow us to separate the effects of TOC concentration and NOM fraction, in a previous study (Mosqueda-Jimenez et al., 2003a) it was found that under the same operating conditions the TOC concentration did not have an effect on flux reduction when the ORW was compared with CORW, and the normalized flux reduction after six days of test was exactly the same. Therefore in this case, the effect of the NOM fraction could be attributed to the size of the NOM molecules in the feed solution.

The flux reduction for membranes without PVP was similar to that experienced by membranes with low PVP content, and smaller than that experienced by membranes with high PVP concentration in the casting solution. From Fig. 7.7a, it can be said that using either low PVP or no PVP in the casting solution should give statistically the same permeate flux reduction. In terms of feed fraction, Fig. 7.7c shows that HMW and unfractionated water resulted in flux reductions in the same range. However the flux reductions with HMW (and unfractionated) were different from those with LMW. These trends were expected given similar results for NOM deposition. Therefore, in order to reduce fouling (and NOM deposition) either a membrane with low or no PVP in the casting solution would be preferable. Moreover, less fouling will be expected when NOM molecules in water have smaller sizes (less than 3,000 Daltons).

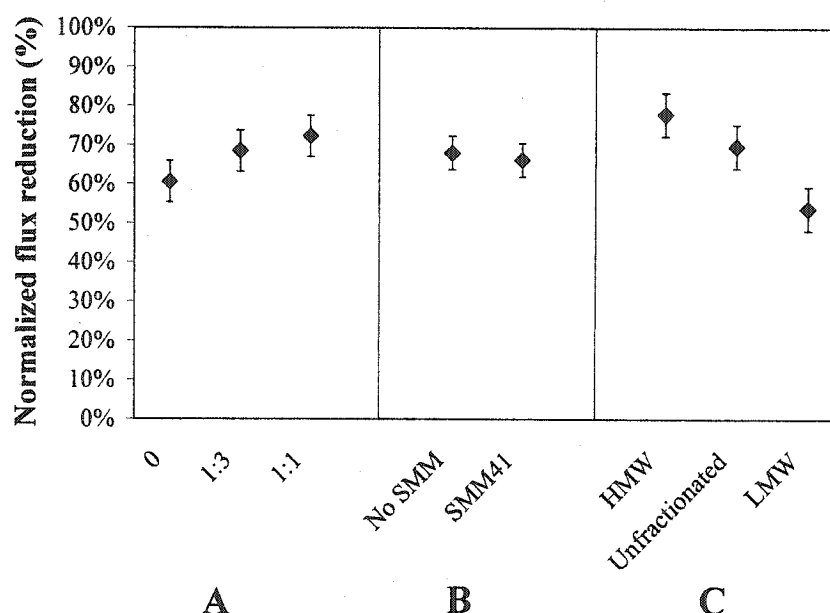


Fig. 7.7 Main effects of independent variables on the normalized flux reduction. A = PVP/PES ratio in the casting solution, B = Without and with SMM, C = Nature of feed water

Somewhat similar results have been observed in other studies. When fractionating water from the Tar River with UF, Nilson and DiGiano (1996) concluded that the high-molecular-weight NOM was probably responsible for most of the permeate flux decline. On the other hand, using commercial humic acid, Lin et al. (2000) found that the fraction

with apparent molecular weight in the range from 6.5 to 22.6 kDaltons exhibited the worst flux decline.

7.4.6 Final flux (permeation rate)

The only variable that had a statistically significant effect on the permeate flux at the end of the experiment was the fraction of NOM with a $P\text{-value}_{\text{fraction}}$ of 0.000 (Table 7.4). Final flux results were reproducible and had a standard deviation of approximately 6% for membrane coupons prepared under the same manufacturing conditions. Examining the plot of main effects of PVP/PES (Fig. 7.8a), it was concluded that membranes prepared with casting solutions with PVP gave a slightly higher final flux than those without PVP. In the case of the fraction, the permeation rate obtained at the end of the experiment with LMW was much higher than those obtained by unfractionated and HMW feed water.

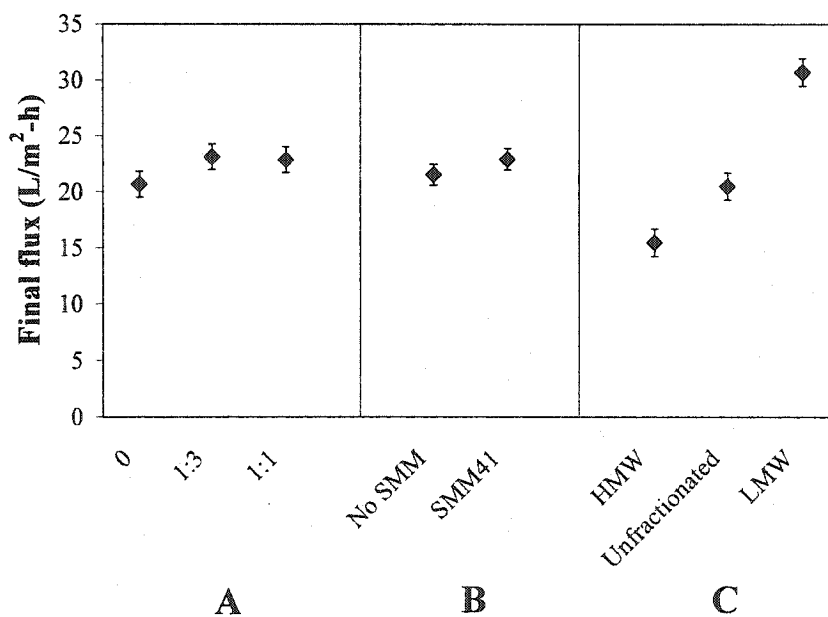


Fig. 7.8 Main effects of independent variables on the final permeate flux. A = PVP/PES ratio in the casting solution, B = Without and with SMM, C = Nature of feed water

7.4.7 Contact angles

The contact angles of the six different membranes used in this study were measured in order to elucidate the reason for the lack of effect of the SMM on the independent variables. According to Fig. 7.9, even when the addition of SMM caused a slight increase in hydrophobicity (greater contact angle), the difference is not statistically significant. It seems that the SMM migration reported in Section 7.4.2 was not sufficiently high to have caused a significant increase in hydrophobicity. When PVP was used as additive, the impact of the SMM41 was not even observed in the pore size (Table 7.2). This seems to indicate that the small effect of the SMM was overshadowed by the effect of the PVP. To ensure a complete coating of the SMM on the PES membranes, attempts were made to prepare composite membranes. For details, please refer to Appendix M.

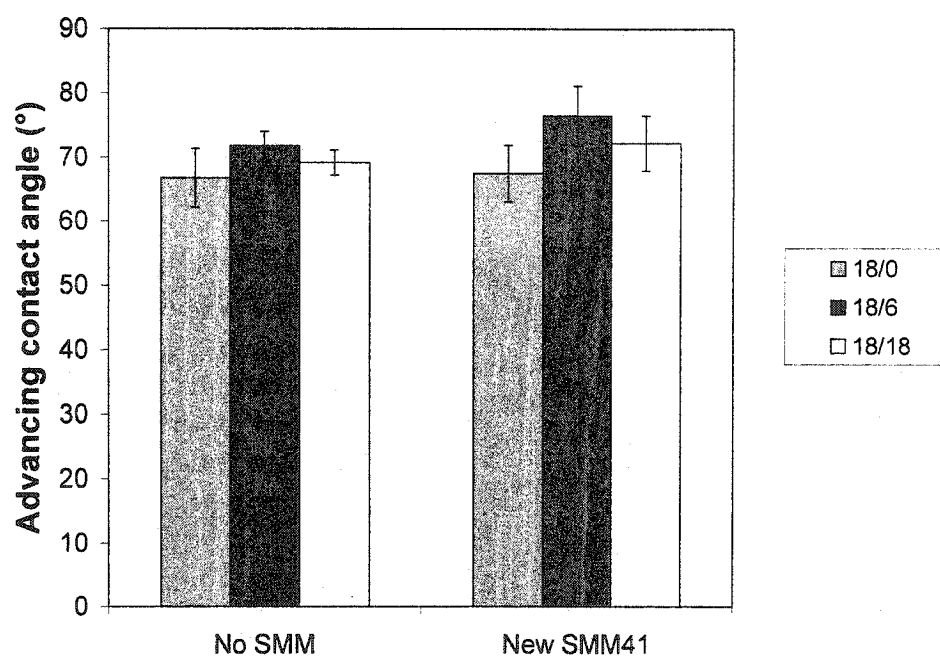


Fig. 7.9 Advancing contact angles for the three different membranes

7.4.8 Responses and independent variables

Based on the results shown above, it was concluded that although the surface modification slightly improved the membrane performance (Figures 7.4, 7.5, 7.7, 7.8), the improvement was not statistically significant. Moreover, the optimum performance could be achieved when the molecular weight of NOM in feed water was less than 3,000 Daltons. It should be noted that the NOM in the Ottawa River water has an unusual molecular weight distribution, even for a surface water. Several researchers have found that 50% or more of the NOM in surface waters has a molecular weight less than 5,000 Daltons (Chadik et al., 1991; Jacangelo et al., 1994; Braghetta et al., 1997). Hence, it is believed that these membranes will perform at their highest level when treating groundwater, since generally NOM from groundwaters has smaller molecules than NOM from surface waters. On the other hand, according to Amirtharajah and O'Melia (1990), NOM with molecular weight less than 10,000 Daltons are not removed with high efficiency by coagulation-flocculation. Therefore, in the case of surface water, the integration of coagulation as a primary treatment and UF with these membranes as a secondary treatment would have favourable results in terms of flux reduction, achieving high levels of TOC removal.

Membranes prepared with 1:1 PVP/PES ratio showed higher membrane fouling and NOM deposition than the membranes prepared without PVP. Moreover, the processing of high-viscosity solution is rather difficult (Kesting, 1985). Membranes prepared with low PVP content (1:3 PVP/PES ratio) performed very similarly to membranes without PVP. Although the PWP of the low PVP content was higher than that of the membranes without PVP, when challenged with CORW they suffered the same flux reduction and NOM deposition, and their final flux was just slightly higher. However, in terms of manufacturing suitability, membranes prepared with casting solutions that contain a PVP/PES ratio of 1:3 are better, since their viscosity is higher, allowing them to retain their integrity throughout gelation (Kesting, 1985). Furthermore they are mechanically stronger than the membranes without PVP (Cabasso et al., 1976).

7.5 Conclusions

1. It was found that surface modification did not significantly impact the performance of 18 wt % PES membranes. The addition of PVP had a greater impact than the addition of SMM, however some of the impacts were positive (i.e., higher permeation rates) and some were not (i.e., greater fouling).
2. The independent variable that had the most important effect on all the response variables (TOC removal, NOM deposition, normalized flux reduction or final flux) was the fraction of NOM used in the feed water: The higher molecular weight NOM caused greater fouling. Thus, membrane performance is significantly impacted by feed water quality.
3. The best performance of the experimental membranes will be achieved when prepared either with low or no PVP in the casting solution. Membranes with PVP/PES ratio of 1:3 had the additional advantage of better casting properties (i.e., more viscous solution) and higher mechanical strength.
4. The TOC removal for these membranes was relatively high (compared with reported results for UF membranes), approximately 65% for the unfractionated concentrated Ottawa River water.

7.6 Acknowledgements

We acknowledge Materials and Manufacturing Ontario (MMO), Natural Sciences and Engineering Research Council of Canada (NSERC) and CONACyT (Mexico) for their financial support.

7.7 References

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Notation

α = significance level related to the probability of rejecting a true hypothesis.

A = PVP/PES weight ratio (factor with three levels: 0, 1:3, 1:1)

B = SMM (factor with two levels: absence or presence of SMM in the casting solution, i.e., No SMM, and SMM41)

C = nature of the feed water (fraction of the NOM) (factor with three levels: HMW, unfractionated, LMW)

$C_{p(t)}$ = permeate concentration at time t.

C_f = feed concentration.

d_1 = depth 1 from the surface of the membrane.

d_2 = depth 2 from the surface of the membrane.

Fluorine _{d_1} = Fluorine content at depth 1.

Fluorine _{d_2} = Fluorine content at depth 2.

$PR_{(t)}$ = permeate flux (product rate) at time t.

P-value, associated with a calculated F ratio = the area under the F distribution to the right of the calculated F ratio (Devore and Farnum, 1999).

PWP = pure water permeation rate.

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

Based on the results of this research, the following general conclusions can be made:

1. The smaller ultrafiltration continuous-flow cells are an effective substitute for the EPA-recommended SEPA CF cells in the evaluation of new membrane materials. They yielded very similar TOC removals and flux decline, and required a membrane coupon of one eighth the size. In addition, when the feed flow rate is low, a single pump can be used to simultaneously drive six of these cells, so that six different coupons can be evaluated at the same time. When six cells are used in series, neither the effect of the experimental runs nor that of the test cells order was statistically significant on any of the response variables studied.
2. The experimental membranes removed between 60 and 70% of the TOC, which are very high removals for ultrafiltration membranes. This is due to the tightness of the membranes (aided by intensive membrane precompaction), and the high apparent molecular weight of the Ottawa River NOM. These removals appeared to be further enhanced by fouling effects, such as cake formation and pore narrowing.
3. For Ottawa River water there was a compromise between TOC removal and membrane water production. Thus, for a particular application, it is necessary to decide whether an increase of TOC removal is worth the consequent reduction of water production and vice versa.
4. XPS results demonstrated that the three SMMs migrated to the surface; however, this did not result in an increase of the contact angles or improved overall performance. Since low or no evaporation times were used during the manufacturing of the experimental membranes, the effect of the SMMs was observed only in terms of a modification of the pore size distribution and not in

terms of increase of hydrophobicity. Attempts to increase surface hydrophobicity by using longer evaporation times and surface coating with SMM solution consistently yielded defective membranes.

5. In general, the surface active character of the SMMs decreased the size of the pores (MWCO) and increased the number of pores per unit area in comparison with the unmodified membranes. In most of the cases, permeation rate of the modified membrane was smaller than the unmodified membranes, causing a decrease on flux reduction and NOM deposited on the top of the membranes at the end of the six-day experiments with concentrated Ottawa River water, while TOC removal did not increase significantly. Thus, the hypothesis about the impact of SMMs was found to be correct, since there was a reduction of the susceptibility to fouling and an increase of TOC removal. However, the improvement was very marginal.
6. SMM41 was the most promising SMM since the best PES-SMM41 membranes had similar fluxes to those of the unmodified membranes, and experienced slight less fouling and NOM deposition. Given the slight benefit achieved, the addition of SMMs does not appear to be worthwhile.
7. The performance of the membranes when challenged with three different NOM fractions of CORW differed significantly indicating that membrane performance is water dependent. Low-molecular-weight NOM, as that encountered in most groundwaters, and coagulated surface waters, causes less membrane fouling, and higher permeate fluxes, however its TOC removal was lower.

8.1.1 Minor conclusions

1. The very popular dead-end cells used at lab-scale testing are not recommended in the evaluation of a given membrane, since their performance is very different from that of the continuous-flow cells.

2. The effect of membrane compaction was very important in membranes prepared with polyethersulfone (PES) as base polymer. Therefore it is important to take this into account during the study of fouling.
3. Precompaction of the membranes caused a deformation of their structure producing tight UF membranes with low permeation rates and relatively high TOC removals, placing the performance of these membranes in the low end of the UF range, close to that of the NF membranes.
4. Increasing the solvent evaporation time or increasing the PES concentration had an effect in the same direction as that of the surface modification, i.e., they also decreased the MWCO of the membranes and the permeation rate, causing a decrease in the amount of NOM deposited. A higher solvent evaporation time significantly increased the TOC removal and decreased the final flux.
5. Membranes prepared with 18 wt % of PES were preferred, because membranes prepared with low PES content were fragile, making their manipulation harder, and possibly compromising their use for water treatment applications. Raising the PES concentration to 21 wt % did not significantly improve the membrane performance.
6. The most important effect of PVP additions was a significant increase of PWP. However, when present in a 1:1 PVP/PES ratio it also increased significantly the fouling with CORW. Thus, its impact was somewhat positive or somewhat negative depending of which of these two criteria are considered more important. When employed at a PVP/PES ratio of 1:3, flux reduction and TOC removal were similar to those of membranes prepared without PVP, with a slight increase in permeability and better casting properties (i.e., more viscous solution) and higher mechanical strength. The effect of surface modification of membranes that contain PVP was statistically insignificant.

8.2 Recommendations

In order to improve the understanding of all the phenomena involved in membrane studies, the following recommendations are suggested:

1. Incorporation of a pre-filter in front of the membrane test cells in order to eliminate the effect of extraneous sources of fouling.
2. When testing membranes prepared under different manufacturing conditions, use of a minimum of seven PEG solutions with different molecular weights during the solute transport characterization to improve the confidence in the determination of the parameters of the pore size distribution.
3. Incorporation of a back-feed controller, that allows the automatic adjustment of the water bath temperature.
4. Use of several membrane coupons, for each manufacturing conditions, randomizing its location in the train of cells and in the order of the test runs to eliminate extraneous sources of variability.
5. Test of the effect of different sources of water, including ground water and coagulated surface-waters on the performance of these new membranes.
6. Comparison of the performance of these lab-prepared membranes with that of large-scale commercial membranes, under the same test conditions.
7. Thorough characterization not only of the feed waters, but of the foulants collected on top of the membranes at the end of the experiment.
8. Test of higher evaporation times for SMM41-modified membranes.
9. Modeling of the permeate flux reduction in order to gain more knowledge on the fouling mechanisms.

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APPENDIX A

TEST OF A SECOND WATER SOURCE AND A SECOND COMMERCIAL MEMBRANE

Besides the Ottawa River water, a second water source was tested, a highly coloured water, from the Mer Bleue Bog (MBBW), in Ottawa. The purpose of this test was find if there were advantages to using a natural high TOC water versus an artificially TOC concentrated water. The same protocol followed in the test of ORW and CORW for the continuous-feed cells (described in Section 3.2.1.5) was used. MBBW was more highly coloured water than ORW, and the TOC concentration of the MBBW was almost the same as that of CORW, i.e., the five-fold concentrated ORW.

To be able to compare results in this study with previous works, for some tests the HO51 membrane was substituted by the YM3 membrane (Millipore, Bedford MA). The 63.5-mm diameter YM3 membrane discs were cut to fit in the RO and UF cells. This membrane was just like the membranes used in the AMWD determinations, and it is made of a regenerated cellulose membrane with a nominal MW of 3,000 Daltons. The same test protocol was repeated using CORW as the feed source. Results from these tests are presented later in this Appendix (see Section "Test of a second membrane").

Test of a second water source

MBBW was a very brown water. The TOC concentration of MBBW was 36 ppm, while for CORW it was 28 ppm. MBBW was evaluated using the same commercial membranes and conditions as described in Chapter 4. Results for precompaction and PWP determination are presented in Fig. A.1. They correspond to averages calculated based on two to six repeats. At the beginning of the test, all the HO51 membrane coupons had statistically the same initial flux. However, the effect of precompaction was more important in the case of the membrane coupons challenged later with MBBW. The reason of this difference is unknown, since Milli-Q water and the same operating pressures and times were used for the different runs. Nevertheless, it is believed that some external factor in the run might have contributed to this difference, i.e., residues inside the piping

system, and to a lesser extent slight experimental differences in pressure, temperature, feed flow, etc.

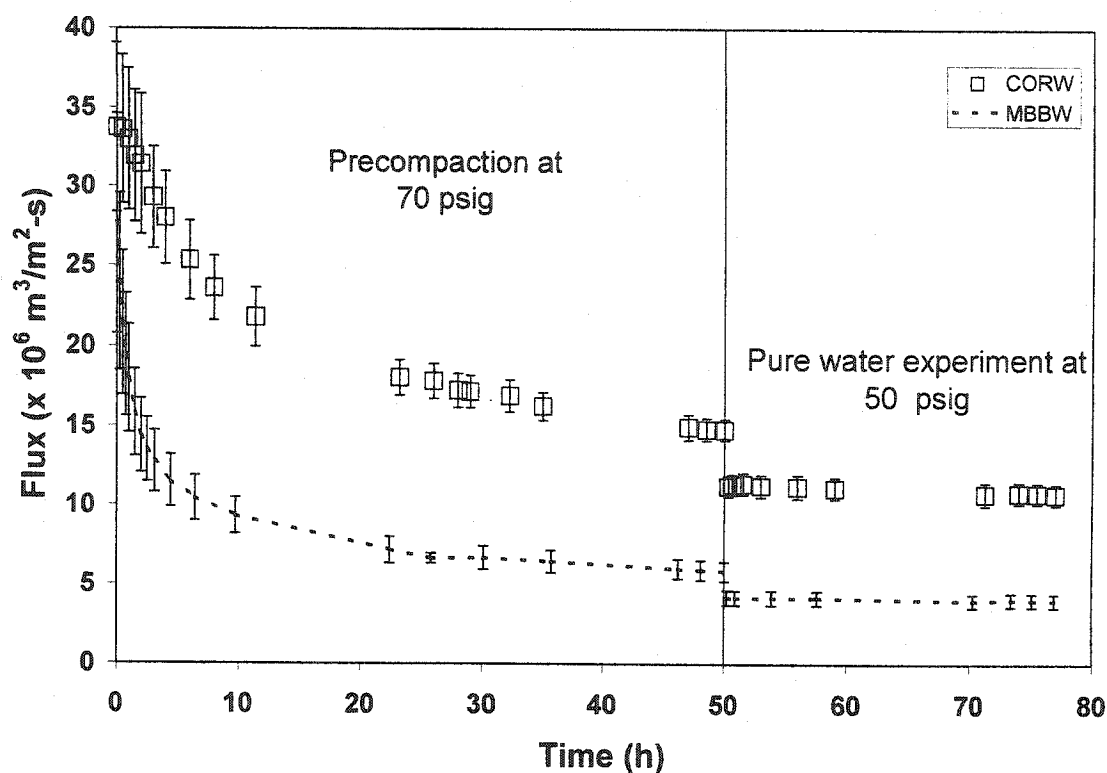


Fig. A.1. Flux reduction during precompaction protocol for membranes used later for test with CORW and MBBW

Afterwards, when the feed solution was changed from Milli-Q water to either CORW or MBBW, the relative flux reduction was more important in the case of the CORW (Fig A.2a). However it was observed that the final absolute fluxes for membranes challenged with MBBW were very similar to those final absolute fluxes for the membranes whose feed was CORW (Fig A.2b). It seems that independently of the intermediate effect of precompaction and membrane fouling, at the end all the HO51 membranes had the same final permeate flux. Given that the precompaction effect was unexpectedly different in both cases it was not possible to conclude if the use of MBBW was more advantageous than the use of CORW, however as we had available more CORW than MBBW, CORW was used for the rest of the experiments.

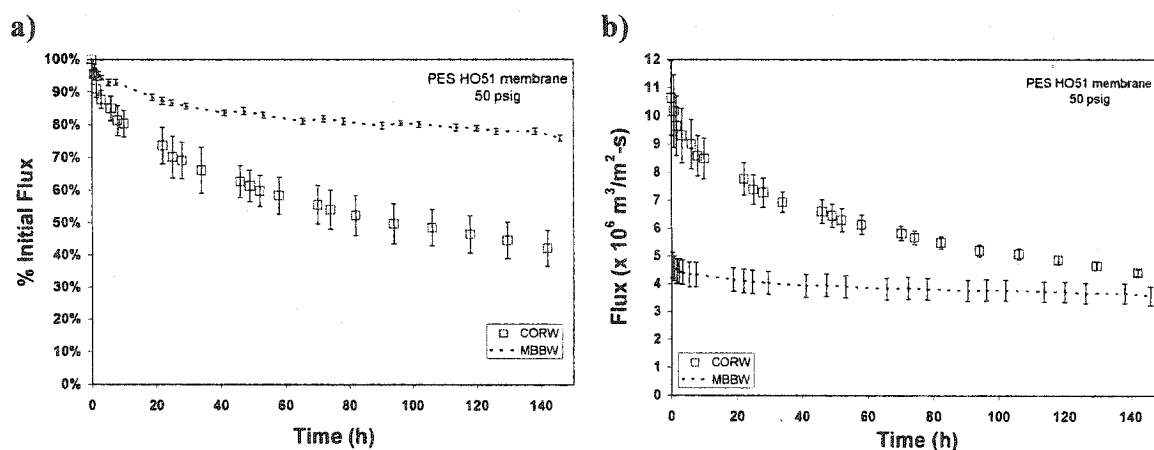


Fig. A.2 Permeate flux reduction observed with concentrated Ottawa River water (CORW) and Mer Bleue Bog water (MBBW)

As the source of NOM in the MBBW was different from that of CORW, the same PES membrane (HO51) showed different TOC removals. They were more than 95% for MBBW and around 80% for CORW (Fig. A.3a). The UV absorbance removals were 99% and close to 90% for MBBW and CORW, respectively (Fig. A.3b). As the UV absorbance removals were higher than the TOC removals, these membranes preferentially remove the aromatic/hydrophobic NOM fraction (Amy and Cho, 1999; Cho et al., 2000b).

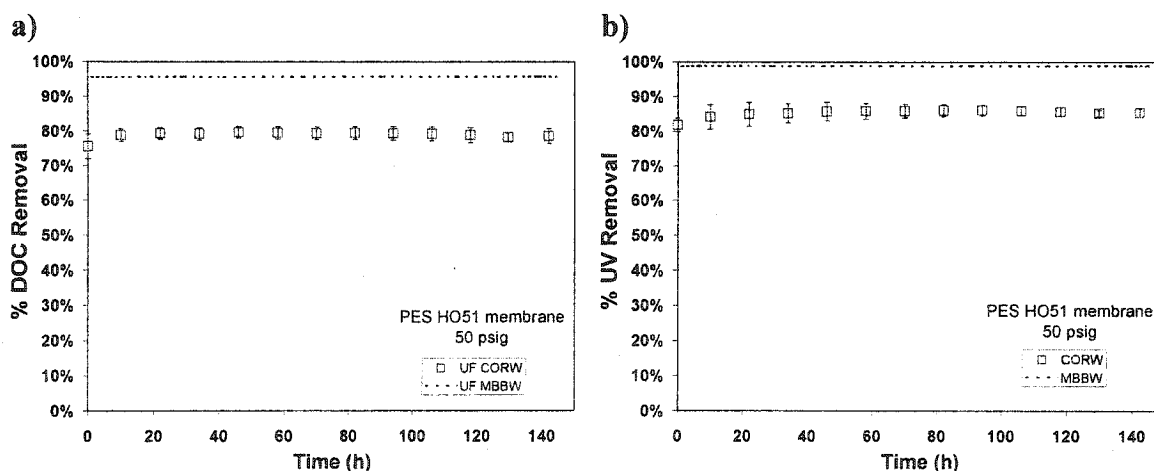


Fig. A.3 DOC and UV removal from CORW and Mer Bleue Bog water

Higher removals for MBBW were presumably due to the removal of NOM with higher molecular weight, which is consistent with the observation of a higher colour. Higher

colour is frequently associated with the higher molecular weight fraction of NOM, as observed in Chapter 7, when different fractions of the CORW NOM were used.

Test of a second membrane

In order to determine the difference in performance among several membrane materials and to be able to compare results in this study with previous works, a second commercial membrane, commonly used in laboratory testing, YM3, was also employed. YM3 is a regenerated cellulose membrane. In this section, the performance of commercially-available membranes was compared with that of one of the experimental SMM-modified membranes. This is important in the sense that it helps to establish if the performance of the experimental membranes is superior to that of the commercial membranes. PES/SMM41 is the membrane tested during the second stage, prepared with 18 wt % PES and SMM41, without solvent evaporation time. As discussed in Chapter 7, the difference in performance when tested with CORW between PES/SMM41 membrane and the membrane prepared with PVP/PES ratio of 1:3 was very small, therefore, the former membrane is representative of the best performing experimental membranes.

The effect of precompaction on HO51 and YM3 membranes was described in Chapter 4. In Fig. A.4b it is observed that when challenged with CORW, the initial flux of the PES membrane, HO51, and the regenerated cellulose membrane, YM3, was statistically the same. The initial flux of the SMM-modified membrane (PES/SMM41) was higher than that of the commercial membranes, however at the end of the 6-day experiment its average permeate flux was 33% lower than that of the YM3 membrane. The permeate flux of the experimental PES membrane was always higher than that of the HO51 membrane; its average final flux was 26% higher. YM3 membrane showed a lower flux reduction when filtering CORW for 6 days (Fig. A.4a), while the flux reduction for both PES membranes was statistically the same. This difference is directly related to the material that constitutes these membranes, regenerated cellulose in the case of YM3, and PES for HO51 and the experimental membrane.

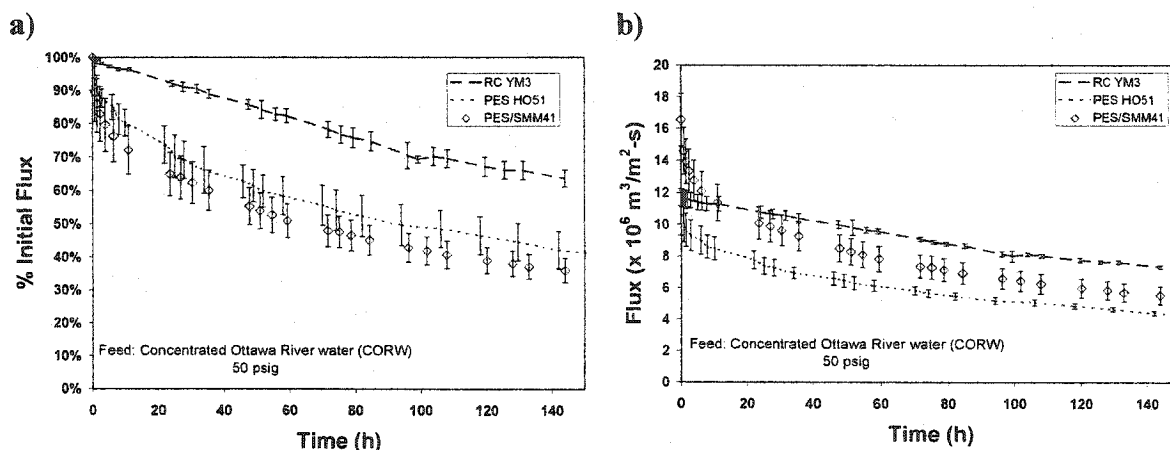


Fig. A.4 Comparison of the permeate flux reduction for HO51 and YM3 membranes and experimental membrane

It is observed, in Fig. A.5a that the low-fouling YM3 membrane showed lower DOC removal (ca. 50%) compared with the approximate 80% removal of the PES HO51 membrane. Cho et al. (1999a) observed DOC removals of 51.1% for an agricultural drain (DOC = 47.8 ppm) when testing the YM3 membrane. It is believed that membrane fouling was contributing to enhance the removal in the case of the HO51 membranes. UV removals were higher than the DOC removals for both types of membranes, nevertheless YM3's removal was more than 13% smaller than HO51's (Fig. A.5b). Experimental membrane achieved DOC and UV removals in between the commercial membranes. PES/SMM41 membrane achieved a DOC removal 15% higher than the "low-fouling" YM3 membrane.

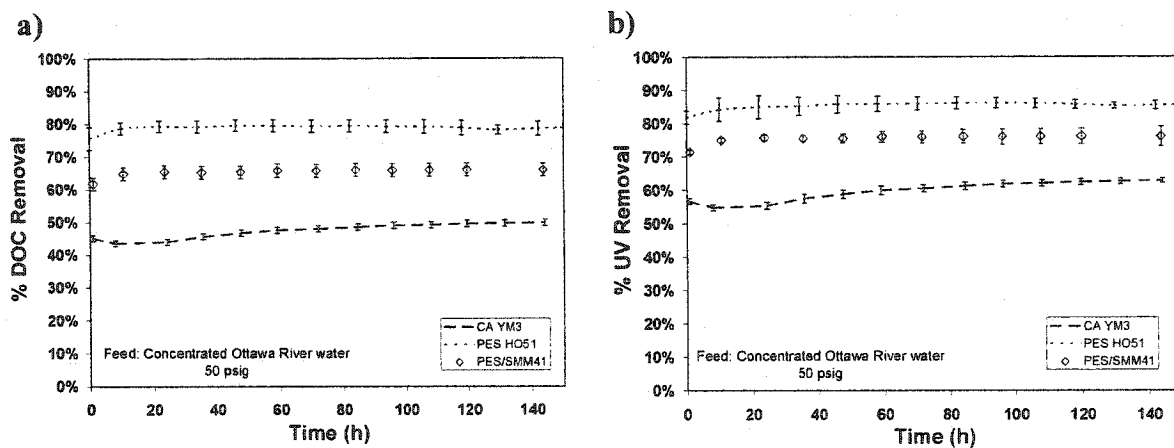


Fig. A.5 Comparison of the a) DOC and b) UV removals achieved with HO51 and YM3 membranes and experimental membrane

Once again the trade-off between DOC removal and membrane productivity was observed both with commercial and experimental membranes. Furthermore, the performance of the experimental membrane proved to be comparable to the commercial membranes tested. It is worth noting that both YM3 and HO51 are very tight UF membranes and they are not representative of the UF membranes used in large-scale applications.

APPENDIX B

CLEANING TESTS AND ASSESSMENT OF CONTRIBUTIONS TO FOULING

After the filtration of CORW or ORW, the pressure was released to remove any concentration polarization that resulted from the membrane's rejection of NOM under forced permeation as mentioned by Cho et al. (1999a), and PWP was measured using Milli-Q water. This way, based on the resistances-in-series model, from the difference between PWPs before and after CORW (or ORW) filtration it was possible to separate the magnitude of fouling from the concentration polarization (Cho et al., 1999a). Then the membranes were flushed with Milli-Q water for at least half an hour and PWP was measured again using fresh Milli-Q water. Afterwards, the membranes were removed from the cells and soaked in 0.1 N NaOH solution overnight, then, they were placed in their respective cells, flushed with Milli-Q water and the PWP was measured once more. In a second test, after flushing with Milli-Q water and measuring the PWP, the membranes were cleaned with the same caustic solution, but this time in-situ (without removing the membrane coupons from their cells). It is ideal to place the membranes back in the cells exactly in the same position as they were during the fouling test, which is why the in-situ cleaning was performed. However, this type of cleaning implied extra rinsing of the whole system in contrast with the membrane cleaning outside of the cells.

A blank test refers to the use of Milli-Q water instead of river water, following the same protocol. When a blank test was performed with the HO51 membrane, a decrease on the flux was observed (Fig. B.1), even after precompaction. It is worth noting that Fig. B.1 does not show the precompaction stage, it starts at the PWP determination performed after precompaction. Upon release of the pressure after filtering Milli-Q water for 144 h, a flux recovery of ca. 18% was detected. However when PWP was measured again at 345 kPa gauge (50 psig), the flux continued decreasing. It would appear that part of the flux reduction with Milli-Q water was due to further compaction of the membrane, and the rest was due to concentration polarization or fouling caused by extraneous solids (as explained in Chapter 4).

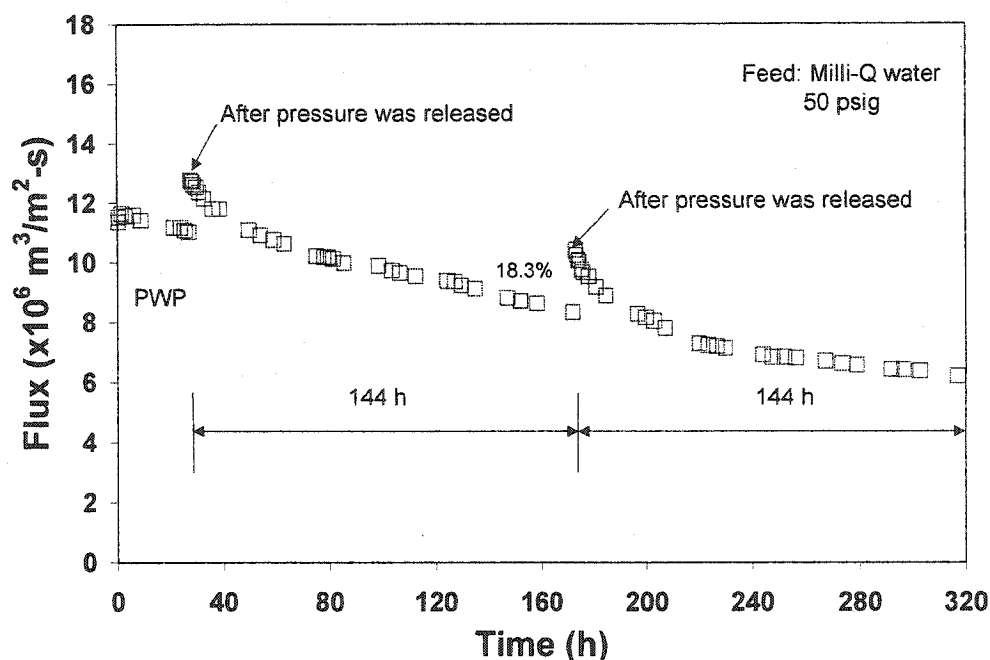
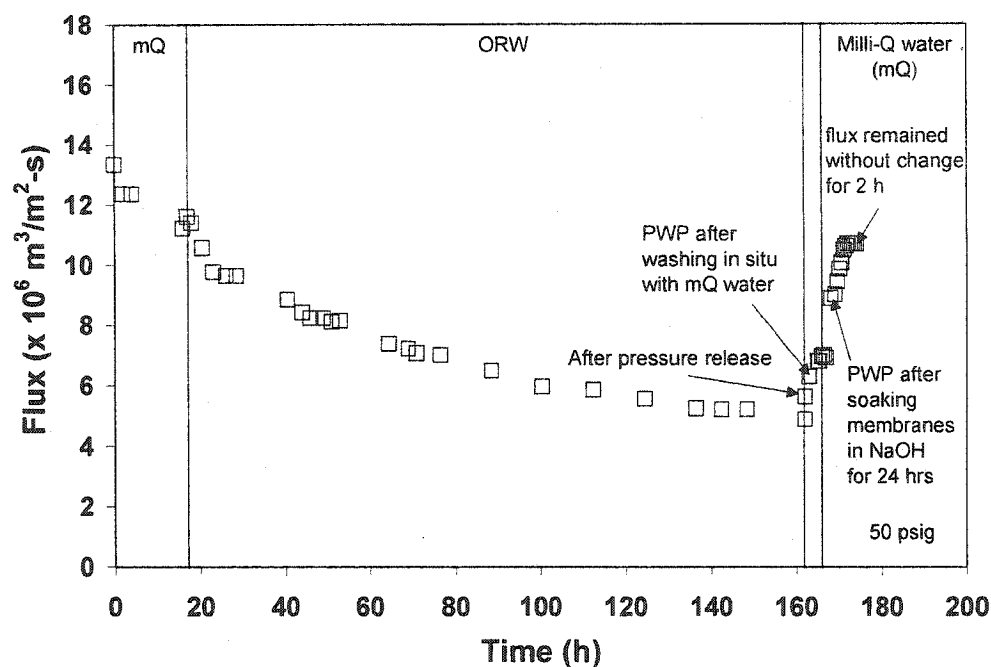


Fig. B.1 Flux reduction with pure water

The cleaning procedures that were used to evaluate the different contributions to fouling are described above. A new test was done with new membrane coupons. After measuring the flux reduction with ORW ($t = 162$ h in Fig. B.2), the pressure was released and the PWP was again determined. As shown in Fig. B.2, the PWP was 7% higher than the final PR. Since concentration polarization results from the membrane retention of solutes under forced permeation, it can be said that this recovery was due to the elimination of concentration polarization. Then, the system was flushed with Milli-Q water for 2 h and PWP recovered by an extra 29%. According to Cho et al. (1999a), this recovery was due to the elimination of the gel layer. Finally, after HO51 membranes were removed from the cells and soaked in NaOH for 24 h, the PWP of the cleaned membranes had a further recovery of 63%, due to the elimination of the weakly adsorbed material (Cho et al., 1999a). Comparing the initial PWP (after precompaction of the new membranes) to the final PWP of the cleaned membranes, the effect of fouling due to irreversible adsorption of NOM in the membrane was a flux reduction of 14%.



**Fig. B.2 Impact of ex-situ cleaning after filtration of Ottawa River water.
Membrane: PES HO51**

When the same protocol was repeated with CORW but cleaning in-situ with NaOH, no fouling was observed, and flux was recovered completely (Fig. B.3). It is believed that the reason for the difference between the two cleaning procedures was the disturbance of the system caused when the membranes were soaked in the caustic solution outside of the cells (i.e., membrane coupons are unlikely to be placed back in exactly the same position as they were prior to cleaning). The outer area of the coupon was pressed against the o-ring and it was not subject to fouling, if the coupon was misplaced in the cell, this outer area would have a different behaviour compared to the rest of the coupon.

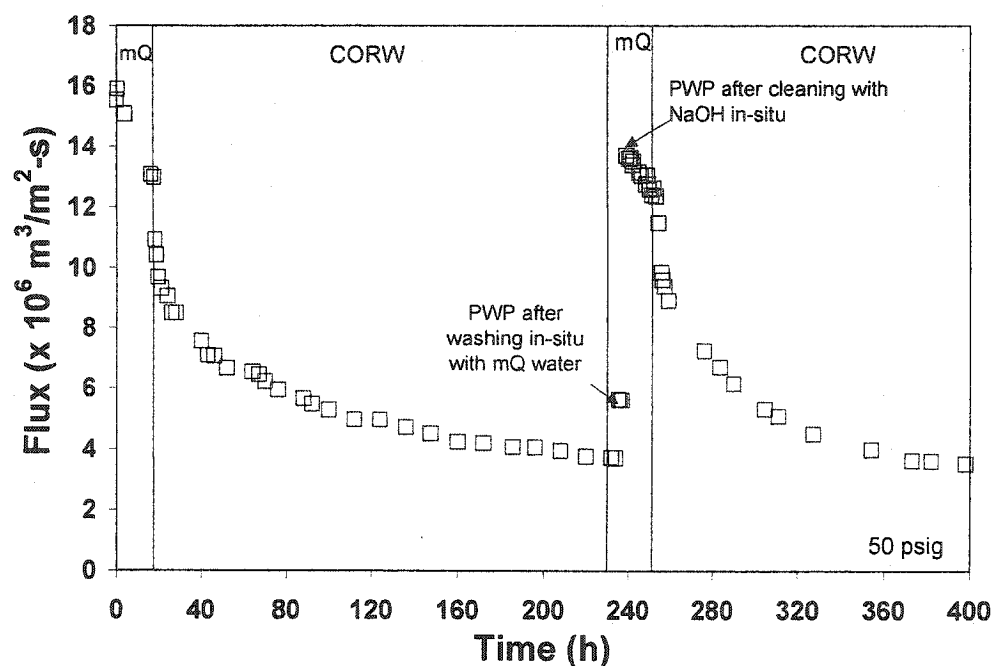


Fig. B.3 Impact of in-situ cleaning after filtration of concentrated Ottawa River water. Membrane: PES HO51

In accordance with these data, based on the resistances-in-series model, the most important contribution to flux reduction corresponded to the weak adsorption of solids that were eliminated with NaOH (Table B.1). The difference observed between the contributions of adsorption to flux reduction with ORW and with CORW might be due to either the characteristics of the water or the in-situ cleaning with NaOH in the second case.

Table B.1 Contribution to flux reduction

	ORW	CORW
Concentration polarization	6 %	17 %
Gel layer	22 %	10 %
Weak adsorption	46 %	73 %
Irreversible adsorption	26 %	0 %
Total	100 %	100 %

The results presented in this section were obtained with UF test cells, since other continuous flow test cells behaved very similarly. Tests using the Amicon cell and the

static cell showed no effect of irreversible fouling by CORW NOM with the HO51 membranes tested (Fig. B.4). The initial permeation rate was completely recovered after cleaning with NaOH. Thus, it is likely that the irreversible adsorption was due to particles or molecules lost in the concentration process.

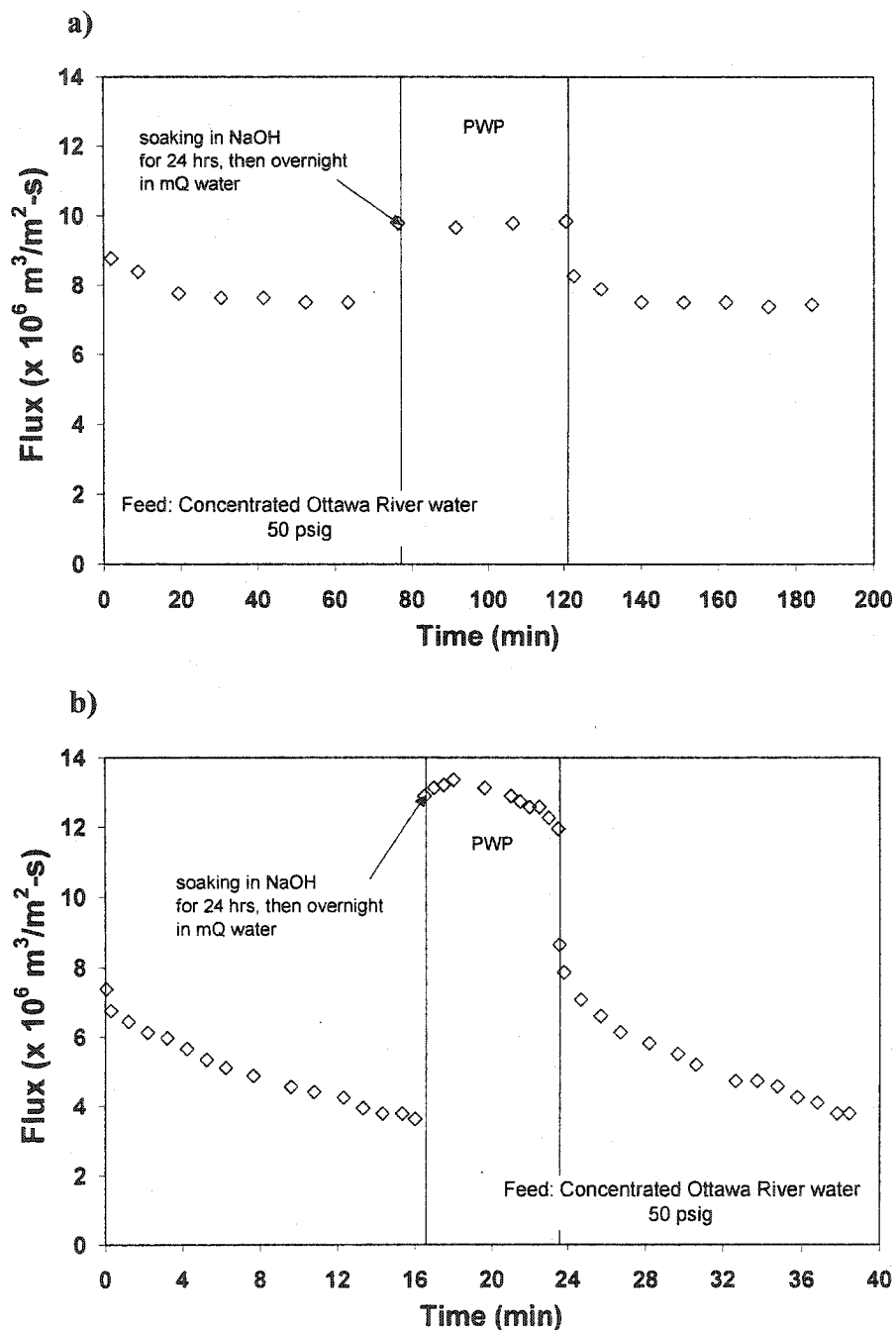


Fig. B.4 Cleaning procedure for batch cells: a) Amicon cell and b) Static cell.
Membrane: PES HO51

APPENDIX C

STATIC CELL

In Chapter 4 several test cells were evaluated, including the Amicon stirred UF cell. A second dead-end cell, the static cell, was also evaluated. Some results are presented in this appendix. The flux reduction using CORW in the static cell was very close to that in the Amicon cell (presented in Chapter 4) (Fig. C.1). On the other hand, the static (or batch) cell showed a higher continuous decrease in flux with CORW than with ORW (Fig. C.1). However, it is worth noting that the concentration inside the cell increased geometrically as water is filtered. This increase was proportional to the initial concentration.

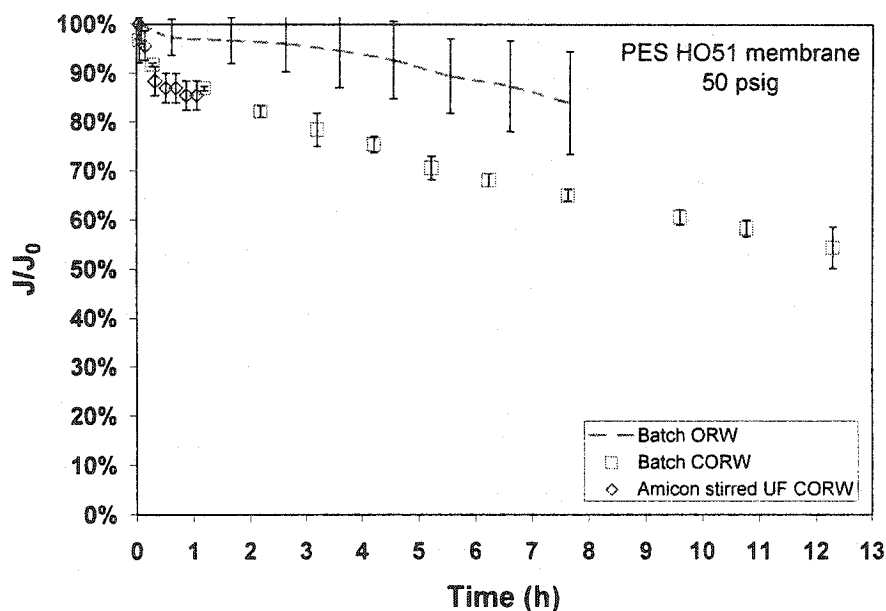


Fig. C.1 Relative flux for batch cells.

Contrary to the increase in permeate concentration when using the Amicon cell, presented in Chapter 4, permeate concentration for the static cell was constant during the experiment (Fig. C.2). Thus, as the bulk concentration increased with filtered volume, the % DOC rejection increased. DOC removals were close to 20% in the case of ORW and more than 40% for CORW. It is likely that the greater amount of dissolved solids favoured the removal in the case of the CORW.

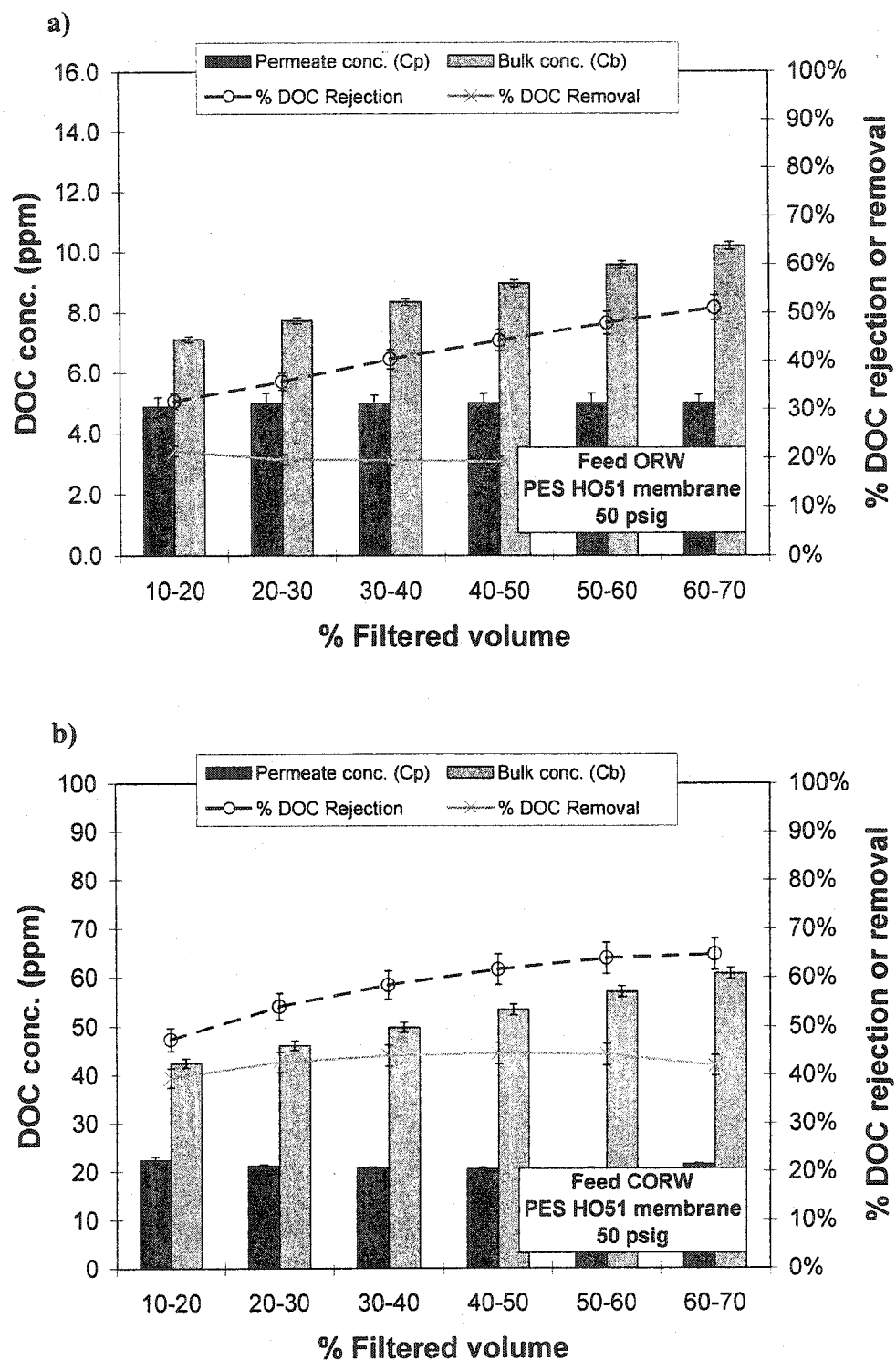


Fig. C.2 DOC removals in the static cell using: a) Ottawa River water and b) concentrated Ottawa River water

APPENDIX D

PRELIMINARY TESTS

In order to find the limits of the factorial design used during the second stage of this study, several membranes were prepared to perform some preliminary tests. Membranes prepared with different amounts of PES with and without PVP were challenged with CORW, during preliminary tests, as explained in Chapter 3. Figure D.1, shows that the initial flux (after precompaction) of membranes prepared with the same ratio PES/PVP was the same, even when the PES concentration was different (i.e., 10 and 15 wt %). The initial flux of the membrane prepared with 15 wt % PES and no PVP was slightly higher, but when the PES concentration was increased to 18 wt %, the initial PR decreased significantly. In spite of these differences, the final flux of the four membranes was statistically the same. Data presented in figures correspond to measurements performed at least in duplicate; up to 5 coupons were tested in the case of the membranes prepared without PVP.

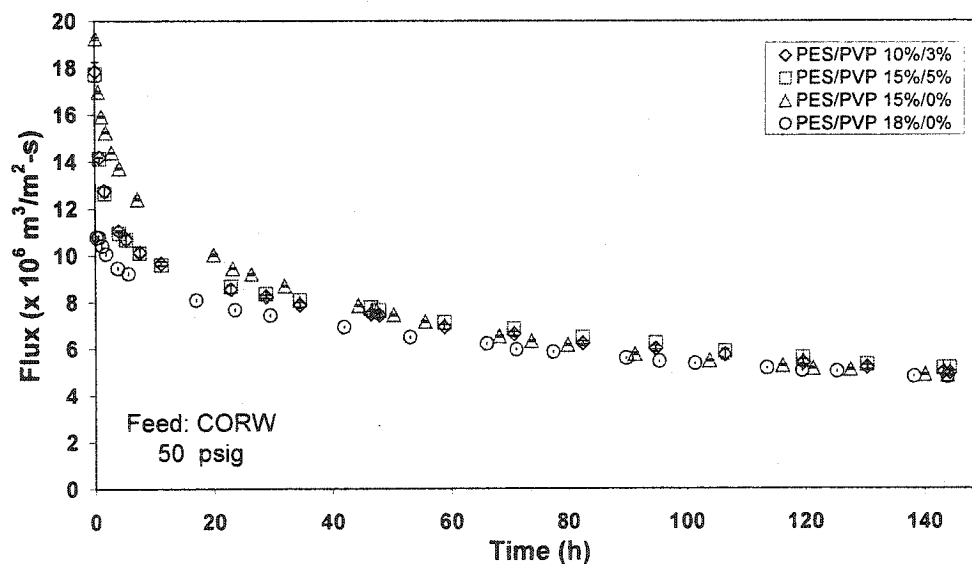


Fig. D.1 Flux reduction for membranes without SMM prepared for preliminary tests.

Consequently when these data was put in terms of relative flux (J/J_0), the flux reduction of the membrane prepared with 18 wt % PES and no PVP, was significantly smaller than that reached after the same period with the other three membranes, as shown in Fig. D.2.

It is worth noting that each membrane was tested separately in different experimental runs, thus, there was no influence between the results of individual types of membranes.

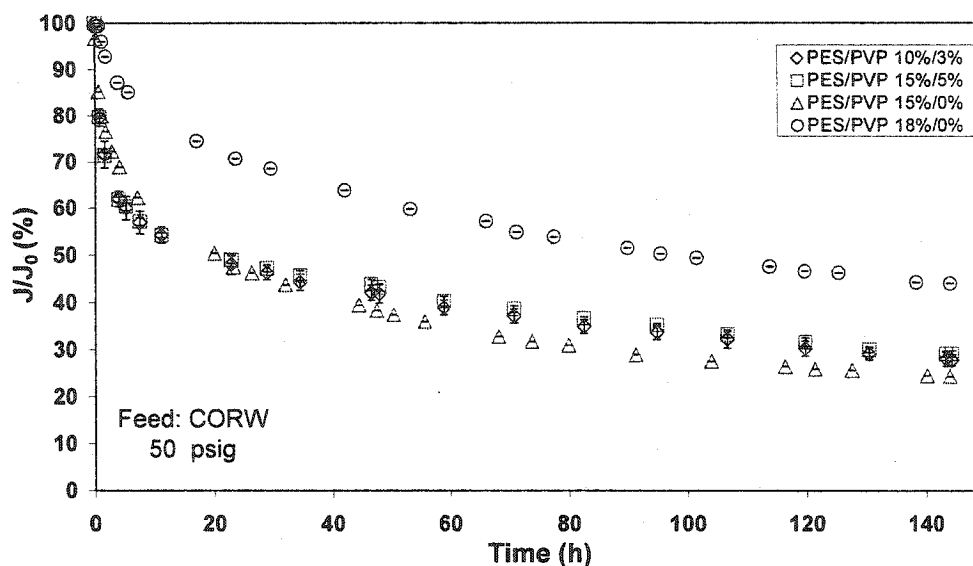


Fig. D.2 Relative flux for membranes without SMM prepared for preliminary tests.

Solute transport data (PEG probe) was used to characterize the membranes. Laboratory prepared PES membranes were compared together with the HO51 membrane. Results are presented in Fig. D.3 and D.4. When the ratio PES/PVP was the same, increasing the PES concentration in the casting solution caused a decreased in the average pore size, while surface porosity was very similar. The addition of PVP to the 15 wt % PES solution caused a significant increase in the average pore size (MWCO), while the number of pores and surface porosity decreased. HO51 membrane was the tighter membrane of all with higher amount of pores per unit area. These results are presented in Table D.1.

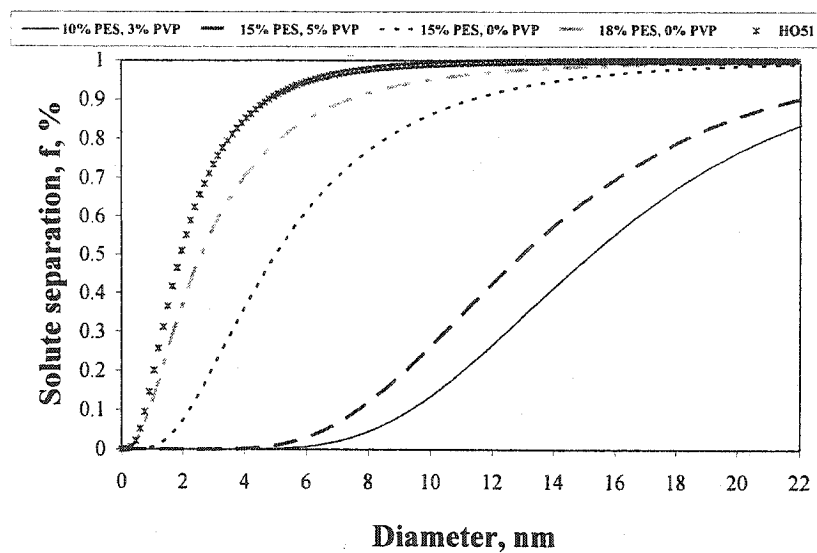


Fig. D.3 Solute separation as a function of the solute diameter for preliminary membranes.

Table D.1 Characteristics of preliminary membranes and commercial PES membrane

	HO51	10% PES, 3% PVP	15% PES, 5% PVP	15% PES, 0% PVP	18% PES, 0% PVP
μ_p	1.9	15.2	13.0	5.0	2.6
σ_p	2.04	1.46	1.51	1.89	2.27
MWCO	7	157	127	36	17
N	380	7	8	47	84
S_p	0.31%	0.09%	0.11%	0.18%	0.15%

μ_p = geometric mean pore size [nm]

σ_p = geometric standard deviation about the mean pore size

MWCO = molecular weight cut-off [kDaltons]

N = pore density [pores/ μm^2]

S_p = surface porosity [%]

In Fig. D.4 and Table D.1, it is observed that membrane HO51 and the membrane prepared with 18 wt % PES had very small pores compared with the other three laboratory-prepared membranes, especially the ones with PVP, which had relatively large pores.

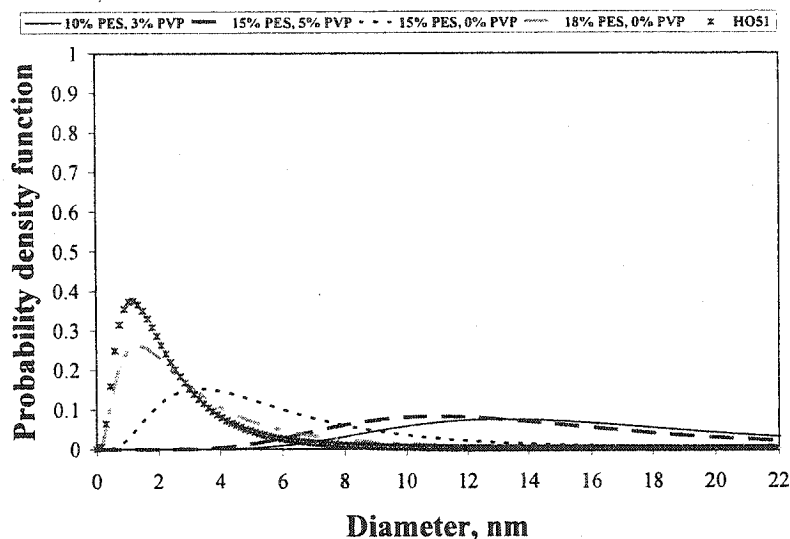


Fig. D.4 Probability density function with respect to the solute diameter.

The change of TOC removal with time graph presented in Fig. D.5 shows the typical increase at the beginning of the test, and in less than 20 h, the removal became stable and remained constant until the end of the experiment. TOC removals were inversely related to the MWCO of the membranes, i.e., HO51 with smallest MWCO had a TOC removal of approximately 80%, while the looser membranes prepared with PVP, had removals close to 55% (Fig. D.6.). However, the latter removal was significantly higher to the value expected in accordance to the AMWD of the NOM in the ORW.

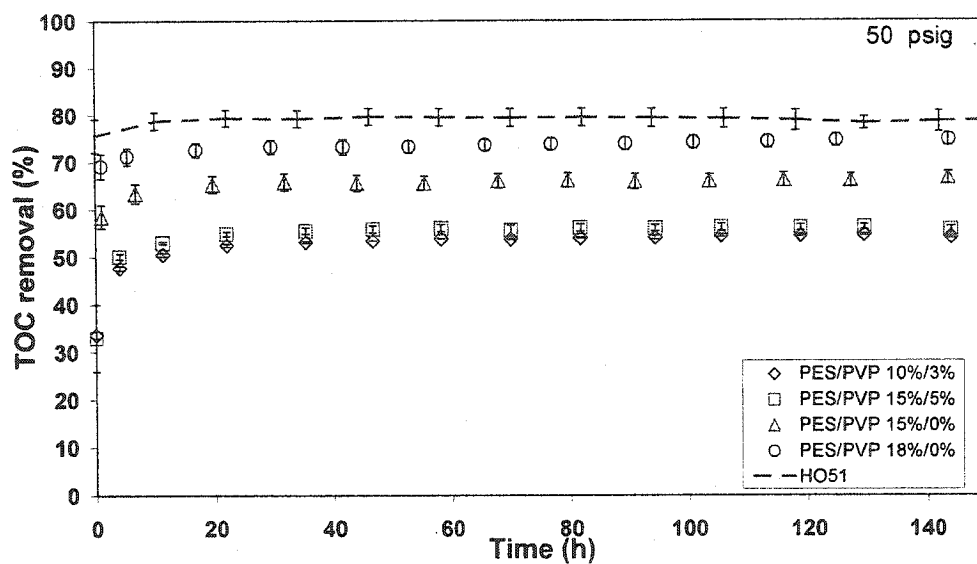


Fig. D.5 TOC removals achieved with preliminary membranes.

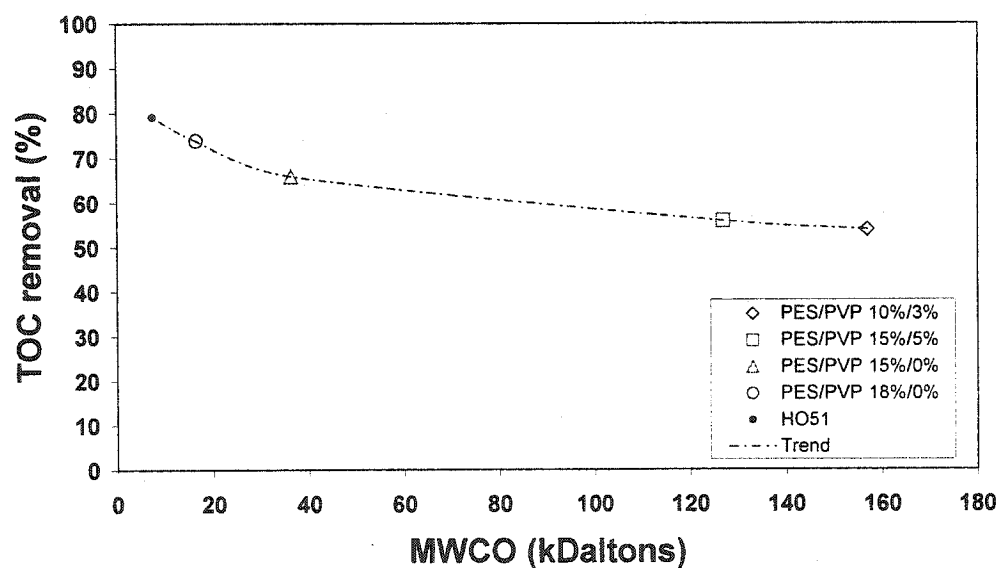


Fig. D.6 TOC removals as a function of membrane MWCO.

When the effect of further precompaction and fouling due to extraneous material (not from the CORW, as explained in Chapter 4) was eliminated through the employment of a blank of Milli-Q water, the effect of just fouling was determined as shown in Fig. D.7. From the comparison between Figures D.2 and D.7, it was found that approximately 40% of the reduction was independent of the NOM in the CORW.

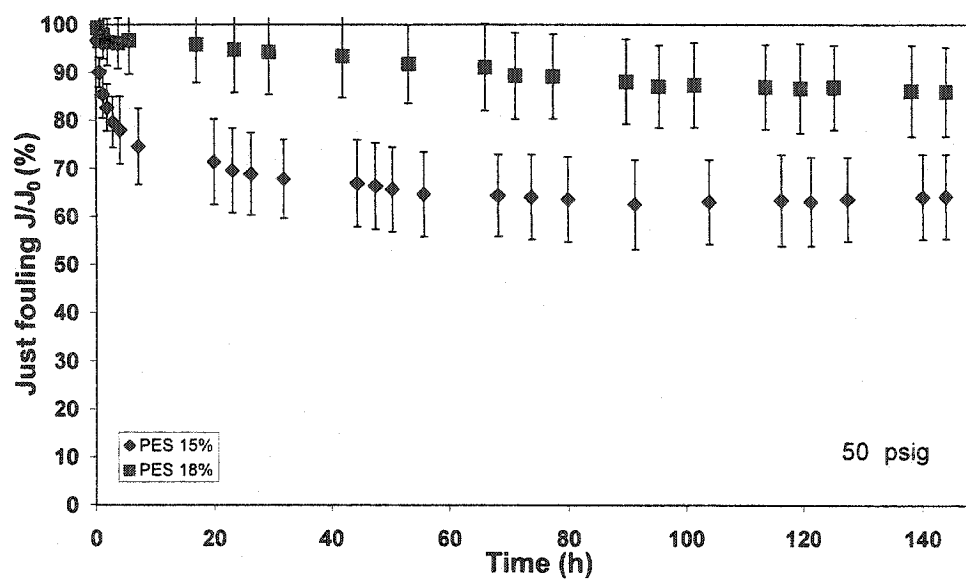


Fig. D.7 Just fouling effect on membranes prepared without PVP during the preliminary tests.

APPENDIX E

EVALUATION OF THE IMPACT OF TEST CELLS AND EXPERIMENTAL RUNS

In order to quantify the source of variability introduced by the test cells and/or the order in the chain of cells, together with the experimental run, a 4×4 graeco-latin square was used. This design allowed the study of 4 treatments, simultaneously with three different blocking variables (Box et al., 1978), as shown in Table E.1.

Table E.1 4×4 graeco-latin square

	I	II	III	IV
1	A α	B β	C γ	D δ
2	B δ	A γ	D β	C α
3	C β	D α	A δ	B γ
4	D γ	C δ	B α	A β

In Table E.2 rows, columns, and greek letters correspond to the three different blocking variables, while the latin letters correspond to the 4 different treatments. In this study, the columns correspond to the test cell, i.e., first, second, etc., cell in the series of cells; while the rows correspond to the different experimental runs. The greek letters correspond to each of the three SMMs tested, together with the unmodified membranes, i.e., α = Additive 1, No SMM; β = Additive 2, SMM DEG; γ = Additive 3, SMM DPS; δ = Additive 4, SMM41. The latin letters correspond to each set of the manufacturing conditions tested. i.e., A = 12 wt % PES, 0 min solvent evaporation time, B = 12 wt % PES, 3 min solvent evaporation time, C = 18 wt % PES, 0 min solvent evaporation time, and D = 18 wt % PES, 3 min solvent evaporation time.

Information for different response variables was collected in the order specified by the graeco-latin square (Table E.1), and ANOVA tests were performed for each response variable.

ANOVA for 4 × 4 graeco-latin square design

ANOVA results are presented in Tables E.2 through E.5. Based on these tables, at a significance level of $\alpha = 0.05$, i.e., the P-value is less than 0.05, the only significant source of variation for the MWCO, PWP, and normalized flux reduction, were the membrane manufacturing variables i.e., solvent evaporation time and PES concentration in the casting solution. Because the differences in TOC removal were very subtle, not even the effects of the membrane manufacturing variables were statistically significant (Table E.4). In all cases, the effect of the runs and the cells was statistically insignificant. This implies that several membrane coupons might be tested simultaneously without expecting any significant effect from the run and cell on the variables of study.

Table E.2 ANOVA test for MWCO

<i>Source of variation</i>	<i>Sum of squares</i>	<i>d.f.</i>	<i>Mean square</i>	<i>F -ratio</i>	<i>P-value</i>
Rows (Runs)	1.65E+09	3	5.50E+08	1.5	0.374
Columns (Cell)	2.45E+08	3	8.16E+07	0.2	0.876
Treatments (Memb: tevap, %PES)	2.29E+10	3	7.63E+09	20.8	0.016
Greek letter (Additive)	2.17E+09	3	7.22E+08	2.0	0.296
Residuals	1.10E+09	3	3.67E+08		
Total	2.80E+10	15			

Table E.3 ANOVA test for flux reduction

<i>Source of variation</i>	<i>Sum of squares</i>	<i>d.f.</i>	<i>Mean square</i>	<i>F -ratio</i>	<i>P-value</i>
Rows (Runs)	0.03	3	0.01	1.739	0.330
Columns (Cell)	0.05	3	0.02	3.085	0.190
Treatments (Memb: tevap, %PES)	0.19	3	0.06	11.002	0.040
Greek letter (Additive)	0.01	3	0.00	0.697	0.613
Residuals	0.03	3	0.01		
Total	0.31	15			

Table E.4 ANOVA test for TOC removal

<i>Source of variation</i>	<i>Sum of squares</i>	<i>d.f.</i>	<i>Mean square</i>	<i>F -ratio</i>	<i>P-value</i>
Rows (Runs)	0.031	3	0.010	1.832	0.316
Columns (Cell)	0.048	3	0.016	2.817	0.209
Treatments (Memb: tevap, %PES)	0.029	3	0.010	1.741	0.330
Greek letter (Additive)	0.011	3	0.004	0.621	0.647
Residuals	0.017	3	0.006		
Total	0.135	15			

Table E.5 ANOVA test for PWP

<i>Source of variation</i>	<i>Sum of squares</i>	<i>d.f.</i>	<i>Mean square</i>	<i>F -ratio</i>	<i>P-value</i>
Rows (Runs)	1087.819	3	362.606	5.490	0.098
Columns (Cell)	379.453	3	126.484	1.915	0.304
Treatments (Memb: tevap, %PES)	4438.158	3	1479.386	22.398	0.015
Greek letter (Additive)	519.561	3	173.187	2.622	0.225
Residuals	198.149	3	66.050		
Total	6623.140	15			

APPENDIX F

PREDICTION EQUATIONS

Separate linear prediction equations were calculated for each SMM type tested during the second stage of the thesis, based on the results of main effects and interactions of the factorial design on each of the response variables. Residuals from an adequately fitted model should behave randomly, i.e., they should not follow a discernible pattern (Devore and Farnum, 1999). Therefore, residual plots were examined in order to detect any unusual behaviour (See Section “Residuals of the prediction equations” later in this Appendix). Equations F.1 to F.20 are the prediction equations for all the performance variables studied, depending on the SMM used in the surface modification. These equations have been simplified to their shortest expression. Since only two levels were tested for each manufacturing variable (two level factorial design), only linear models could be generated. In order to increase the complexity of the models more levels are necessary.

For No SMM:

$$\text{PWP [L/m}^2\text{-h]} = 153.4 + 2.2 t_{\text{evap}} - 6.5 \text{PES}_{\text{conc.}} - 0.3 t_{\text{evap}} \text{PES}_{\text{conc.}} \quad (\text{F.1})$$

$$\text{TOC removal [\%]} = 58.2 - 5.1 t_{\text{evap}} + 0.3 \text{PES}_{\text{conc.}} + 0.5 t_{\text{evap}} \text{PES}_{\text{conc.}} \quad (\text{F.2})$$

$$\text{NOM deposition [g/m}^2\text{]} = 18.0 - 1.2 t_{\text{evap}} - 0.8 \text{PES}_{\text{conc.}} + 0.1 t_{\text{evap}} \text{PES}_{\text{conc.}} \quad (\text{F.3})$$

$$\text{SMM: Norm. flux red. [\%]} = 85.3 + 5.5 t_{\text{evap}} - 1.2 \text{PES}_{\text{conc.}} - 0.5 t_{\text{evap}} \text{PES}_{\text{conc.}} \quad (\text{F.4})$$

$$\text{Final flux [L/m}^2\text{-h]} = -7.2 + 7.4 t_{\text{evap}} + 1.6 \text{PES}_{\text{conc.}} - 0.5 t_{\text{evap}} \text{PES}_{\text{conc.}} \quad (\text{F.5})$$

For DEG:

$$\text{PWP [L/m}^2\text{-h]} = 71.9 + 21.9 t_{\text{evap}} - 2.1 \text{PES}_{\text{conc.}} - 1.6 t_{\text{evap}} \text{PES}_{\text{conc.}} \quad (\text{F.6})$$

$$\text{TOC removal [\%]} = 25.6 + 9.0 t_{\text{evap}} + 2.7 \text{PES}_{\text{conc.}} - 0.5 t_{\text{evap}} \text{PES}_{\text{conc.}} \quad (\text{F.7})$$

$$\text{NOM deposition [g/m}^2\text{]} = 5.81 + 1.9 t_{\text{evap}} - 0.1 \text{PES}_{\text{conc.}} - 0.2 t_{\text{evap}} \text{PES}_{\text{conc.}} \quad (\text{F.8})$$

$$\text{Norm. flux red. [\%]} = 92.3 + 12.9 t_{\text{evap}} - 2.6 \text{PES}_{\text{conc.}} - 0.8 t_{\text{evap}} \text{PES}_{\text{conc.}} \quad (\text{F.9})$$

$$\text{Final flux [L/m}^2\text{-h]} = 18.5 - 2.55 t_{\text{evap}} - 0.1 \text{PES}_{\text{conc.}} + 0.02 t_{\text{evap}} \text{PES}_{\text{conc.}} \quad (\text{F.10})$$

For DPS:

$$\text{PWP [L/m}^2\text{-h]} = 83.0 + 20.3 t_{\text{evap}} - 3.1 \text{PES}_{\text{conc.}} - 1.5 t_{\text{evap}} \text{PES}_{\text{conc.}} \quad (\text{F.11})$$

$$\text{TOC removal [\%]} = 65.6 + 2.4 t_{\text{evap}} - 0.6 \text{PES}_{\text{conc.}} - 0.03 t_{\text{evap}} \text{PES}_{\text{conc.}} \quad (\text{F.12})$$

$$\text{NOM deposition [g/m}^2\text{]} = 29.1 - 5.5 t_{\text{evap}} - 1.5 \text{PES}_{\text{conc.}} + 0.3 t_{\text{evap}} \text{PES}_{\text{conc.}} \quad (\text{F.13})$$

$$\text{Norm. flux red. [\%]} = 70.7 + 22.9 t_{\text{evap}} - 1.0 \text{PES}_{\text{conc.}} - 1.9 t_{\text{evap}} \text{PES}_{\text{conc.}} \quad (\text{F.14})$$

$$\text{Final flux [L/m}^2\text{-h]} = 36.4 - 1.0 t_{\text{evap}} - 1.4 \text{PES}_{\text{conc.}} + 0.02 t_{\text{evap}} \text{PES}_{\text{conc.}} \quad (\text{F.15})$$

For SMM41:

$$\text{PWP [L/m}^2\text{-h]} = 97.7 - 5.4 t_{\text{evap}} - 2.4 \text{PES}_{\text{conc.}} - 0.3 t_{\text{evap}} \text{PES}_{\text{conc.}} \quad (\text{F.16})$$

$$\text{TOC removal [\%]} = 61.1 + 1.5 t_{\text{evap}} + 0.3 \text{PES}_{\text{conc.}} + 0.03 t_{\text{evap}} \text{PES}_{\text{conc.}} \quad (\text{F.17})$$

$$\text{NOM deposition [g/m}^2\text{]} = 17.6 - 1.5 t_{\text{evap}} - 0.9 \text{PES}_{\text{conc.}} + 0.1 t_{\text{evap}} \text{PES}_{\text{conc.}} \quad (\text{F.18})$$

$$\text{Norm. flux red. [\%]} = 106.5 - 16.8 t_{\text{evap}} - 2.8 \text{PES}_{\text{conc.}} + 0.6 t_{\text{evap}} \text{PES}_{\text{conc.}} \quad (\text{F.19})$$

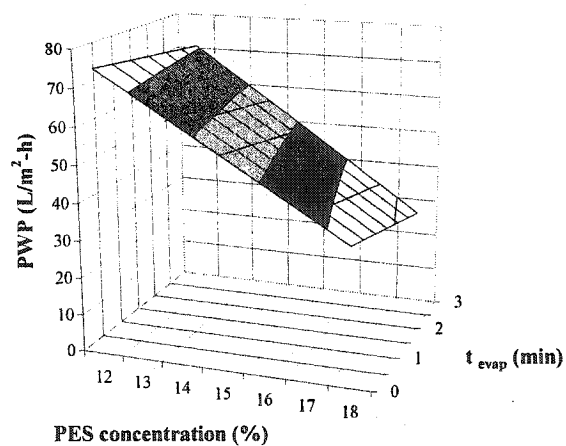
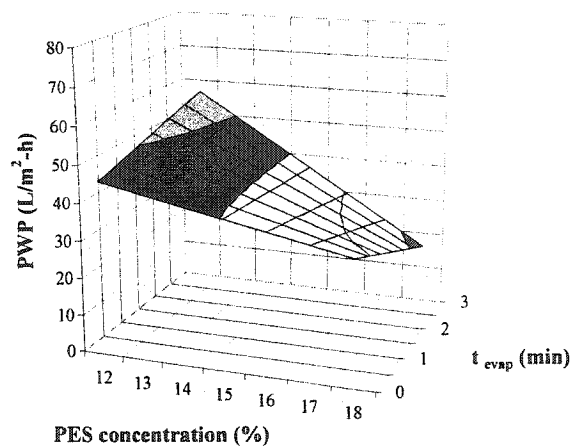
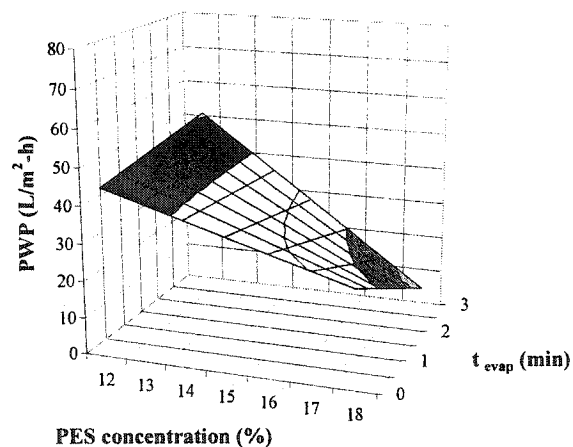
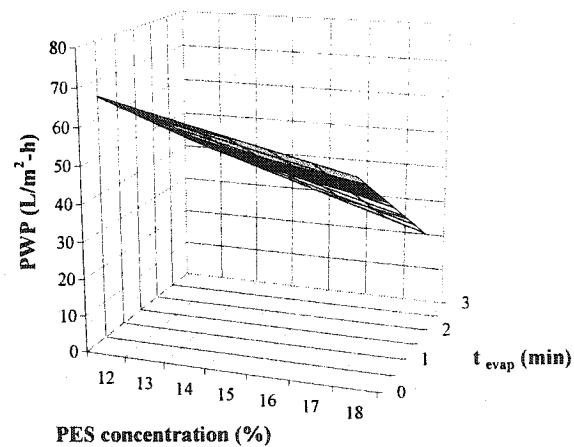
$$\text{Final flux [L/m}^2\text{-h]} = 15.3 + 5.9 t_{\text{evap}} + 0.2 \text{PES}_{\text{conc.}} - 0.5 t_{\text{evap}} \text{PES}_{\text{conc.}} \quad (\text{F.20})$$

In these equations, t_{evap} is the solvent evaporation time in min, and $\text{PES}_{\text{conc.}}$ is the PES concentration in wt % in the casting solution.

Response surfaces

Based on the above prediction equations, forty-nine conditions (in the range tested) were evaluated. PES concentration was evaluated with increases of 1 wt % i.e., 12, 13, 14,..., 18 wt %, and solvent evaporation time with increases of 0.5 min i.e., 0, 0.5, 1.0,..., 3.0 min. Results for the response variables for these 49 conditions are presented in the form of three dimensional graphs also known as response curves.

Figures F.1a to F.1d represent the predicted variation of PWP when PES concentration and solvent evaporation time were changed simultaneously, for each of the SMMs tested in comparison to the unmodified membrane. In each case, these graphs help to establish the ideal conditions necessary to maximize the PWP. It is clear that low PES concentrations maximized the PWP. In the case of the SMM41- modified membranes, the increase of solvent evaporation time decreased the PWP (Fig. F.1). Interactions among the independent variables caused complicated responses as shown in Figures F.1a to F.1d.

a) No SMM**b) DEG****c) DPS****d) SMM41****Fig. F.1 Response surfaces for PWP with forty-nine simulated conditions**

In order to evaluate the general effect of each SMM on the response variables, histograms with the results from the predicted equations were built. The frequencies were arrived at considering the prediction equations for the aforementioned 49 conditions. Figure F.2 shows the behaviour of the PWP as a response to surface modification. The histogram evaluates the probability that a surface modified membrane, within the conditions tested, has a particular PWP. Membranes with highest PWP were No SMM membranes and SMM41-modified membranes, i.e., 65% and 55% of the data tested had PWP higher than 55 L/m²-h, for unmodified and SMM41-modified membranes, respectively. DEG and DPS-modified membranes were well below with 27 and 14%, respectively (Fig. F.2).

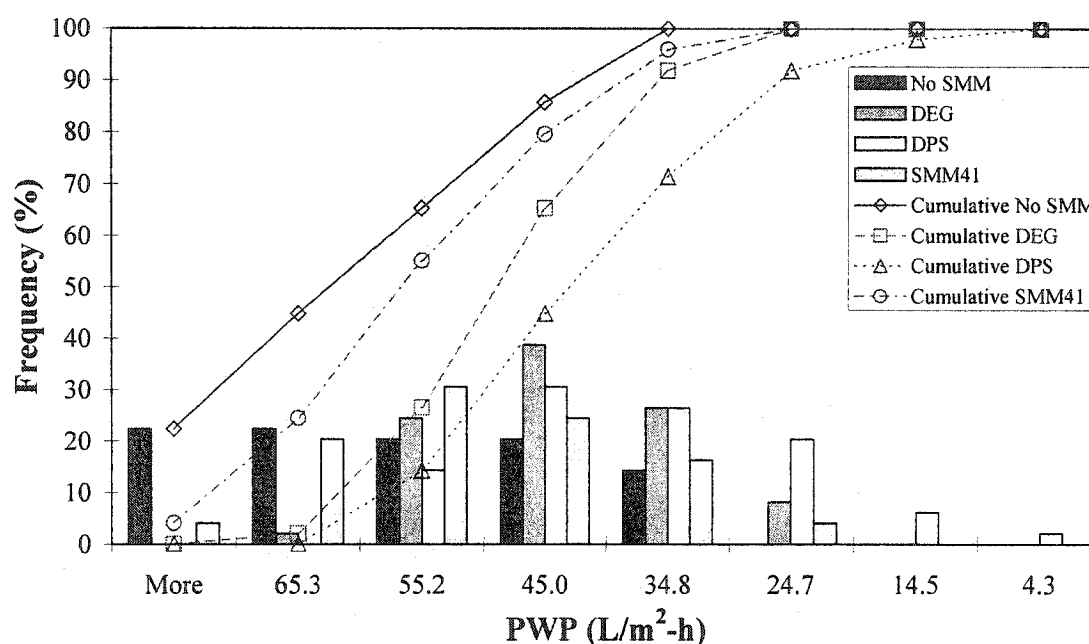
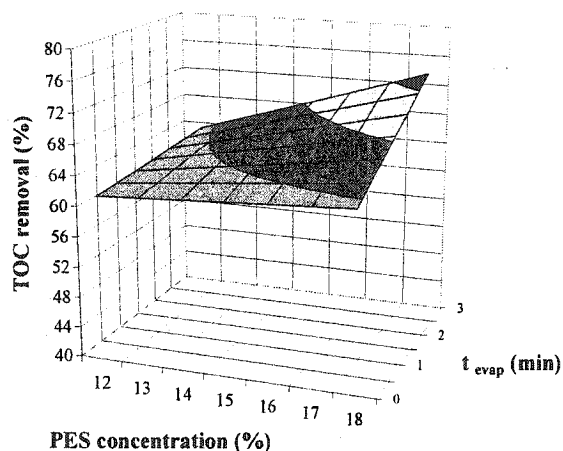


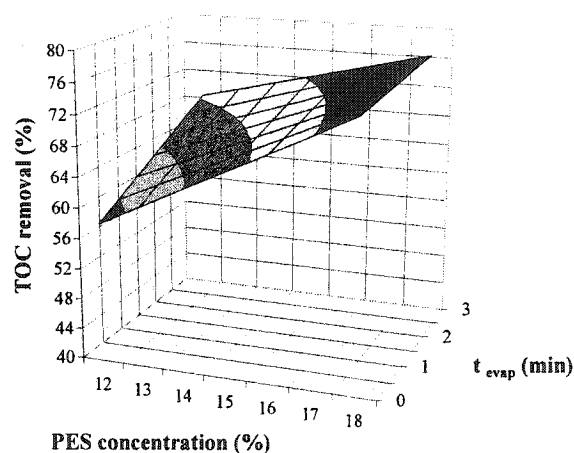
Fig. F.2 Simulation of the change of PWP with surface modification, based on prediction equations

According to Figures F.3a to F.3d, in general, TOC removal increased with PES concentration and solvent evaporation time. DPS-modified membranes were the exception, in this case TOC removal slightly decreased with PES concentration. Therefore, for DEG- and SMM41-modified and unmodified membranes, in order to increase TOC removal, PES concentration and solvent evaporation time should be 18 wt % and 3 min, respectively. The manufacturing conditions that yielded optimal TOC removal were the direct opposite of those yielding the maximum PWP.

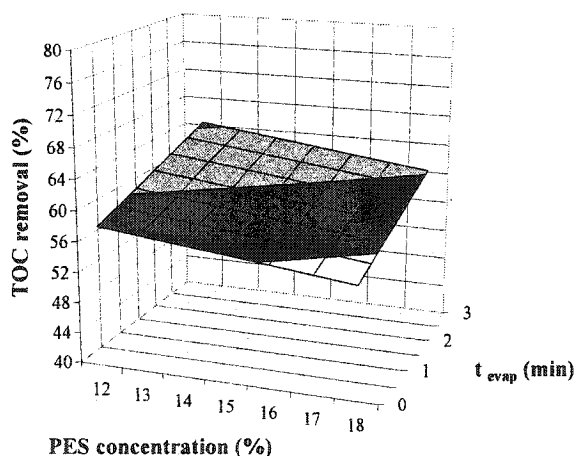
a) No SMM



b) DEG



c) DPS



d) SMM41

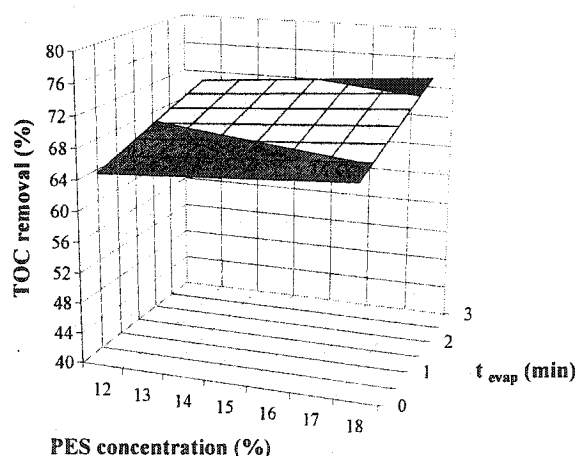


Fig. F.3 Response surfaces for TOC removal with forty-nine simulated conditions

On the other hand, from Fig. F.3d it can be seen that SMM41-modified membranes had the most stable and high TOC removal. The histogram in Fig. F.4 shows that 82% of the conditions tested for SMM41-modified membranes had a TOC removal higher than 70%. While only 69 and 27% for DEG-modified and unmodified membrane, respectively, had the same TOC removal.

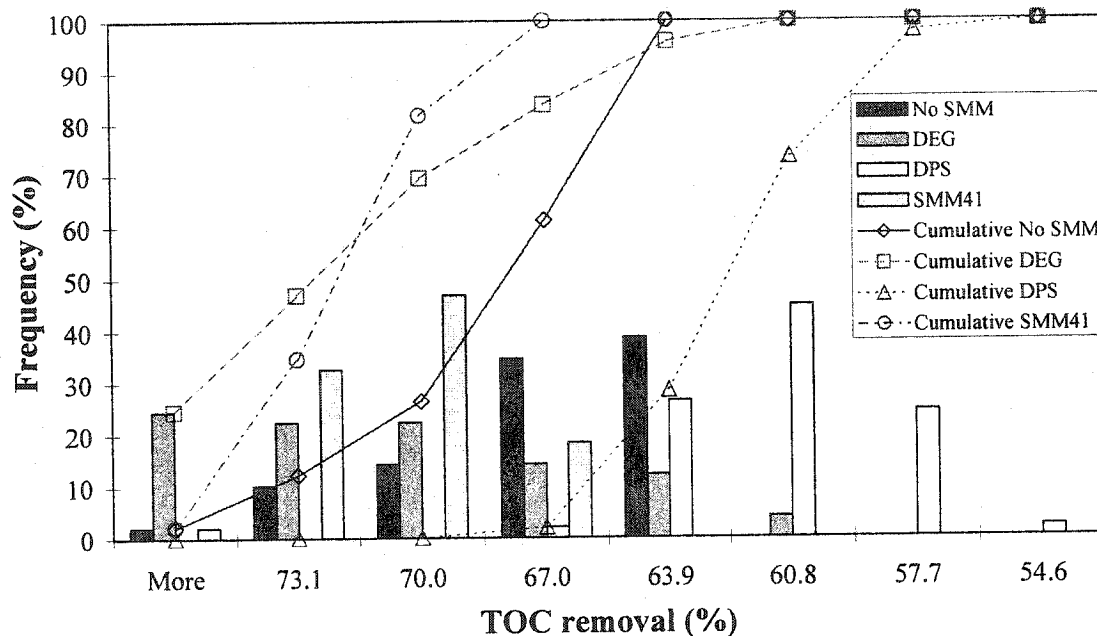
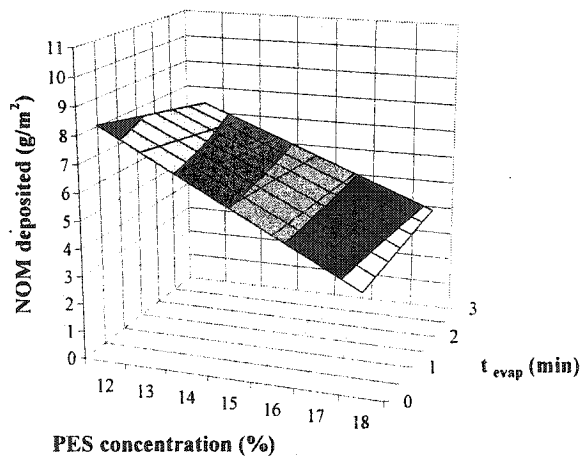


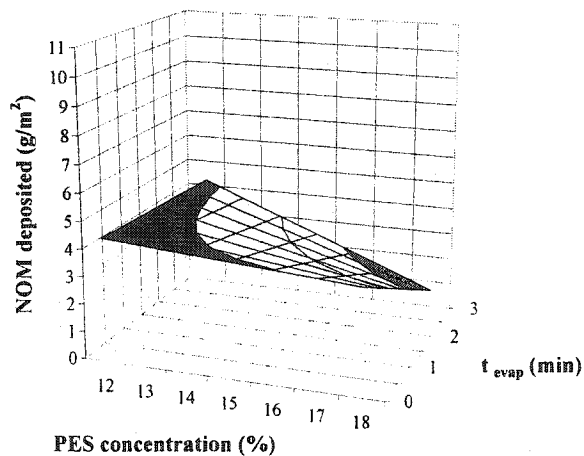
Fig. F.4 Simulation of the change of TOC removal with surface modification, based on prediction equations

The response surfaces for NOM deposition in Figures F.5a to F.5d show a reduction in NOM deposition either with an increase in PES concentration or an increase in solvent evaporation time or with surface modification. As mentioned in Chapter 6, the reduction of water going through the membrane was reflected in the reduction of NOM deposited on top of the membrane at the end of the experiment.

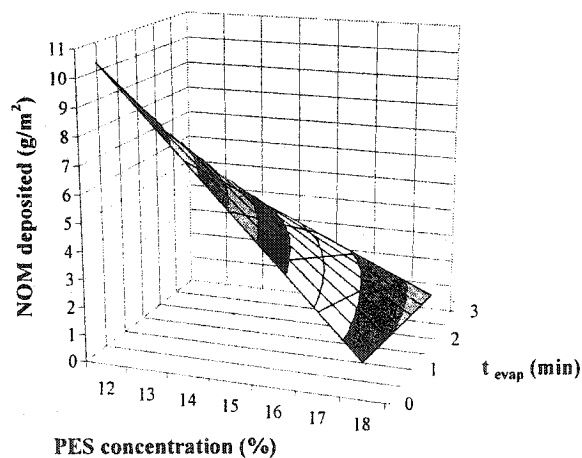
a) No SMM



b) DEG



c) DPS



d) SMM41

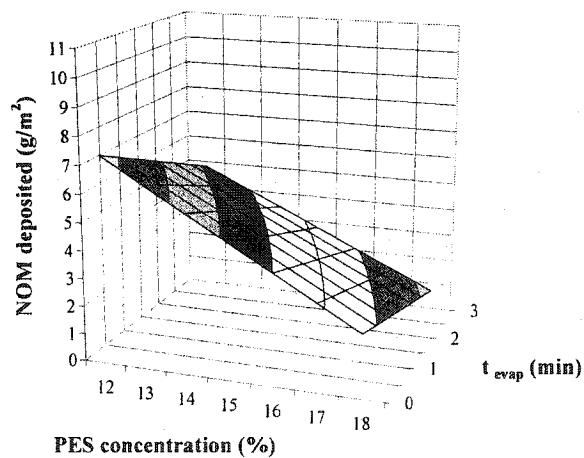


Fig. F.5 Response surfaces for NOM deposition with forty-nine simulated conditions

The histogram in Fig. F.6 shows that DEG-modified membranes had the highest probability of having a lower NOM deposition, followed by SMM41-modified membranes.

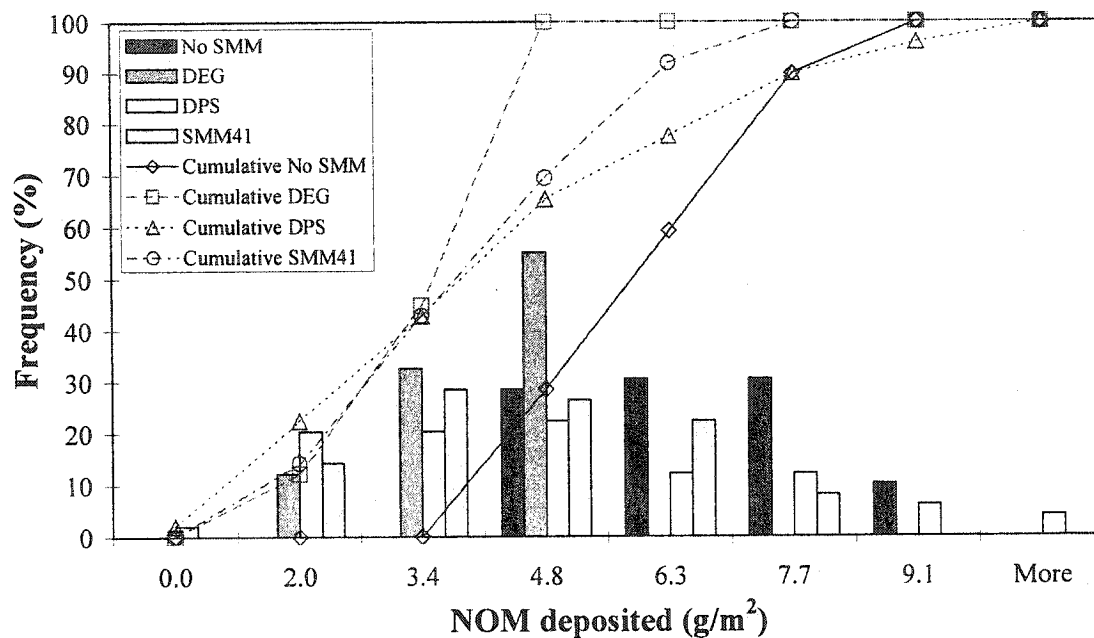
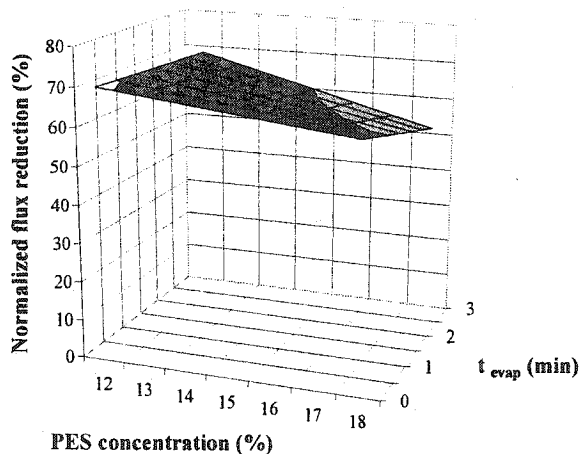


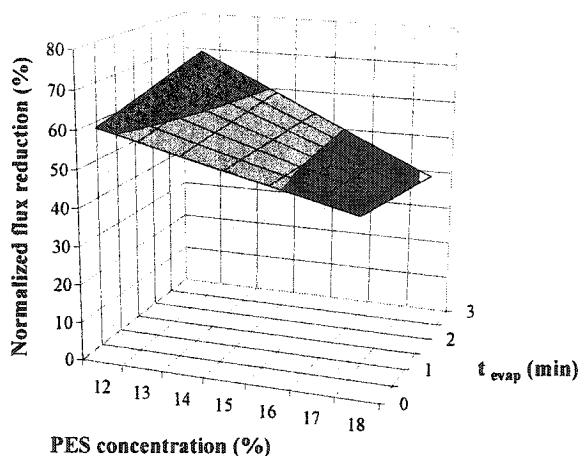
Fig. F.6 Simulation of the change of NOM deposition with surface modification, based on prediction equations

In general, the normalized flux reduction (or fouling) decreased increasing the PES concentration or the solvent evaporation time, and the magnitude of the effect was different depending on the SMM used during the surface modification as is observed in Figures F.7a to F.7d. The unmodified membrane in Fig. F.7a showed a consistently high fouling.

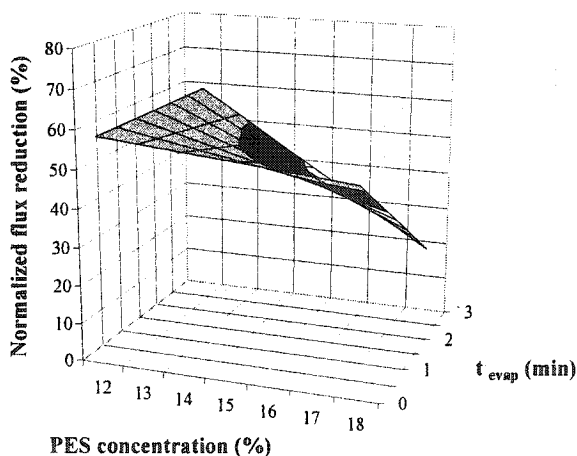
a) No SMM



b) DEG



c) DPS



d) SMM41

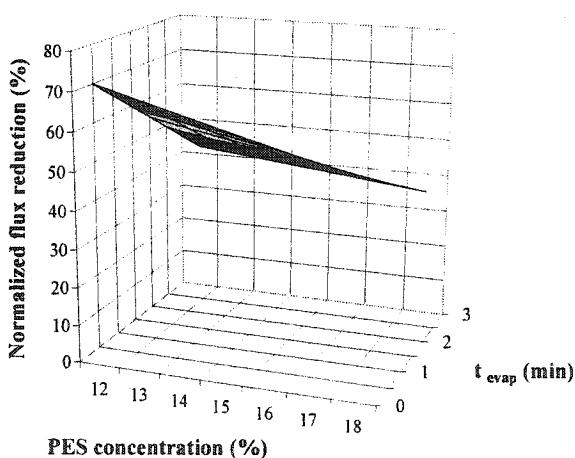


Fig. F.7 Response surfaces for normalized flux reduction with forty-nine simulated conditions

Figure F.8 shows the reduction of fouling by surface modification. DPS-modified membranes had the lowest fouling, however, as observed in Fig. F.2, DPS-modified membranes also had the lowest permeate flux at all the conditions tested. On the other hand, SMM41-modified membranes had low fouling and a relatively high permeation rate.

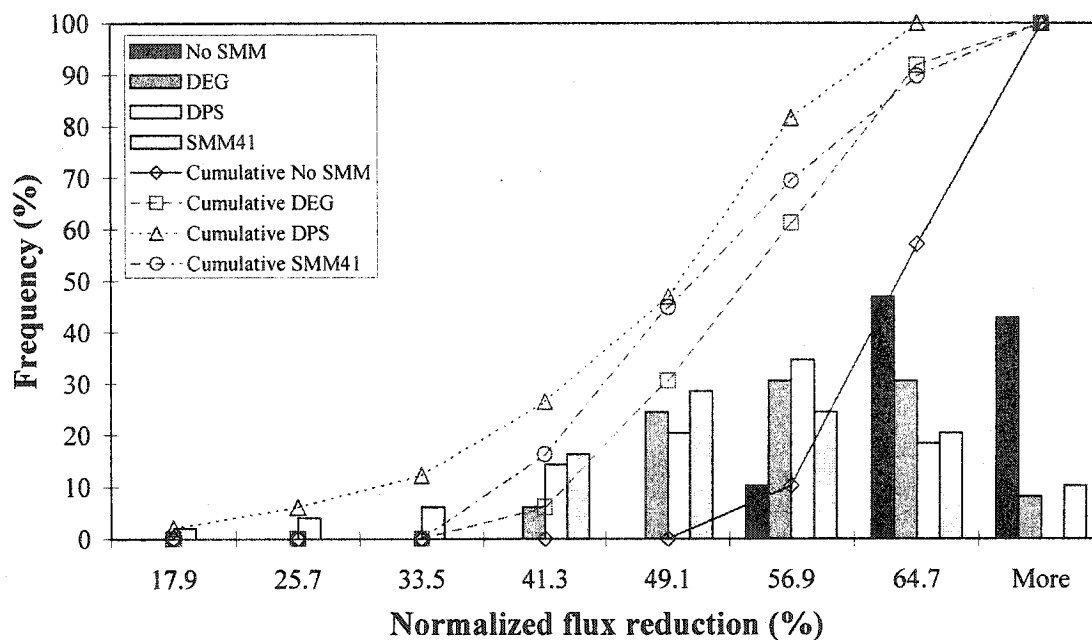
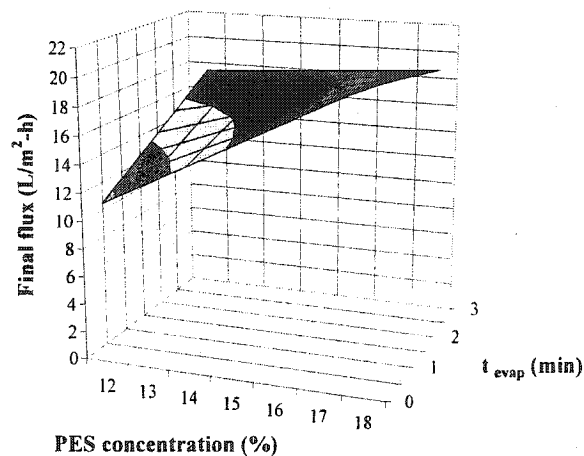


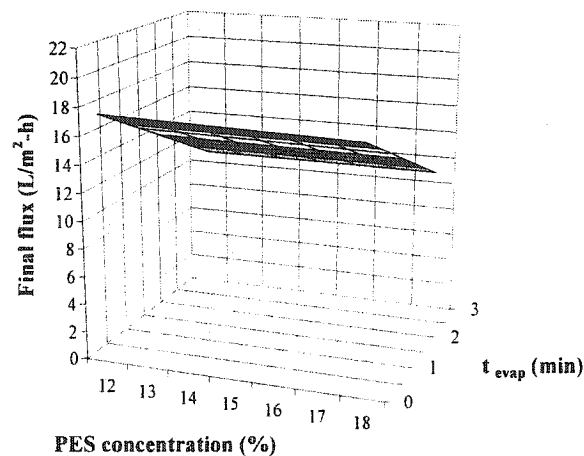
Fig. F.8 Simulation of the change of normalized flux reduction with surface modification, based on prediction equations

The final permeate flux for the simulated surface modified membranes, shown in Figures F.9b to F.9d, generally decreased with PES concentration and with solvent evaporation time. Final permeate flux followed the same trend as the PWP (with the exception of the unmodified membrane) but the effects are more subtle.

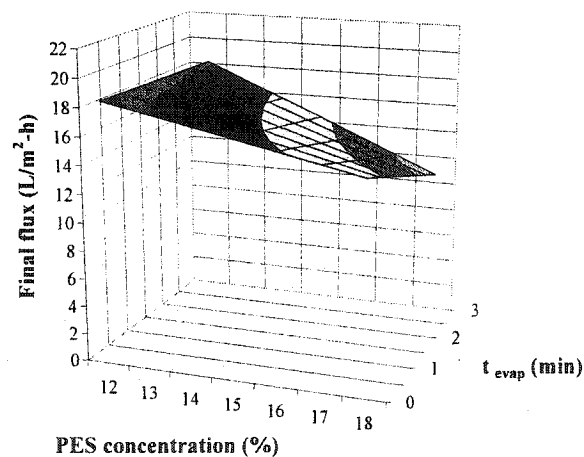
a) No SMM



b) DEG



c) DPS



d) SMM41

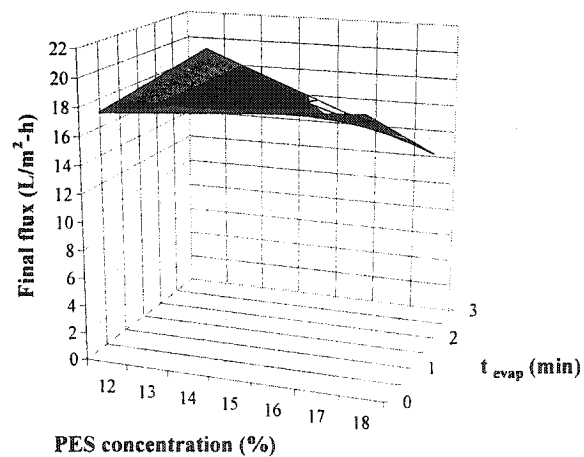


Fig. F.9 Response surfaces for final flux with forty-nine simulated conditions

It is observed in Fig. F.10 that final flux was the highest for the SMM41-modified membranes at all the conditions tested. Although the unmodified membranes showed very similar fluxes, it is observed that, for example, 73% of the SMM41-modified membranes at simulated conditions had a final flux of 17.9 L/m²-h or higher, while only 65% of the unmodified membranes had a final flux in the same range.

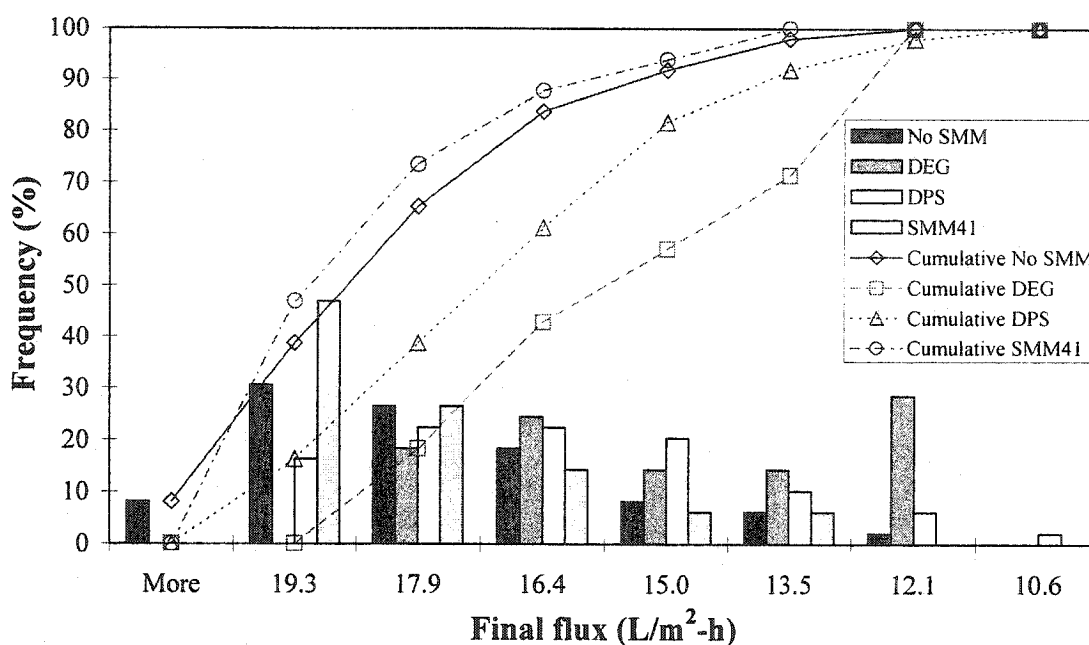


Fig. F.10 Simulation of the change of final flux with surface modification, based on prediction equations

Results presented in this section complement and corroborate the results presented in Chapter 6. In general, a high PES concentration and high solvent evaporation time decreased the permeate flux, causing a decrease in the NOM deposition and membrane fouling (since less river water goes through the membrane) and an increase on TOC removal. Surface modification proved to reduce the NOM deposition and fouling, being SMM41-the most promising SMM, since SMM41-modified membranes showed high permeate fluxes with low fouling and stable high TOC removals.

Residuals of the prediction equations

Figures F.11a-e, show the residuals of the prediction equations presented above. Residuals were calculated from the differences between the observed values and the predicted values (results from the prediction equations or models) for the various response variables. They did not show any discernible patterns, therefore it was concluded that the models fit the data adequately.

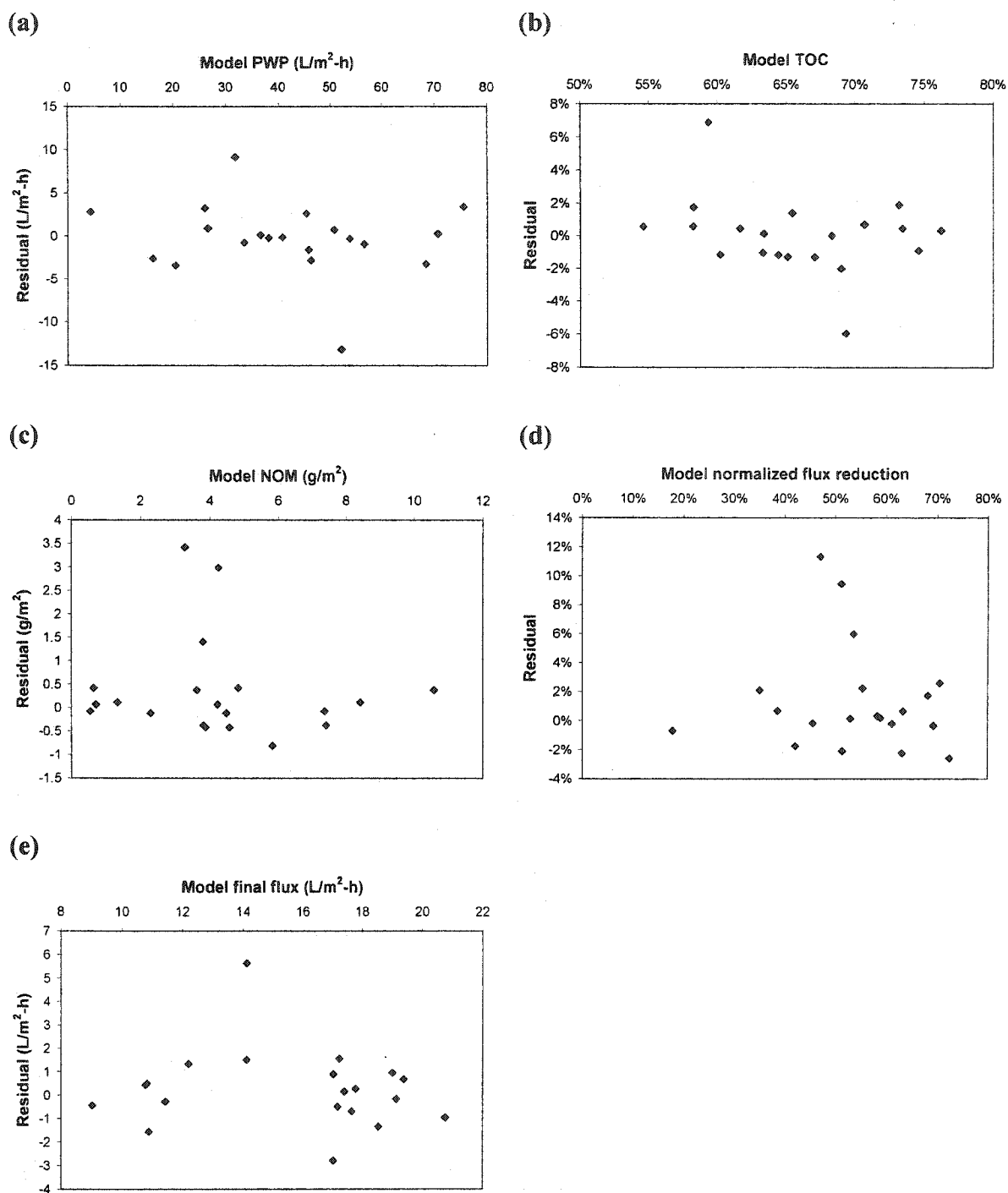


Fig. F.11 Residuals of the prediction equations for a) PWP, b) TOC removal, c) NOM deposition, d) Normalized flux reduction e) Final flux.

APPENDIX G

FLUX REDUCTION WITH PURE WATER

The change on PWP as a function of the amount of water filtered was measured for the membranes tested during the second stage as is shown in Fig. G.1. The total amount of pure water (Milli-Q water) filtered during the 6-day tests for membranes prepared with 12 wt % PES was in the range of 7,000 to 12,000 L/m², while for membranes prepared with 18 wt % PES ranged between 1,000 and 8,000 L/m². The initial flux decrease was important and it tended to level off at the end of the experiment.

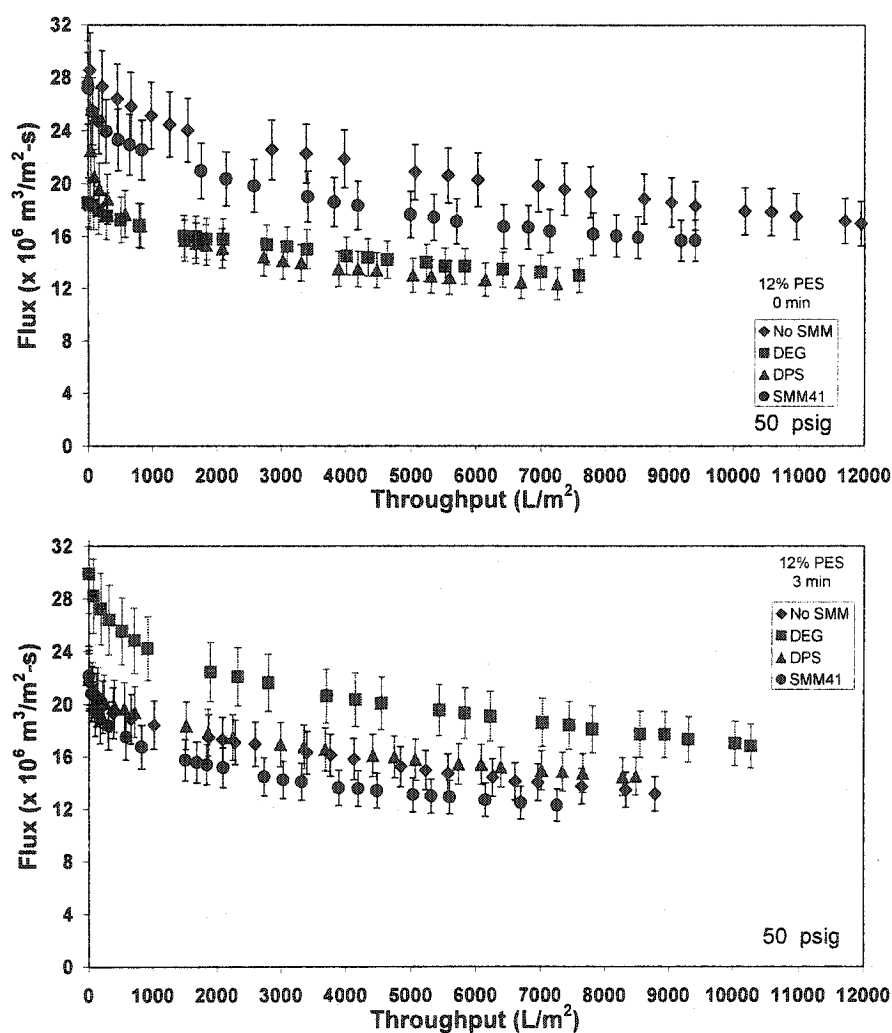


Fig. G.1 Permeate flux reduction for membranes prepared under different manufacturing conditions.

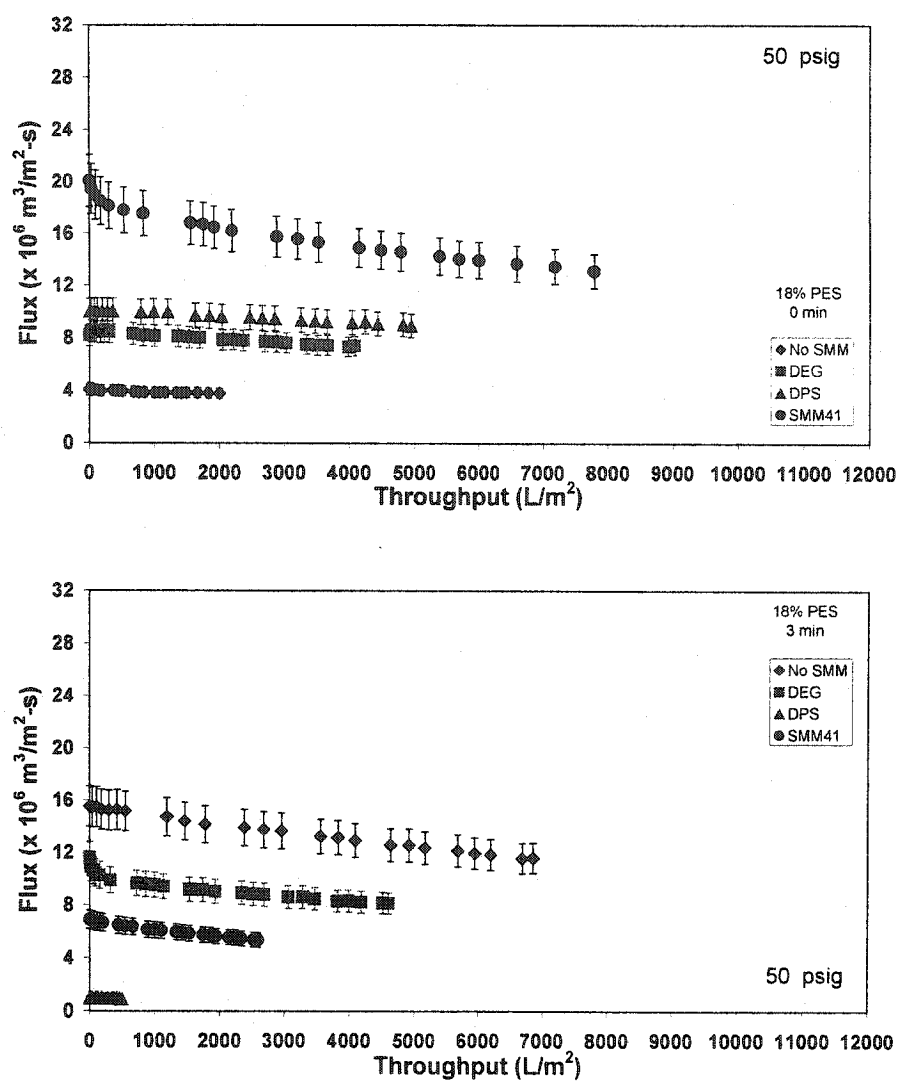


Fig. G.1 (continued) Permeate flux reduction for membranes prepared under different manufacturing conditions.

APPENDIX H

TOPOGRAPHY OF THE MEMBRANE

The AFM was used to observe the surface of the membranes. Figure H.1 shows three-dimensional images of the membrane surfaces prepared under different manufacturing conditions for unmodified and surface-modified membranes.

All AFM images in Fig. H.1 are presented at the same scale to facilitate the comparison among them, i.e., $0.5\ \mu\text{m} \times 0.5\ \mu\text{m}$ scanning area with 40 nm in the Z direction. Light areas correspond to elevated regions (peaks that represent the nodules), while dark areas correspond to low regions (valleys that represent the pores) (Khayet et al., 2003). The surface of the DPS-modified membranes seemed invariably rough, while SMM41-modified membranes generally showed smoother surfaces. Membrane topography may be characterized by several roughness parameters, measurable by AFM. One of the parameters most commonly employed is the mean roughness or R_a (or arithmetic roughness average), which, according to Singh et al. (1998), is the mean value of the surface height relative to the centre plane. The centre plane is defined as that plane that encloses equal volumes above and below it. In other words, R_a is the arithmetic average of the absolute value of the surface variation from the mean.

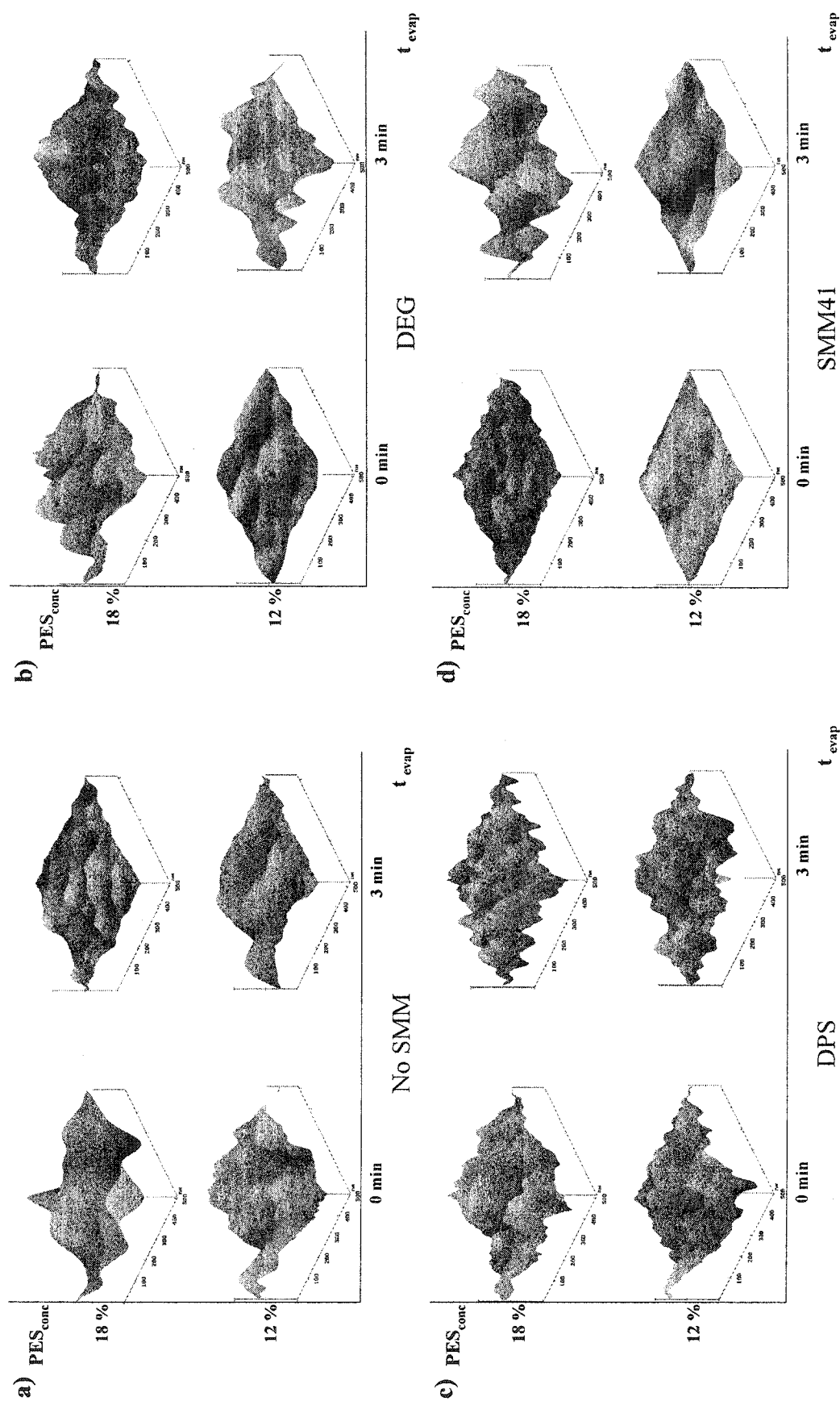


Fig. H.1 Atomic force microscopy images of the top of unmodified membranes prepared under different manufacturing conditions. X divisions correspond to 100 nm, and Z divisions to 20 nm

According to Fig. H.2, in general R_a tended to decrease when the PES concentration in the casting solution increased, except in the case of the SMM41-modified membranes. This decrease was expected, since as the polymer concentration increases in the casting solution (and the MWCO of the membranes becomes smaller), the nodule aggregates are more compact, and the roughness decreases (Khayet et al., 2003). The solvent evaporation did not have a clear trend on the surface roughness. SMM41-modified membranes had, in general, a smoother surface, except in the case of the membrane prepared with 18 wt % and 3-minute solvent evaporation time, which showed an exceptionally high roughness. DEG and DPS-surface modification seemed to slightly increase the surface roughness. It is believed that the differences in trends were due to heterogeneity of the surfaces. A greater number of observations would have been necessary to have more confident estimations of the roughness of these membranes. At least four different $1\text{ cm} \times 1\text{ cm}$ samples, randomly selected from different locations of a membrane sheet, should be analyzed, and from each square as many observations and measurements as possible should be made.

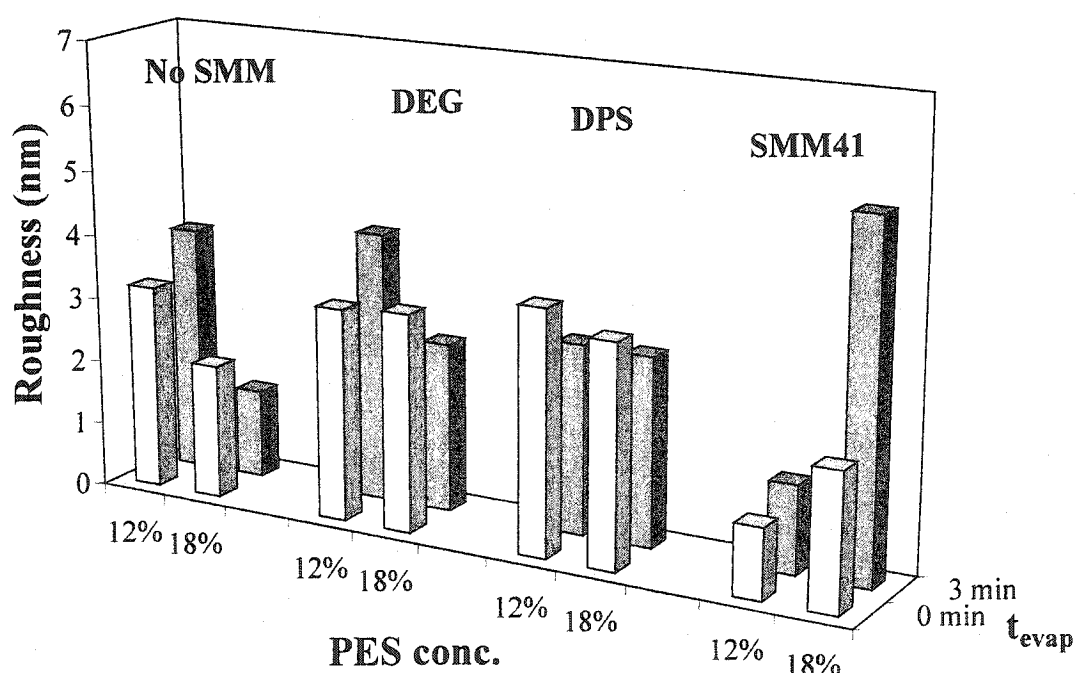


Fig. H.2 Mean roughness (R_a) of different membranes measured with AFM

In order to find any possible relationship between mean roughness and membrane performance, performance variables were plotted against R_a . Figure H.3 shows that there

was no strong relationship between NOM deposition and mean roughness since no clear pattern was observed.

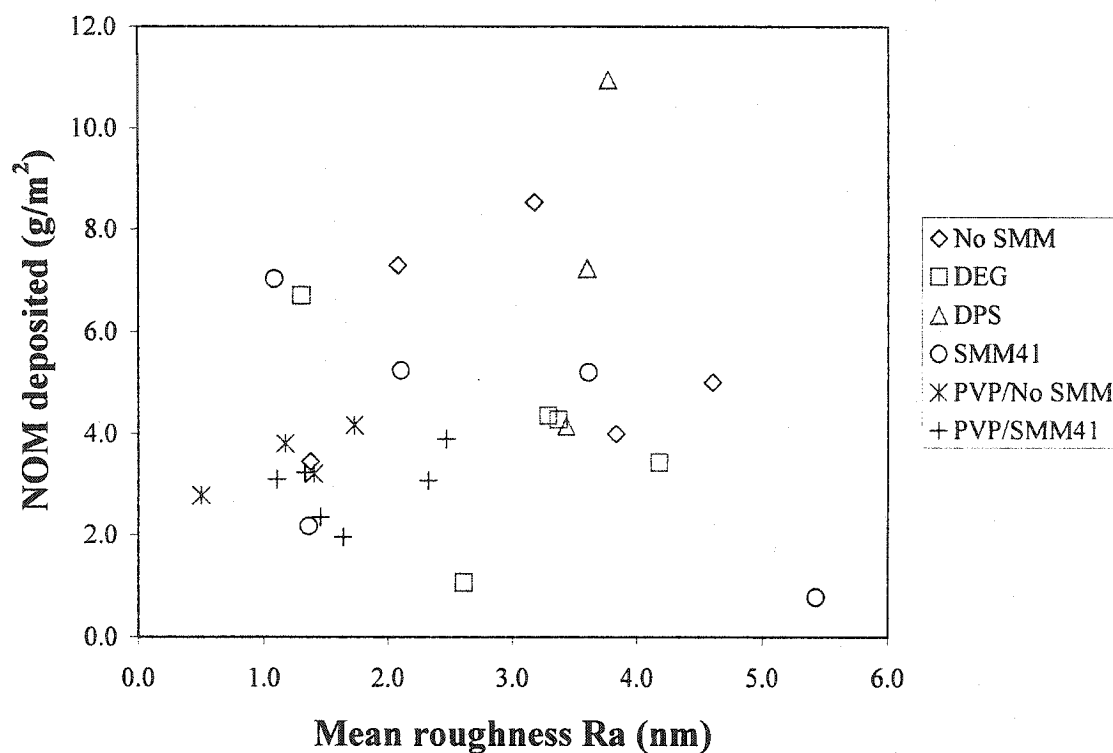


Fig. H.3 Scatter plot of NOM deposited as a function of mean roughness for membranes prepared using different additives

When the PWP and the final flux were plotted against the mean roughness in Figures H.4a and H.4b, SMM41-modified membranes gave evidence of a negative relationship, indicating that as the membrane surfaces were rougher the permeation rate was lower, in other words, a smoother surface favours a higher permeate flux. In other cases the relationship among these variables was not as evident.

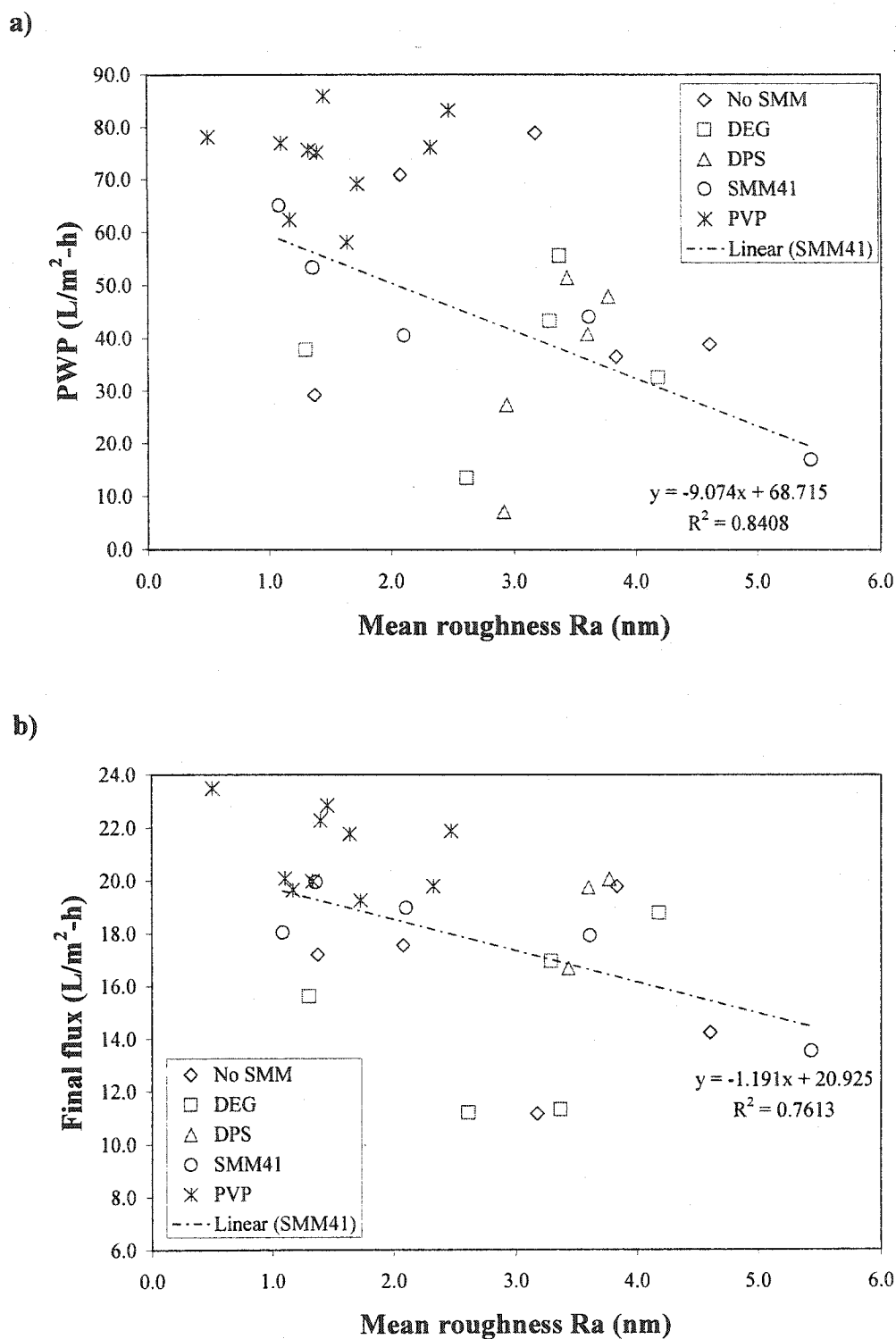


Fig. H.4 Scatter plot of: a) PWP and b) final permeate flux as a function of mean roughness for membranes prepared using different additives

APPENDIX I

SCANNING ELECTRON MICROSCOPY IMAGES

Some SEM images were previously presented in Chapters 5 and 7. This appendix presents SEM images for membranes prepared within this thesis. SEM images for membranes prepared during the second stage of this study are presented in Figures I.1 to I.4. Figures I.5 and I.6 show the SEM images for membranes prepared with PVP and without evaporation time, during the third stage of this study. The topography of the latter membranes is observed in the AFM images in Figures I.7 and I.8.

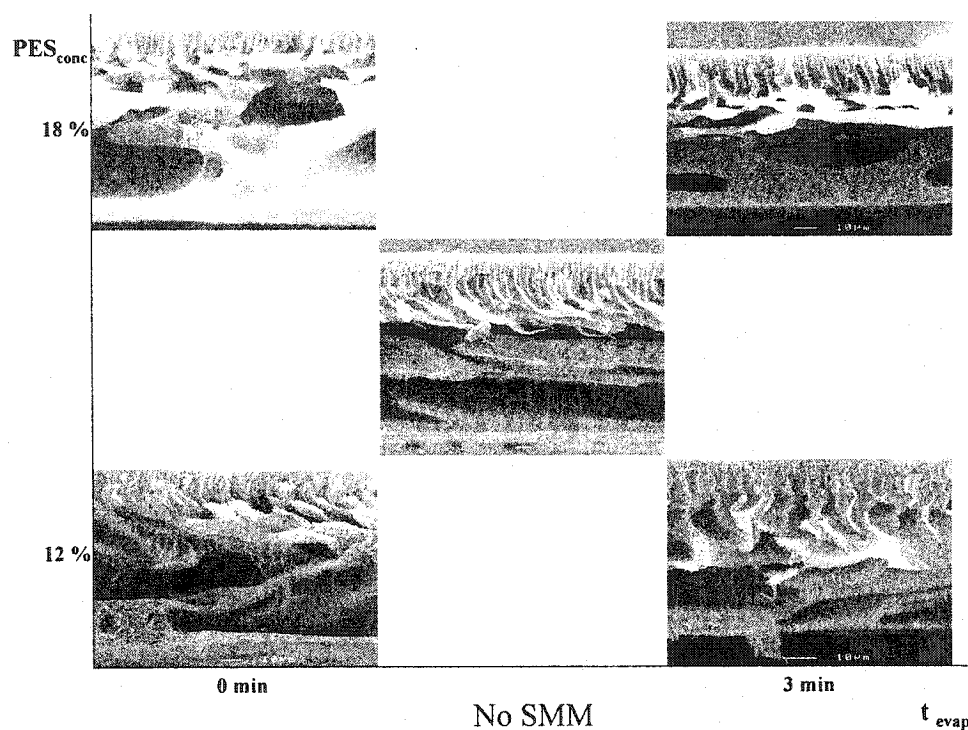


Fig. I.1 SEM images for unmodified membranes prepared under different manufacturing conditions.

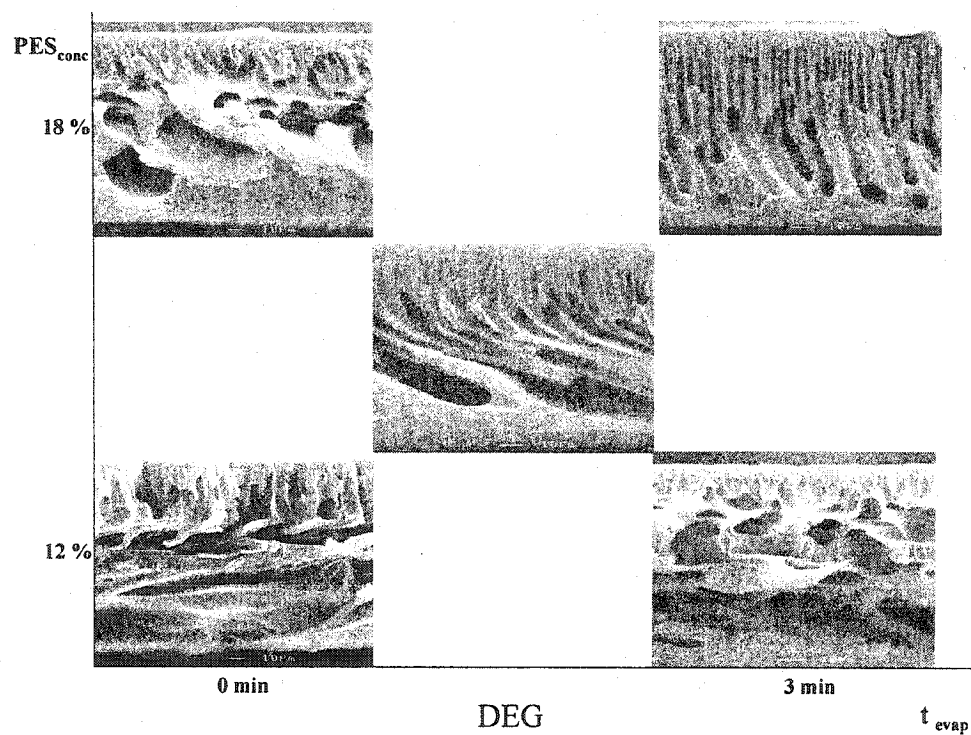


Fig. I.2 SEM images for DEG-modified membranes prepared under different manufacturing conditions.

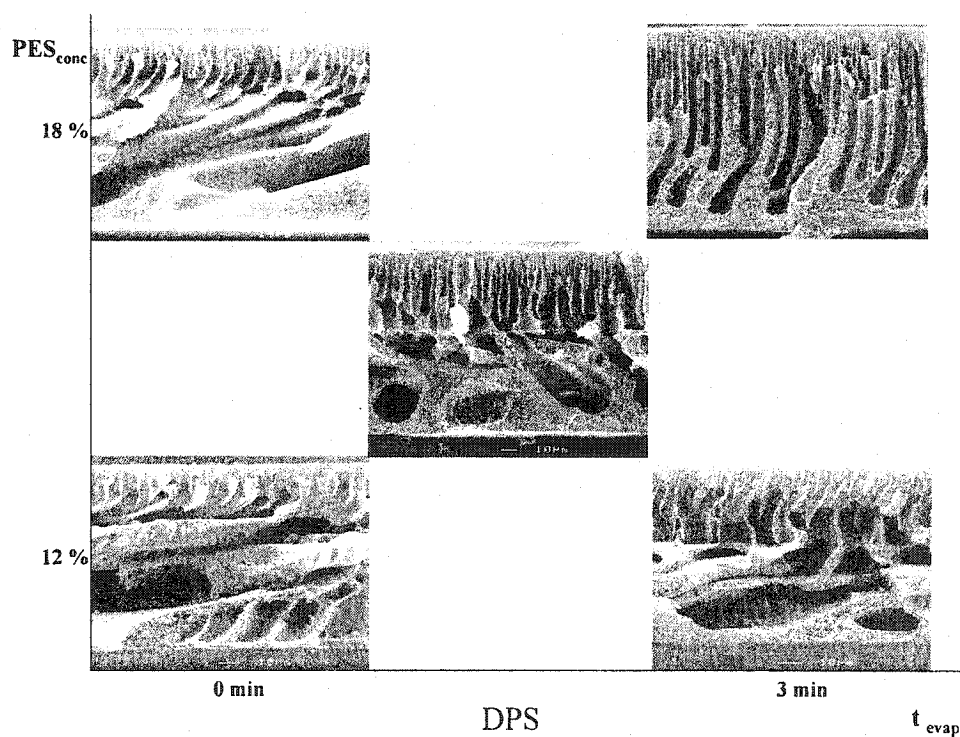


Fig. I.3 SEM images for DPS-modified membranes prepared under different manufacturing conditions.

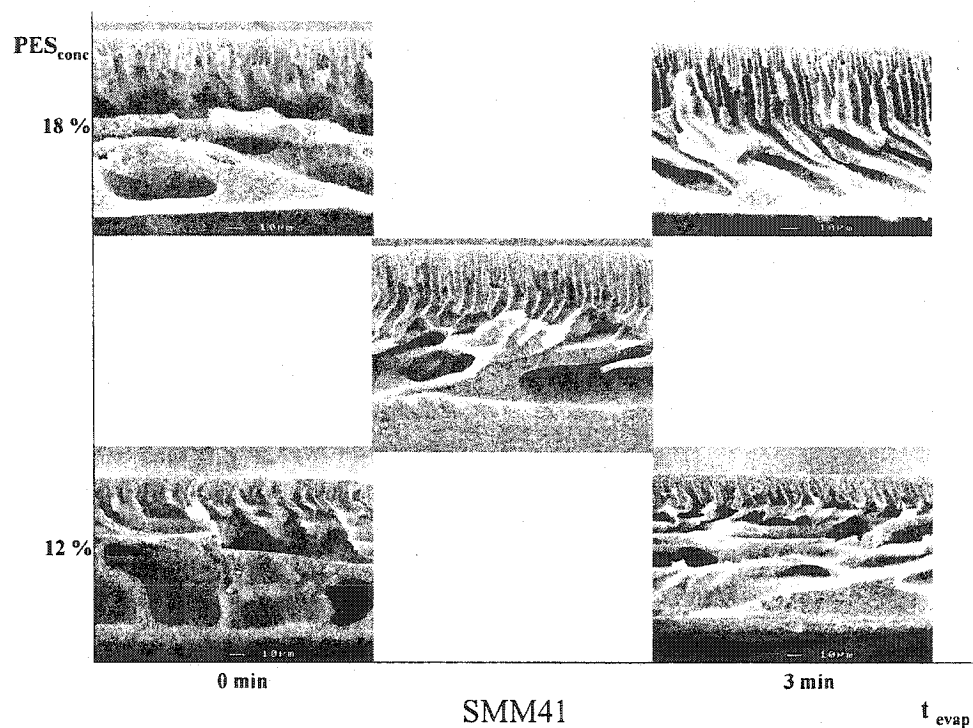


Fig. I.4 SEM images for SMM41-modified membranes prepared under different manufacturing conditions.

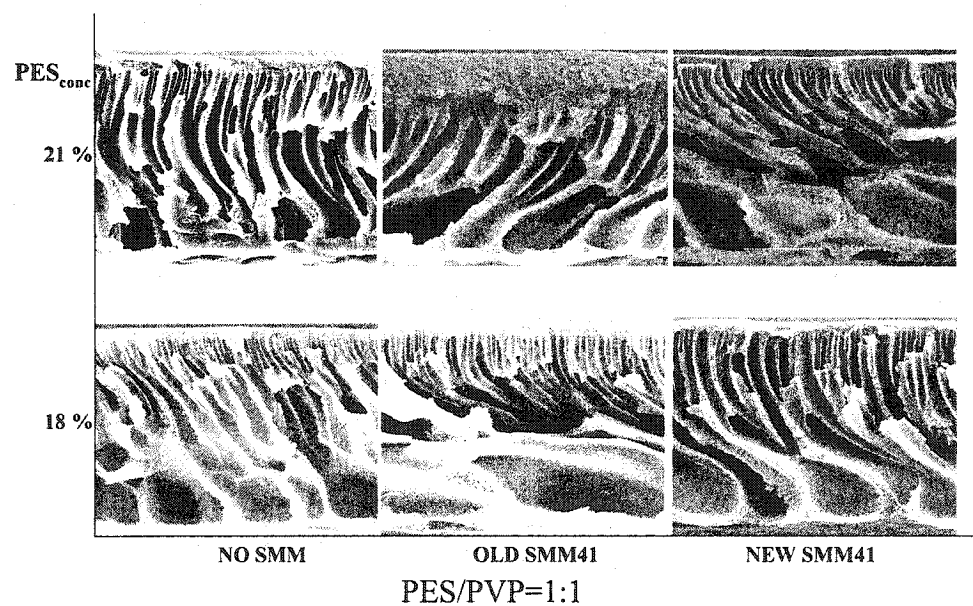


Fig. I.5 SEM images for unmodified and SMM41-modified membranes prepared with PES/PVP ratio = 1, with 18 or 21 wt % PES.

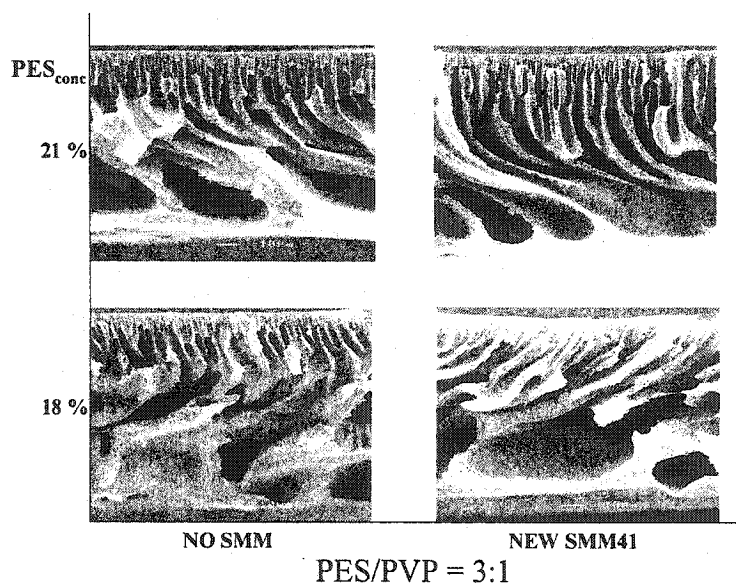


Fig. I.6 SEM images for unmodified and SMM41-modified membranes prepared with PES/PVP ratio = 3:1, with 18 or 21 wt % PES.

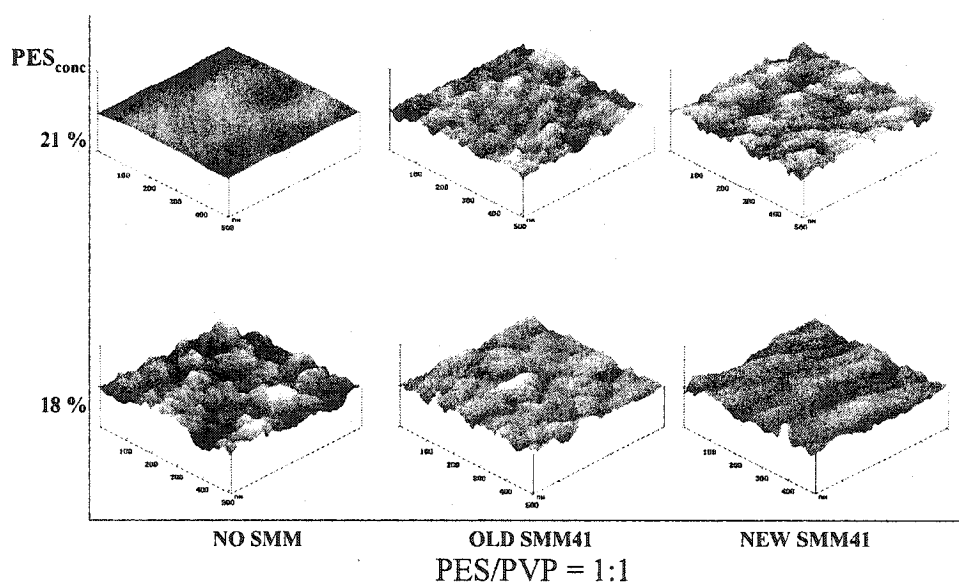


Fig. I.7 AFM images for unmodified and SMM41-modified membranes prepared with PES/PVP ratio = 1, with 18 or 21 wt % PES. X divisions correspond to 100 nm, and Z divisions to 20 nm

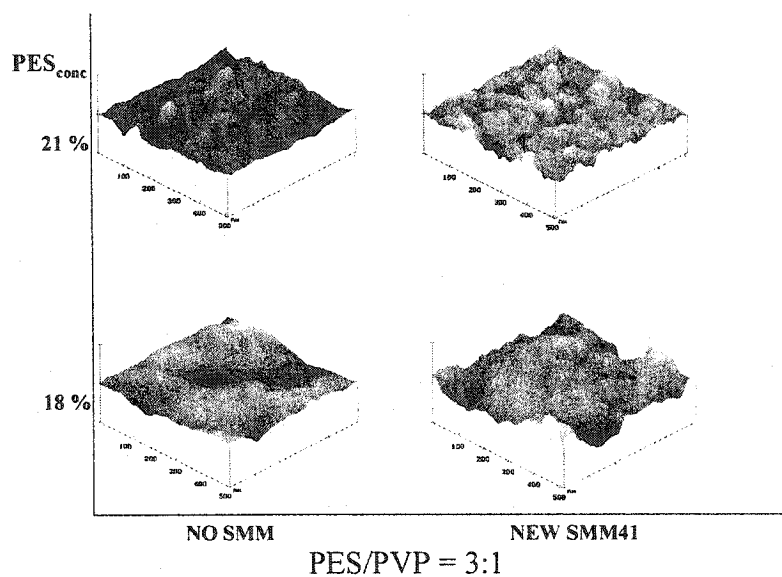


Fig. I.8 AFM images for unmodified and SMM41-modified membranes prepared with PES/PVP ratio = 3:1, with 18 or 21 wt % PES. X divisions correspond to 100 nm, and Z divisions to 20 nm

APPENDIX J

MEMBRANES PREPARED WITH 21 WT % PES

During the last stage of this study, PES concentrations in the casting solution were increased to 21 wt %, since previous tests demonstrated that increasing PES concentration enhanced the membrane performance (Chapter 6). It is worth noting that the casting solutions prepared with 21 wt % PES were extremely viscous and harder to manipulate. Results obtained with membranes prepared with PVP and 21 wt % in the casting solution are compared with membranes prepared with 18 wt % in Figures J.1 to J.4. These figures show that, in general, the performance of the membranes prepared with 21 wt % PES, along the 6-day experiments, was statistically the same as that of the membranes prepared with 18 wt %. Although the relative flux reduction (J/J_0) of the SMM41-modified membrane prepared with 21 wt % PES and 7 wt % PVP in Fig J.2 was slightly different to the rest of the membranes, it is observed in Fig J.1 that the absolute permeate flux was statistically the same.

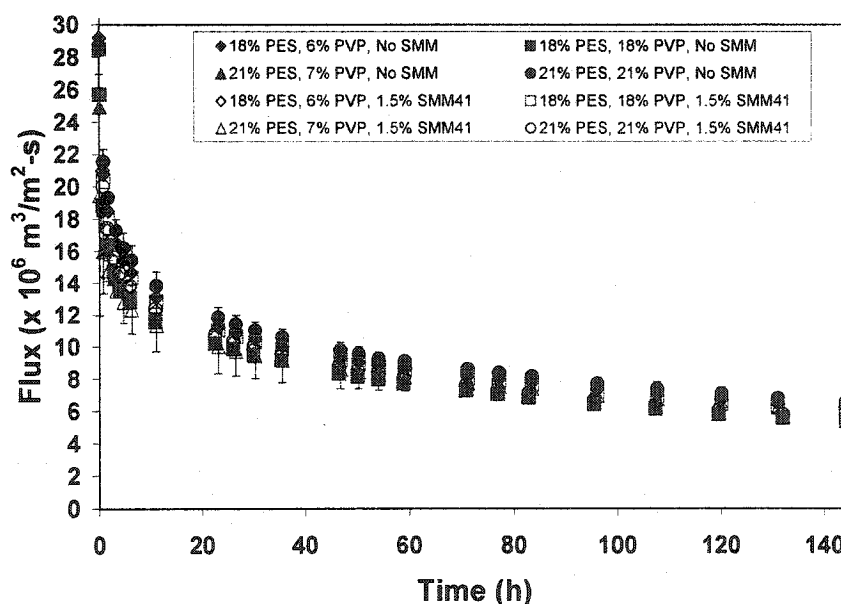


Fig. J.1 Permeate flux reduction with time for unmodified membranes (filled symbols) and SMM41-modified membranes (empty symbols).

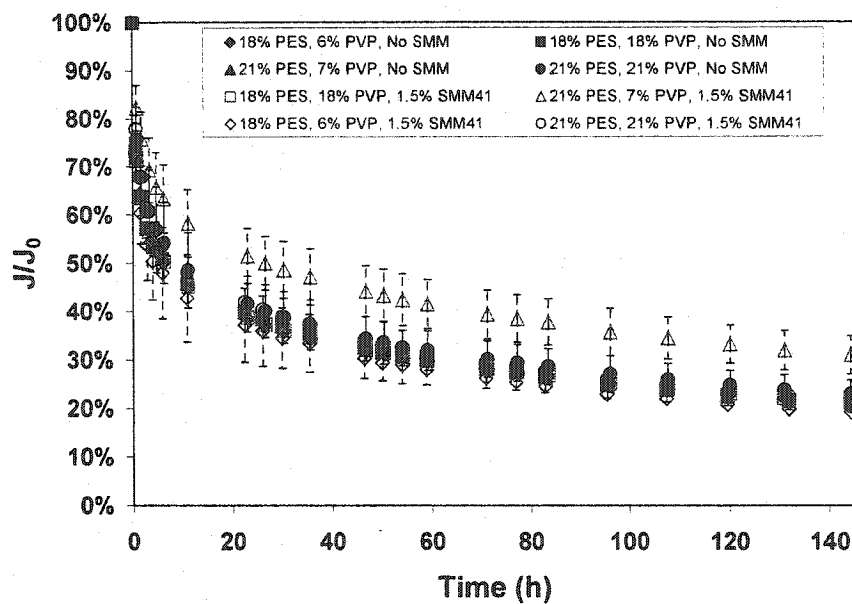


Fig. J.2 Change of the relative flux with time for unmodified membranes (filled symbols) and SMM41-modified membranes (empty symbols).

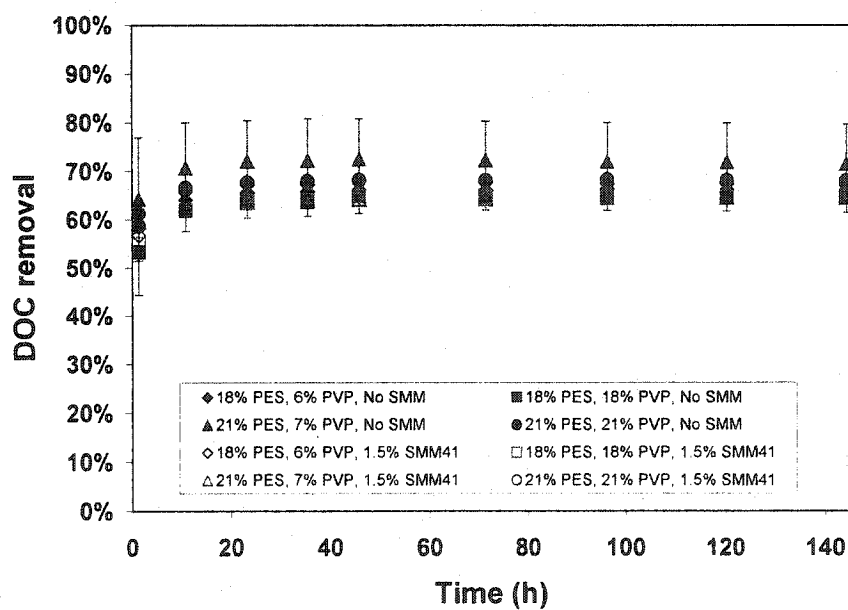


Fig. J.3 Change of DOC removal with time for unmodified membranes (filled symbols) and SMM41-modified membranes (empty symbols).

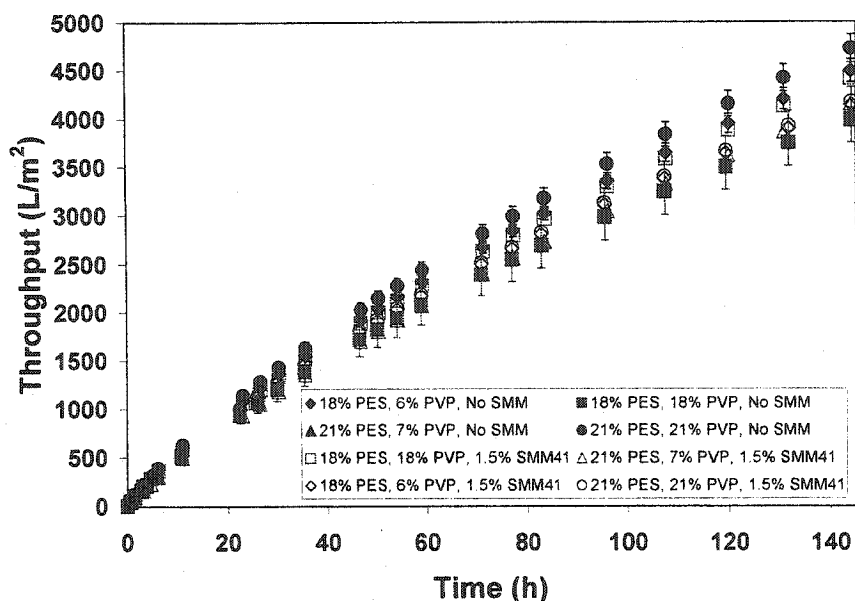


Fig. J.4 Change of throughput with time for unmodified membranes (filled symbols) and SMM41-modified membranes (empty symbols).

In order to evaluate the effect of the manufacturing variables, ANOVA test were performed for each response variable studied. Results are presented in Tables J.1 and J.2. No significant effect (at a 5% level of significance) of any of the manufacturing variables was observed on the response variables. Only in the case of the final flux, the effect of PES concentration $\times$ PES/PVP $\times$ SMM and that of PES concentration $\times$ PES/PVP interaction, were statistically significant (Tables J.1 and J.2). Entries in bold in Tables J.1 and J.2 indicate statistically significant effects in these test.

Table J.1 P-values for membrane characteristics.

		MWCO	Pore size	Porosity	Pore density	PEG 35K
x_1	PES conc.	0.091	0.230	0.916	0.467	0.098
x_2	PES/PVP	0.274	0.186	0.861	0.268	0.448
x_3	SMM type	0.869	0.740	0.128	0.809	0.502
x_1x_2	PES conc.and PES/PVP	0.858	0.626	0.704	0.680	0.847
x_1x_3	PES conc.and SMM type	0.748	0.681	0.561	0.693	0.553
x_2x_3	PES/PVP and SMM type	0.600	0.586	0.098	0.357	0.552
$x_1x_2x_3$	PES conc., PES/PVP and SMM type	0.848	0.703	0.373	0.434	0.863

Table J.2 P-values for membrane performance variables.

		PWP	NOM	TOC	Flux reduction	Final flux
x_1	PES conc.	0.160	0.315	0.368	0.389	0.168
x_2	PES/PVP	0.106	0.422	0.633	0.971	0.345
x_3	SMM type	0.686	0.478	0.561	0.917	0.304
x_1x_2	PES conc.and PES/PVP	0.128	0.541	0.713	0.595	0.028
x_1x_3	PES conc.and SMM type	0.293	0.690	0.442	0.409	0.211
x_2x_3	PES/PVP and SMM type	0.471	0.393	0.589	0.581	0.655
$x_1x_2x_3$	PES conc., PES/PVP and SMM type	0.580	0.341	0.413	0.298	0.000

Since based on these results we can conclude that increasing the PES concentration in the casting solution from 18 wt % to 21 wt % did not significantly improve the performance of the SMM-modified or unmodified membranes, these results were not included in any of the chapters of this thesis.

APPENDIX K

TEST OF DIFFERENT NOM FRACTIONS

Some results of the test with different NOM fractions were presented in Chapter 7. Figures K.1 and K.2 show the normalized permeate flux and TOC removals for all the membranes prepared.

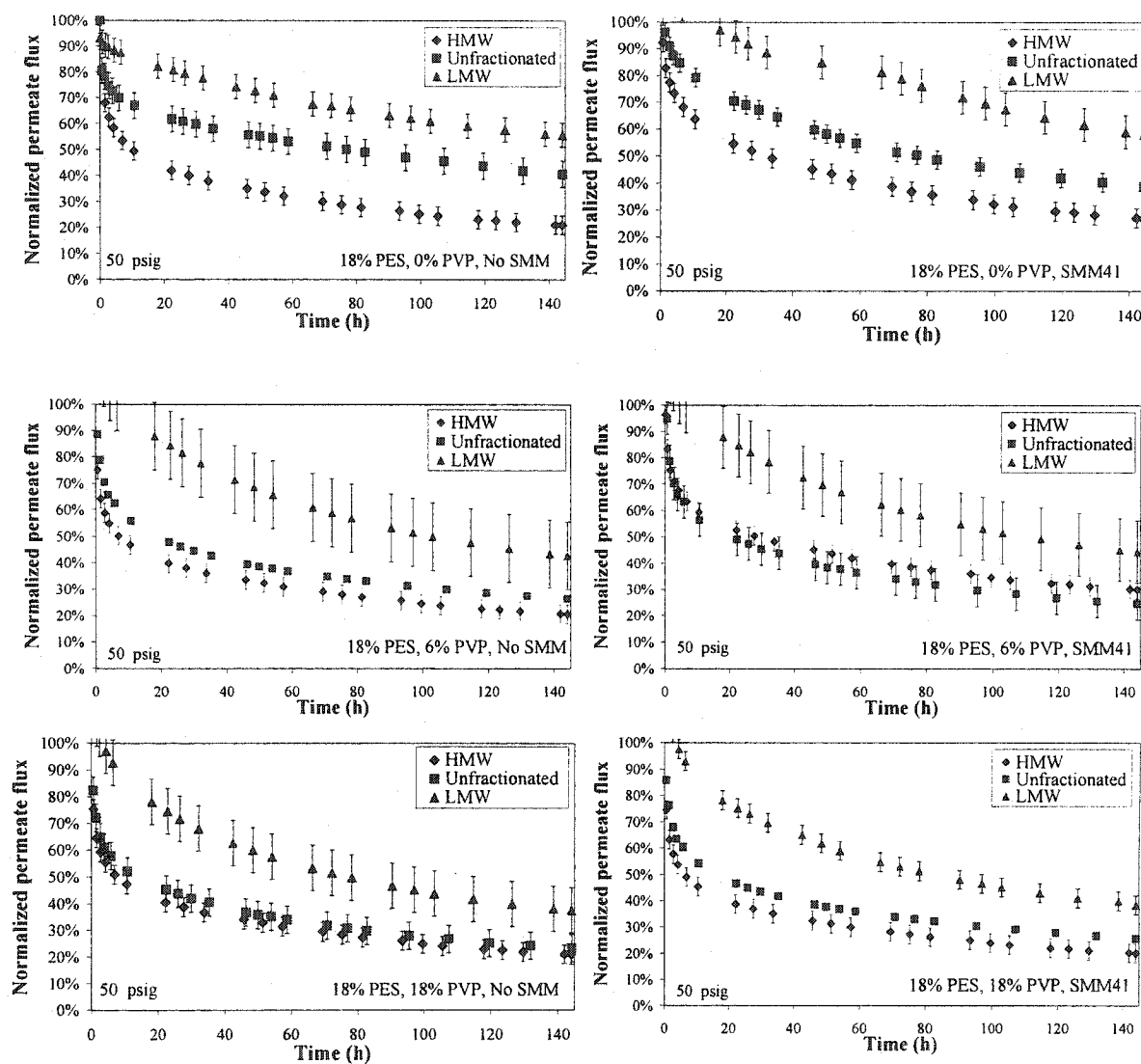


Fig. K.1 Reduction of normalized permeate flux for membranes prepared under different manufacturing conditions

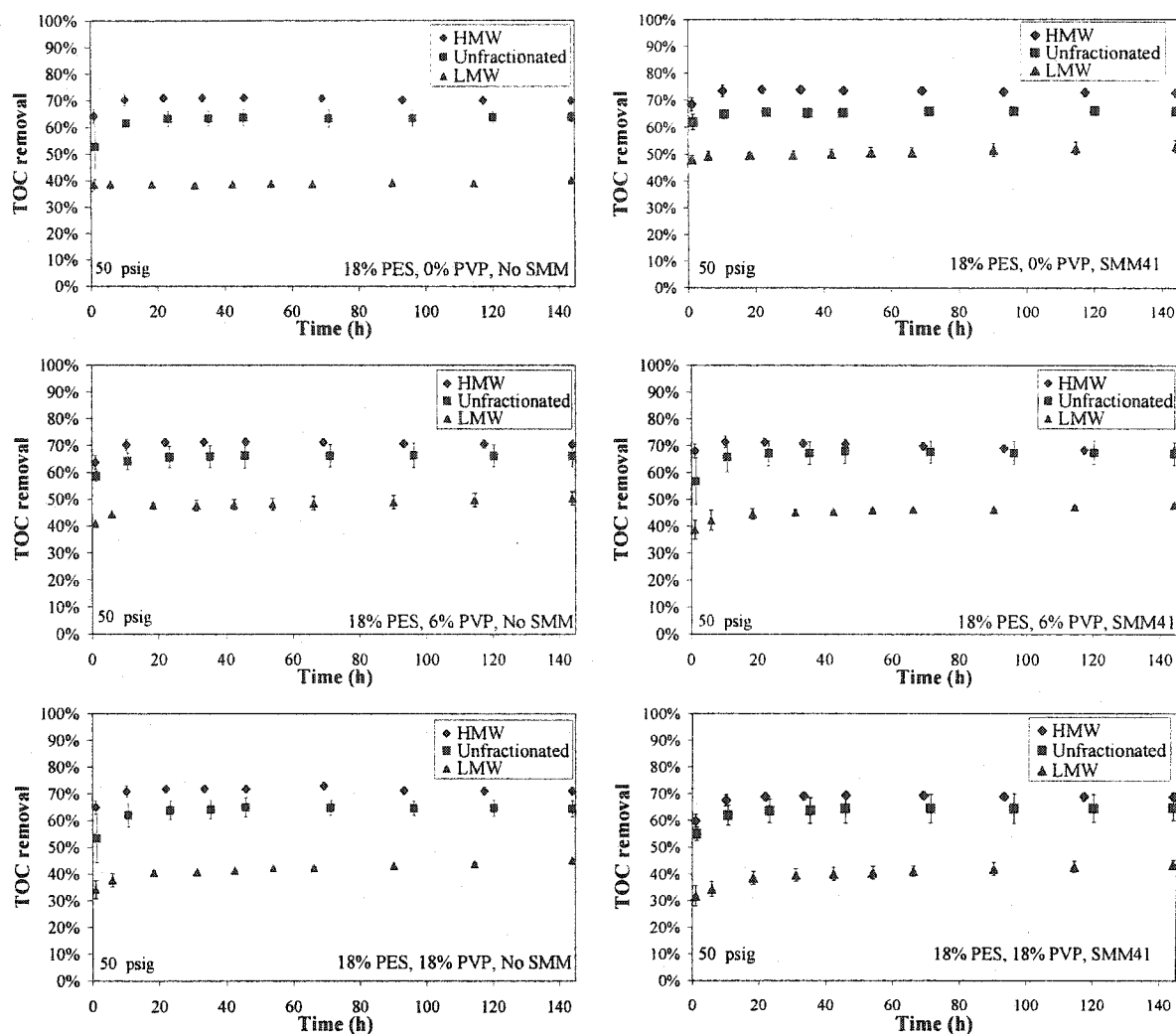


Fig. K.2 Change of TOC removal with time for membranes prepared under different manufacturing conditions

APPENDIX L

SMM41 BATCHES

Different batches of SMM41 were used during the second and third stages of this study. Although their molecular weights were the same, their fluorine content was not. Therefore, an ANOVA was performed to test if the batch had any significant effect on any of the performance variables. Tables L.1 and L.2 show the P-values associated with the manufacturing conditions. At a significance level of $\alpha = 0.05$, batch type only had a significant effect on the amount of fluorine measured on top of the membrane surface, which is reasonable (Tables L.3 and L.4.) since the fluorine content in the raw material was different. Fluorine concentration at the surface of the membranes modified with high fluorine content SMM41 was 4.1 ± 0.6 % and that at the surface of the membranes modified with low fluorine content SMM41 was 1.4 ± 0.7 %. Therefore, we can conclude that higher fluorine concentration at the surface had no apparent impact on membrane performance.

Table L.1 P-values for membrane characteristics.

		MWCO	Pore size	Porosity	Pore density	PEG 35K
x_1	PES conc.	0.374	0.545	0.993	0.933	0.410
x_2	SMM type	0.822	0.949	0.817	0.794	0.875
x_1x_2	PES/PVP and SMM type	0.727	0.815	0.700	0.738	0.771

Table L.2 P-values for membrane performance variables

		PWP	NOM deposition	TOC removal	Flux reduction	Final flux	F content
x_1	PES conc.	0.273	0.964	0.344	0.584	0.001	0.094
x_2	SMM type	0.780	0.386	0.998	0.718	0.108	0.000
x_1x_2	PES/PVP and SMM type	0.930	0.459	0.865	0.973	0.170	0.243

APPENDIX M

PREPARATION OF COMPOSITE MEMBRANES

During the surface modification of the PES membranes, the additive migrates to the surface of the membrane; however, one way to be sure that the membrane surface is completely covered with SMM is by coating the PES membrane using SMM.

In coating the surface of the PES membrane, the first step was finding a solvent that was able to dissolve the SMM but did not dissolve the PES sublayer. SMM41 was added to beakers containing equal amounts of different solvents and stirred for over 24 h at room temperature. The solubility of SMM41 was determined in the various solvents by visual observation, i.e., the clear solutions indicating that the SMM41 dissolved well in the given solvent. Table 3.6 shows the properties of the solvents, taken from Kim et al. (2000).

Table M.1 Solvent properties used in membrane coating (Kim et al., 2000)

Solvent	Molecular weight	P _v (kPa) ^a	Viscosity (cP)	T _b ^b	Evaporation ^c
Methanol	32.0	17.0	0.6	64.7	6.3
Ethanol	46.1	7.9	1.2	78.5	8.3
Isopropanol	60.1	6.1	2.3	82.5	11
2-Methoxyethanol ^d	76.1	-	1.7	125	34
2-Ethoxyethanol ^e	90.1	0.71	2.2	135	4.3
2-Butoxyethanol ^f	118.0	0.15	3.3	171	140

^a P_v: vapour pressure at 25 °C

^b Boiling point at 760 mm Hg

^c Evaporation time ratio of test solvent to diethyl ether

^d Ethylene glycol monomethyl ether (methyl cellosolve HOCH₂CH₂OCH₃)

^e Ethylene glycol monoethyl ether (cellosolve HOCH₂CH₂OC₂H₅)

^f Ethylene glycol monobutyl ether (butyl cellosolve HOCH₂CH₂OC₄H₉)

After trying all these solvents, 2-methoxyethanol seemed like a good candidate, since it was the only solvent able to dissolve the SMM41. Next, it was necessary to perform the measurement of the solvent uptake by PES films. Therefore, dense films were prepared using a 5 wt % solution of PES in NMP poured on moulds made with glass plates with aluminium rings. The films were dried in an oven at 90°C for 3 days. Next, the films were peeled and their dry weight was determined. The films were soaked in 2-

methoxyethanol at room temperature. However, after 5 h the PES films broke into pieces. Thus, it was impossible to continue with this coating procedure.

Later, another old technique to prepare the composite membranes was attempted. This technique was invented in 1964 by Peter Francis (Francis, 1966), however it became obsolete when newer and more effective techniques were invented. In this case, a dilute solution (5 wt %) of SMM in cyclohexanone was prepared. SMM41 was the only SMM soluble in cyclohexanone at room temperature. For DPS and DEG it was necessary to warm the solution to 50 or 60°C. The resultant solutions were somewhat turbid, while the SMM41 solution was a clear yellowish solution. Then the solution was filtered using the same kind of filters used for the casting solutions (i.e., Teflon PTFE 47-mm discs with pore size of 5.0 μm). The solution was allowed to degas. Then, it was poured onto the surface of water, in the empty area of a ring holder. The solution spread spontaneously over the water surface inside of the ring. An evaporation period of two hours was allowed, and afterwards, the ultrathin membrane was transferred to the top surface of the porous substrate membrane. The thickness of these flat films was measured using a micrometer (Miituty No. 293-761-30, Japan).

Attempts to coat PES membranes with SMM using the technique developed by Peter Francis (Francis, 1966) were not successful. The main problem was that the SMM solution in cyclohexanone did not spread uniformly on the surface of the water, and SMM films had wrinkles or bubbles. These little defects became cracks with aging. The films were also very tacky when wet and brittle when dry. Figures M.1 and M.2 show the defects encountered in films prepared with SMM41 with low and high fluorine content, respectively. These two SMM41s had statistically the same weight-average and number-average molecular weights (M_w and M_n , respectively), however their fluorine contents were very different i.e., 18 and 3 wt % for the high and low contents, respectively.

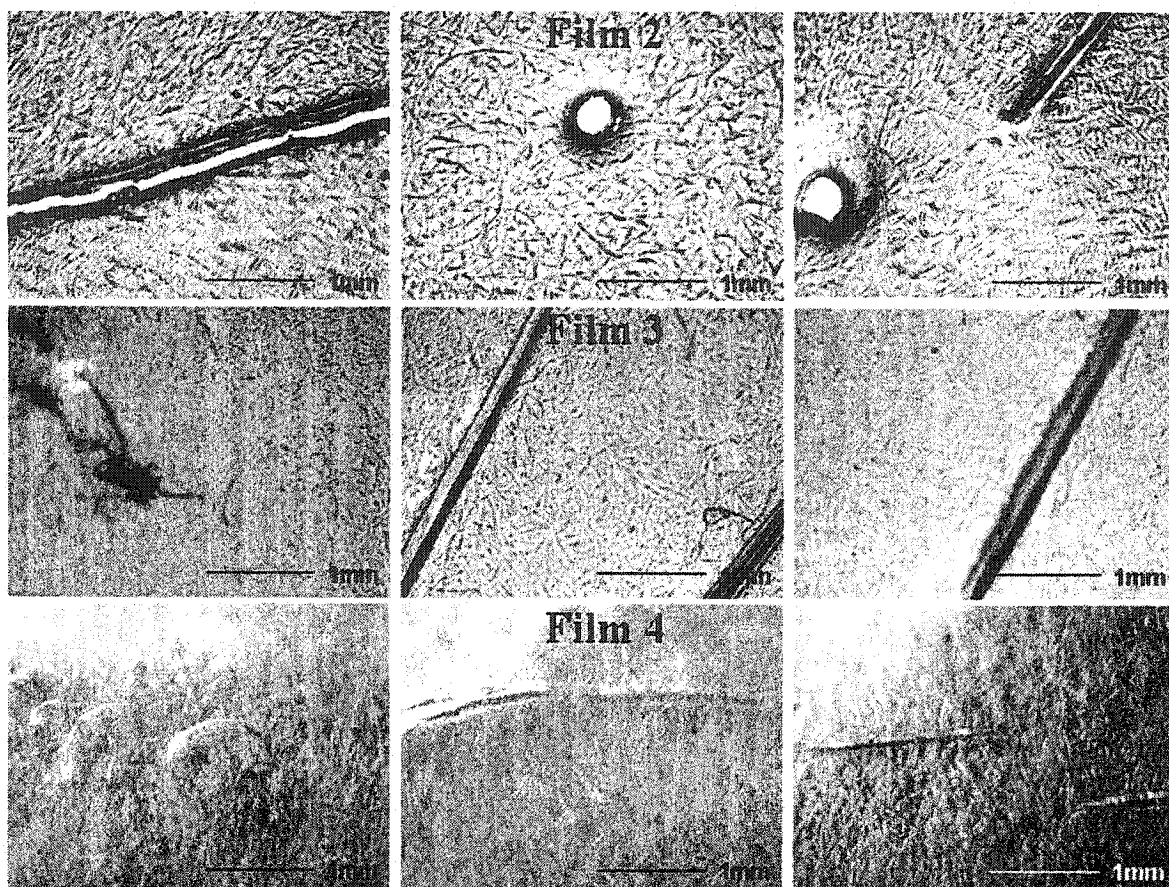


Fig. M.1 Optical microscope images of SMM41 (low fluorine content) films. Films in the last row have a filter paper as support

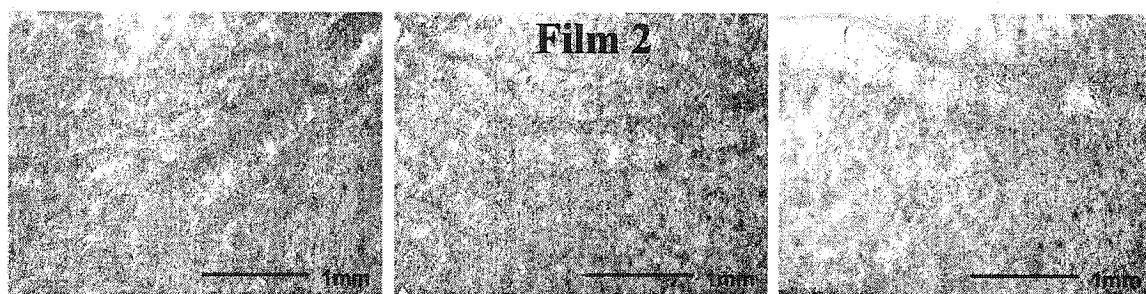


Fig. M.2 Optical microscope images of SMM41 (high fluorine content) films

Figure M.3 shows that independent of their thickness and fluorine contents, the advancing contact angles of the SMM41 films were statistically the same as those reported in the literature (Pham et al., 1999; Ho et al., 2000). However, the receding contact angle was significantly higher, and consequently the hysteresis was smaller. It is believed that this difference is due to the presence of PVP (and different solvent) in those films reported in the literature, causing a different SMM orientation in the surface. Films

prepared in this study were prepared with just SMM and solvent; therefore, they were more homogeneous. Even when the average contact angles for the low and high fluorine content SMM41s seemed different, the variability among readings was around 7%. Thus, statistically advancing and receding angles for the low and high fluorine contents SMMs were the same.

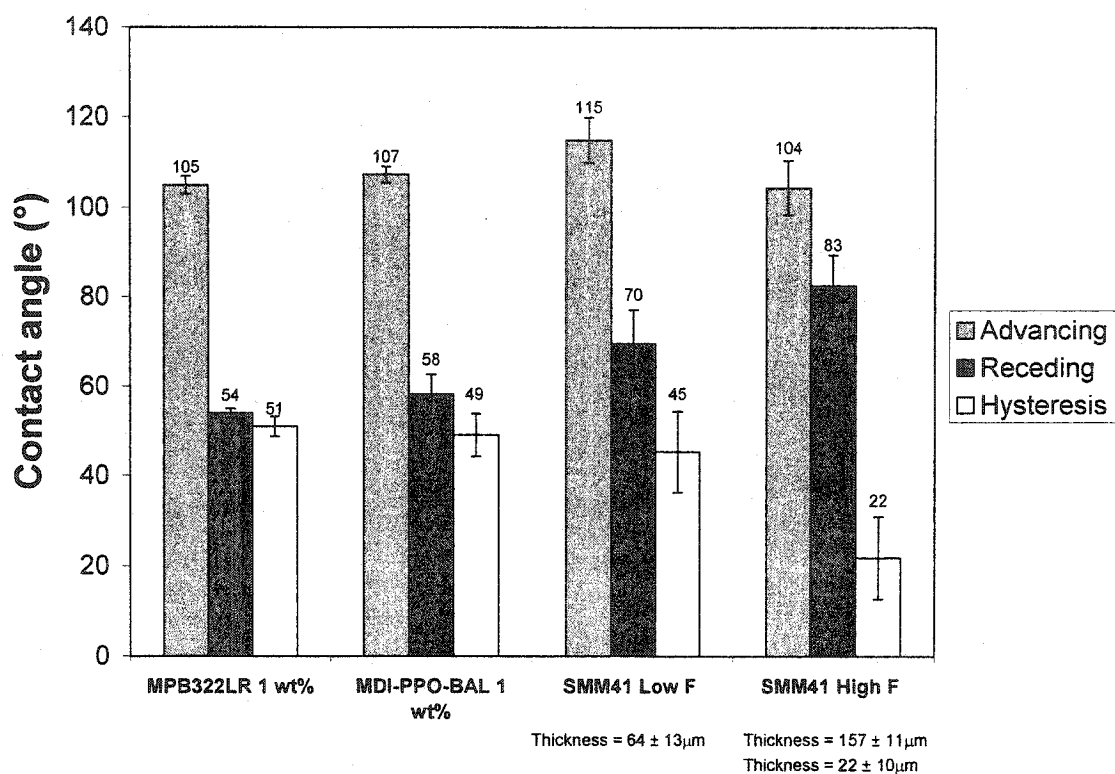


Fig. M.3 Advancing and receding contact angles of SMM41 films compared with data from the literature. MPB322LR is a membrane film prepared by Pham et al. (1999) and MDI-PPO-BAL was prepared by Ho et al. (2000)

APPENDIX N

TOC SURROGATES

Approximately one fifth of the samples collected were analyzed for TOC concentration. UV ($\lambda = 254$ nm, 1-cm cell) was used as its surrogate in the rest of the samples, i.e., the UV measurements were used in conjunction with TOC vs. UV calibration curves. The calibration curves were checked for each run, to verify that they did not change (Fig. N.1).

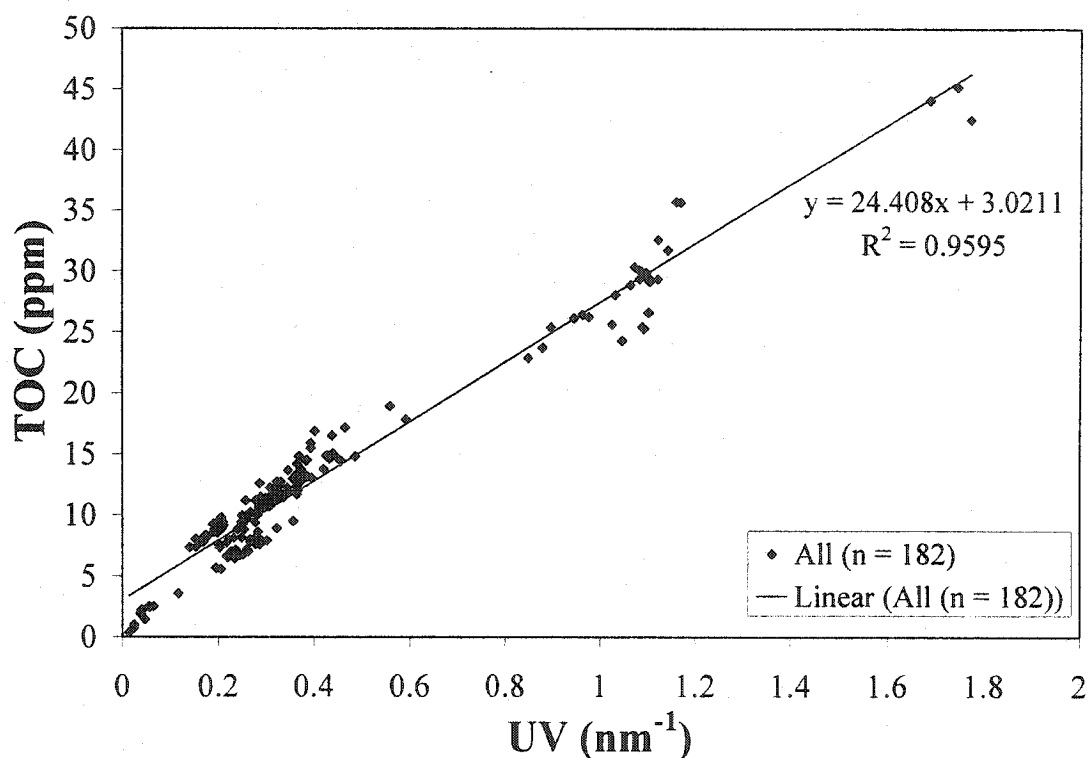


Fig. N.1 Calibration chart