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M.A.Sc. (Environmental Engineering)
GRADE / DEGREE

Program of Environmental Engineering
FACULTÉ, ÉCOLE, DÉPARTEMENT / FACULTY, SCHOOL, DEPARTMENT

Evaluation of Novel Polyethersulfone Membranes Developed Using Charged Surface Modifying Macromolecules for the Removal of Pharmaceutically Active Compounds and Endocrine Disrupting Compounds from Drinking Water

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EVALUATION OF NOVEL POLYETHERSULFONE MEMBRANES DEVELOPED USING CHARGED SURFACE MODIFYING MACROMOLECULES FOR THE REMOVAL OF PHARMACEUTICALLY ACTIVE COMPOUNDS AND ENDOCRINE DISRUPTING COMPOUNDS FROM DRINKING WATER

by

Anne-Marie Garand-Sheridan

M.A.Sc. Thesis

submitted to the Faculty of Graduate and Postdoctoral Studies

In partial fulfillment of the requirements for the degree of

M.A.Sc. in Environmental Engineering

January 2008

Department of Civil Engineering

(Ottawa-Carleton Institute of Environmental Engineering)

Faculty of Engineering

University of Ottawa

Your file Votre référence
ISBN: 978-0-494-48456-2
Our file Notre référence
ISBN: 978-0-494-48456-2

CERTIFICATE OF EXAMINATION

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is accepted in partial fulfillment of the requirements of the degree of

Master of Applied Science in Environmental Engineering

in the

Department of Civil Engineering

For my beautiful little sister, Bronwen. Je t'aime beaucoup.

For Amy, I could not have done this without you.

ACKNOWLEDGEMENTS

I would like to extend my sincere appreciation to Dr. Narbaitz for giving me the opportunity to work on this project as well as for his technical and moral support throughout. I am also very grateful to Dr. Matsuura for his invaluable knowledge and enthusiasm throughout this project.

My special thanks to Dr. Tabe of the Ontario Ministry of the Environment and Dr. Jasim of the Walkerton Clean Water Center, for their sponsorship of this project and their valuable feedback.

I am especially grateful to Amy Westgate and Dr. Dipak Rana for their collaboration, thoughts and knowledge during the project, as well as the synthesis of the novel CSMMs by Dr. Rana.

My most sincere thanks to Mr. Louis Tremblay and Mr. Franco Ziroldo from the Dept. of Chemical Engineering, Mr. John Perrins from the Dept. of Mechanical Engineering and Mr. Fransisco Aposaga from the Dept. of Civil Engineering for their invaluable knowledge, technical assistance and support.

I am indebted to Dr. Droste, Dr. Kennedy, Dr. Ormeci, Dr. Fernandes, Dr. Nistor and Mr. Tremblay for sharing their knowledge as well as for their support and encouragement. Thank you for your wisdom and enthusiasm.

Un gros merci à Mme. Yolande Hogan et Mlle. Manon Racine, pour leur support et amitiés, et surtout leur bonne humeur et sourires!

Thank you to the University of Ottawa for providing Admission and Excellence Scholarships and to NSERC for the Postgraduate Scholarship.

A great big **thanks!** to my colleagues and friends in the department, in particular Amy, Vienna, Elizabeth, Omar, Dillon, Isil, Nuno, Muna, and Younes. Thank you for your camaraderie, friendship and assistance. Also, a special thank you to Bilal who patiently put up with the noisy pump.

Finally, I would like to thank Amy, without whom this would not have been possible, and my family, Maman, Dad and Bronwen, who continue to support, encourage and believe in me. Merci.

ABSTRACT

The increasing concern over potential health effects of pharmaceutically active compounds (PhACs) and endocrine disrupting compounds (EDCs) in drinking water has led to an increase in assessment of drinking water treatment plant efficiencies at removing these emerging micropollutants. For the most part, tight commercial membrane processes such as nanofiltration (NF) and reverse osmosis (RO) successfully eliminate PhACs and EDCs, however these are costly processes and infrequently implemented in North American treatment facilities. The more frequently used microfiltration (MF) and loose ultrafiltration (UF) membranes are ineffective in the removal of these compounds.

This thesis focuses on developing tight charged ultrafiltration (UF) membranes which could effectively remove PhACs and EDCs from drinking water without compromising flux and cost. The approach centers on developing the membrane surface charge by incorporating charged surface modifying macromolecules (CSMMs) as additives. Four CSMMs (MDI-PPG-HBS, MDI-PEG_{200}-HBS, MDI-PEG_{400}-HBS, MDI-DEG-NDS) were evaluated at three different casting conditions for poly(ether sulfone) (PES) based membranes. The modified membranes were compared to controls (without CSMMs) and one commercial membrane (NF270, Dow/Filmtec). Membrane properties including flux, molecular weight cut off, surface porosity, charge and hydrophilicity were evaluated and compared to the removal of four representative PhACs and EDCs (sulfamethazine, carbamazepine, bisphenol A and ibuprofen) at the mg/L-level.

The experimental membranes only achieved a temporary partial removal of the PhACs and EDC tested, thus further development is required. Given the temporary target compound removal and the large membrane pores, size exclusion and charge repulsion are not the dominant removal mechanism. From the removal pattern, and the fact that removal increased with increasing solute hydrophobicity, it is assumed that initial removal is caused by adsorption to the membrane. The membranes developed were tight by conventional ultrafiltration standards but did not achieve the performance desired.

In general, it was found that the CSMM-modified membranes did not significantly outperform the control membranes. CSMM-modified membranes tested generally produced less hydrophilic membranes with increasing pre-gelation time or PES concentration, in comparison to the control membranes. Pre-gelation time (i.e., three minutes versus no pre-gelation time) increases membrane porosity, and therefore flux is increased, without compromising removal. Increased PES concentration (i.e., 20% PES in comparison to 18% PES) yields more distinct effects from the different CSMMs. From these results, the most promising casting condition appears to be 20% PES and the CSMMs achieving the best removal are MDI-PEG_{400}-HBS and MDI-PPG-HBS. As increased surface porosity was achieved, continuing this line of research by optimizing membrane preparation conditions to decrease the pore size may produce the desired characteristics. It is recommended that further tests be performed at increased PES concentrations and with pre-gelation time to achieve better results.

RÉSUMÉ

Récemment, la détection de produits pharmaceutiques (PhACs) et substances perturbateurs du système endocrinien (EDCs) dans l'eau potable a accrue l'inquiétude concernant les effets néfastes de ces solutés sur la population humaine. Cette inquiétude a aussi accrue l'évaluation des unités de traitement d'eau potable afin de déterminer l'efficacité des différentes étapes de purification pour l'elimination des PhACs et EDCs. La filtration par membrane commerciale, telle l'osmose inverse (RO) ou la nanofiltration (NF), est un procédé qui élimine une grande partie des PhACs et EDCs, réaliseant des taux d'élimination entre 50 et 95+%. Le cout d'implémentation, par contre, est élève et le taux de production d'eau potable est faible, ce qui fait que la majorité des usines d'eau potable nord-américaines n'utilisent pas cette technologie. Les technologies plus populaires telles la microfiltration (MF) et l'ultrafiltration (UF) sont incapable d'éliminer les composés en question.

Le but de cette thèse est de développer de nouvelles membranes d'ultrafiltration (UF) en utilisant des macromolécules chargées (CSMMs) qui chargeraient la surface. Ces membranes auraient l'avantage d'éliminer les PhACs et EDCs tout en produisant économiquement un haut taux d'eau potable, en comparaison aux membranes NF et RO. Quatre CSMMs (MDI-PPG-HBS, MDI-PEG_{200}-HBS, MDI-PEG_{400}-HBS, MDI-DEG-NDS) ont été évaluées à trois différentes conditions de préparation pour des membranes à base de polyethersulfone (PES). Ces membranes ont été comparées à des membranes contrôles (sans CSMM) et à une membrane commerciale (NF270, Dow/Filmtec). La perméabilité, le seuil de coupure (MWCO), la porosité, la distribution de la taille de

pores, la charge et l'hydrophobicité des membranes ont été évaluées. Aussi, ces propriétés ont été comparées aux taux d'élimination de trois PhACs et un EDC représentatifs (sulfamethazine, carbamazepine, bisphenol A et ibuprofen) au niveau mg/L.

Les membranes expérimentales ont seulement démontrées une élimination partielle des PhACs et EDC testées donc plus de développent est requis. D'après les résultats d'élimination et la taille des pores, il est impossible que l'élimination soit due à la rejection due à la taille ou la charge, et d'après la courbe d'élimination, et le fait que le taux d'élimination augmente avec l'hydrophobicité des solutés, il est présumé que le phénomène d'adsorption est prédominant. Les membranes développées étaient plus serrées que les membranes UF conventionnelles, par contre n'ont pas réussi la performance désirée.

Généralement, les membranes modifiées par CSMM n'ont pas démontré de grandes améliorations par rapport aux membranes contrôles. En comparant les membranes modifiées (avec CSMM) aux contrôles (sans CSMM), les membranes modifiées étaient plus hydrophobiques avec une hausse de PES ou en augmentant le temps de migration. Le temps de pré-gélation (i.e., trois minutes versus aucun temps) accroit la porosité ce qui augmente la perméabilité mais qui ne diminue pas le taux d'élimination des PhACs ou EDCs. En augmentant la quantité de PES (i.e., 20% PES versus 18% PES), la variation des propriétés sont plus distinctes pour les différents CSMMs. D'après les résultats, la condition de préparation la plus promettante est celle de 20% PES. Les CSMMs ayant les

plus haut taux d'élimination sont le MDI-PEG_{400}-HBS et le MDI-PPG-HBS. Il est suggéré de faire plus de tests à de plus hautes concentrations de PES et avec au moins trois minutes de pré-gélation afin d'obtenir de résultats plus favorables.

NOMENCLATURE

316-SS	316 stainless steel
AOP	Advanced oxidation process
B	Bench scale
BPA	Bisphenol A
CA	Cellulose acetate
CBC	Canadian Broadcasting Corporation
CBZ	Carbamazepine
CSMM	Charged surface modifying macromolecule
CTA	Cellulose triacetate
CTV	Canadian Television
DEG	Diethyleneglycol
DBP	Disinfection by-product
DEET	*N,N*-diethyl-meta toluamide
DI	Deionized water
DMAC	Dimethylacetate
DW	Drinking water
EDC	Endocrine disrupting compound
EfOM	Effluent organic matter
FS	Flat sheet bench scale
GAC	Granular activated carbon
GEM	Gemfibrozil
HBS	Hydrobenzene sulfonate
IB	Ibuprofen
LMH	$L/(m^2h)$
log K_{OW}	Octanol-water partition coefficient
LOQ	Level of quantification
LSMM	Hydrophillic surface modifying macromolecule
MDI	Methyl-diisocyanate
MF	Microfiltration
MQ	Ultrapure lab grade water obtained from Millipore Milli-Q Water System

MW	Mineral water
MWCO	Molecular weight cut off
NDIR	Non-dispersive infrared
NDS	Naphthol disulfonate
NF	Nanofiltration
NMP	1-Methyl-2-pyrrolidone
NOM	Natural organic matter
NP	Nonylphenol
NSAID	Non-steroidal anti-inflammatory drugs
NSF	Normalized standard flux
P	Pilot scale
PA	Polyamide
PAC	Powdered activated carbon
PAN	Polyalcrylonitrile
PC	Polycarbonate
PCP	Personal care product
PE	Polyethylene
PEG	Poly(ethylene glycol)
PEG_{200}	Poly(ethylene glycol) with molecular weight of 200Da
PEG_{400}	Poly(ethylene glycol) with molecular weight of 400Da
PEO	Poly(ethylene oxide)
PES	Poly(ether sulfone)
PF	Plate and frame
PhAC	Pharmaceutically active compound
pK	Dissociation constant
PP	Polypropylene
PPCP	Pharmaceuticals and personal care products
PPG	Poly(propylene glycol)
ppmC	parts per million Carbon (mg Carbon/L)
PS	Polysulfone
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride

PWP	Pure water permeability
RO	Reverse osmosis
RWW	Reclaimed wastewater
SC	Dead-end stirred cell
SFT	Solute filtration test
SMM	Surface modifying macromolecule
SMZ	Sulfamethazine
TFC	Thin film composite
TOC	Total organic carbon
UF	Ultrafiltration
ULPRO	Ultra low pressure reverse osmosis
UV	Ultraviolet
WTP	Water treatment plant
WWTP	Wastewater treatment plant
XF	Cross-flow
XFSC	Cross-flow stirred cell

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CHAPTER 1

INTRODUCTION

1.1 Background

Due to recent advances in analytical techniques, a number of pharmaceutically active compounds (PhACs) and endocrine disrupting compounds (EDCs) are being detected in water samples. Surface and ground water surveys show that these emerging micropollutants primarily originate from wastewater effluents and are either persistent or pseudo-persistent, due to their constant introduction. The environmental concentration of PhACs and EDCs ranges from ng/L to μg/L and varies widely as a function of location (i.e., upstream discharges, degree of dilution, type of wastewater treatment), demographics and prescription habits as well as season. Effects on aquatic biota are widely reported for EDCs, generally skewing population sex ratios (having either androgenic or estrogenic effects). In recent years, studies reporting the effects of pharmaceuticals and personal care products (PPCPs) on aquatic biota have increased, however the effects of these contaminants is much less widely known. Although many effects are reported, the chronic effects of subtle changes may not be known for some time. The detection of these compounds in drinking water raises the question of effects to human populations. Effects to humans are unknown: acute effects are unlikely due to the low concentrations however, long-term effects are cause for concern since they could be subtle, having cumulative and possibly irreversible effects.

The efficiency of drinking water treatment plants at removing PPCPs and EDCs is varied. Conventional treatment does not appear to significantly decrease concentrations; the

performance of advanced technologies, such as adsorption via activated carbon, oxidation and membrane filtration, is more promising, with removals ranging from 50 to 95+%. The key hurdles in removing these micropollutants are: i) their small size and very low concentration, ii) the wide range of properties, iii) the cost of the additional water treatment processes required, and iv) the cost and availability of analytical techniques. Membrane technologies appear to be a viable technology since, for tight membranes, they can completely retain these solutes without the formation of by-products (as seen with oxidation). The major drawbacks of tight membrane processes are their higher operating cost and lower water production rate. Currently, only commercial membranes have been evaluated for the removal of PPCPs and EDCs from drinking water.

Membranes can be tailored for specific applications by modifying the membrane manufacturing method. A novel technique for making membranes with improved surface characteristics has been developed over the past 15 years by a group of researchers at the University of Ottawa and the University of Toronto. The surface modifying macromolecules (SMMs) they have developed are polymeric additives tailored for poly(ether sulfone) (PES) membranes used in environmental applications. The advantage of this surface modification method over others is that it only involves a single step casting process. The additives used are tailor-made – having either hydrophobic or hydrophilic properties, as desired. The SMMs are incorporated to the casting solution containing PES and the desired solvent. When the solution is cast, the SMMs rise to the surface, making it more hydrophobic or hydrophilic, depending on the SMM. Applications investigated include pervaporation for the separation of volatile organic

compounds from water (Pham, 1995; Mahmud, 1996; Fang, 1997), biomedical applications (Ho, 1997) and the reduction of natural organic matter (NOM) fouling during drinking water treatment (Mosqueda-Jimenez, 2003; Nguyen, 2005).

1.2 Scope of research

To date, no one unit operation has been shown to effectively remove all PhACs and EDCs from drinking water. Tight membranes (i.e., nanofiltration (NF) and reverse osmosis (RO)) have been shown to remove, with varying degrees of success, a wide range of these emerging micropollutants. The major drawback of tight membranes used for drinking water treatment is their low flux (production rate) and high operating costs. The primary objective of this research project was to develop and test surface modified poly(ether sulfone)-based ultrafiltration membranes tailored for the removal of PhACs and EDCs such that they could be cost-effectively implemented into drinking water treatment plants while achieving high removals. It is hypothesized that since some PhACs and EDCs are charged, the use of charged SMMs may produce membranes that will remove at least some of these compounds via charge repulsion.

The major goals of this thesis were to:

- Conduct a literature review of the occurrence, fate and effects of PhACs and EDCs in the environment and examine the ability of unit operations to remove them during drinking water treatment, specifically investigating the role of membrane processes

- Develop, characterize and test poly(ether sulfone) based ultrafiltration membranes incorporating charged surface modifying macromolecules for the removal of five representative PhACs and EDCs

CHAPTER 2

LITERATURE REVIEW

Emerging contaminants in the aquatic environment and the ability of drinking water treatment plants to remove them is an increasing concern. This literature review focuses on the occurrence, fate and effects of pharmaceuticals, personal care products and endocrine disrupting compounds in the aquatic environment and drinking water plants. As well, the use of membrane processes to remove these contaminants is reviewed. A review of membrane technologies used in water treatment and wastewater treatment, including background on ultrafiltration membranes is presented in the literature review.

2.1 Emerging contaminants in drinking water

Advances in analytical methods have led to the detection of low-level contaminants (micropollutants) in the aquatic environment. These emerging contaminants include:

- Pharmaceuticals: prescription and non-prescription drugs;
- Personal care products (PCPs): ingredients found in soaps, shampoos, cosmetics, cleaning products, detergents, and many other household items;
- Endocrine disrupting compounds: "An exogenous substance that causes adverse health effects in an intact organism, or its progeny, consequent to endocrine function" (Bowman et al., 2002; Nghiem and Schafer, 2002), found in paints, personal care products, plastics, flame retardants, pesticides, cleaning products, and natural and synthetic hormones;
- Pesticides and herbicides: used for agricultural or domestic purposes;
- Ultraviolet (UV) filters: active ingredients in sunscreens and commonly found in many personal care products.

Examples of these contaminants are listed in Table 2.1.

Table 2.1: Examples of emerging contaminants commonly found in the environment

Classification	Compounds	
Analgesics and Non-Steroidal Anti-Inflammatory Drugs (NSAIDs)	Acetaminophen	Indomethacin
	Acetylsalicylic acid	Ketoprofen
	Codeine	Meclocycline sulfosalinicylate
	Diclofenac	Naproxen
	Fenoprofen	Phenazone
	Ibuprofen (IB)	Propyphenazone
Antibiotics	Amoxacillin	Roxithromycin
	Chloramphenicol	Sulfachloropyridazine
	Chlortetracycline	Sulfadiazine
	Ciprofloxacin	Sulfamerazine
	Doxycycline	Sulfamethazine (SMZ)
	Erythromycin	Sulfamethizole
	Lincomycin	Sulfamethoxazole
	Monensin	Tetracycline
	Oxytetracycline	Trimethoprim
	Penicillin G	Virginiamycin M1
UV Filters	Ethylhexyl methoxycinnamate	Octocrylene
	4-Methylbenzylidene camphor	Butyl methoxydibenzoylmethane
	Benzophenone	Octyl methoxycinnamate
Anticoagulants	Warfarin	
Antidepressants	Diazepam	Fluoxetine
Antiepileptics	Carbamazepine (CBZ)	Primidione
Blood Lipid Regulators	Bezafibrate	Gemfibrozil (GEM)
	Clofibric acid *	Fenofibric acid *
Endocrine Disrupting Compounds	Bisphenol A (BPA)	Perfluorooctanoic acid
	Nonylphenol	Perfluorooctyl sulfonate
	Octylphenol	Phthalates
Veterinary Antibiotics	Lasalocid A	Sulfadimethoxine
	Carbadox	Tylosin
Natural and Synthetic Steroids	17α-estradiol	Equilin
	17α-ethynyl estradiol	Estriol
	17β-estradiol	Estrone
	19-norethisterone	Progesterone
	Diethylstilbesterol	Testosterone

* metabolite

Studies have shown that these contaminants of concern are primarily entering the environment through wastewater effluents; their fate and effect in the environment is largely unknown, with the exception of noted impacts from EDCs.

2.1.1 Occurrence, fate and effects of PhACs and EDCs in the aquatic environment

2.1.1.1 Occurrence

It is estimated, from an annual worldwide use of approximately 100,000 tons, that the average person would use 15 g/year (Kummerer, 2004) of prescription pharmaceuticals, however the quantity of PhACs used, and therefore discharged into wastewater treatment plants, may be significantly larger in developed countries, where non-prescription medication is used extensively. Pharmaceutically active compounds are excreted from 30 to 90% in their active or conjugated (polar) forms (Kummerer, 2004; Heberer, 2002a; Andreozzi et al., 2003; Metcalfe et al., 2003b). They are not fully eliminated during wastewater treatment (Heberer, 2002a; Andreozzi et al., 2003). Endocrine disrupting compounds are also frequently detected in industrial and municipal wastewater effluents. Approximately 150 of these compounds have been detected in wastewater effluent, surface and ground water and to a lesser extent within finished drinking water (Zuccato et al., 2006; Boyd et al., 2003; Heberer, 2002a; Stumpf et al., 1999).

Wastewater treatment plants are traditionally not designed for the removal of micropollutants (Petrović et al., 2003b). Wastewater effluents are therefore the primary source of PhACs and EDCs into the aquatic environment (Roberts and Thomas, 2006; Lindqvist et al., 2005; Petrović et al., 2003b; Heberer, 2002a; Andreozzi et al., 2003; Metcalfe et al., 2003b). Other sources are listed in Table 2.2. An increasing number of

studies have been carried out to assess the level and spread of contamination in aquatic compartments. Important studies include: Kolpin et al. (2002), Heberer (2002b), Ternes et al. (2002) and Ferrari et al. (2003).

Table 2.2: Principal secondary sources of PhACs and EDCs into aquatic compartments

Source	References
Aquafarming	Perret et al. (2006); Hirsch et al. (1999)
Hospital effluents	Perret et al. (2006); Sanderson et al. (2004)
Industrial and Pharmaceutical wastewaters	Heberer (2002a); Hirsch et al. (1999)
Landfill leachate	Heberer (2002a); Metcalfe et al. (2003a)
Runoff from land application of biosolids	Roberts and Thomas (2006); Metcalfe et al. (2003a, b)
Runoff from land application of manure	Jones et al. (2004); Hirsch et al. (1999); Metcalfe et al. (2003b)

2.1.1.1.1 Occurrence in wastewater treatment plant effluent

The characterization of contamination throughout wastewater treatment plants (WWTPs) and their effluents has helped determine the removal efficiencies of the different unit operations and assess environmental loads. This is particularly important to determine potential implications to wastewater reuse and impacts to downstream drinking water treatment plants (WTPs) as well as the receiving environment.

Influent concentrations to WWTPs can be predicted by drug usage within the service area whereas effluent concentration estimates may be predicted by the treatment plant efficiency (Liebig et al., 2006; Zuccato et al., 2006; Anderson et al., 2004). In raw wastewater, PhACs and EDCs are commonly detected in the ng/L – mg/L range. Different levels of removal are achieved in treatment plants, with compounds such as

acetaminophen, acetylsalicylic acid, penicillins, tetracyclines, and cephalosporins showing significant or complete removal (Roberts and Thomas, 2006; Andreozzi et al., 2003; Hirsch et al., 1999). Other compounds show increases in concentration over the course of the treatment process, which may be due to re-activation of metabolites (Roberts and Thomas, 2006) or variability in analytical techniques. Studies by Vieno et al. (2006), Lindqvist et al. (2005), Miao et al. (2004), and Tixier et al. (2003) have shown seasonal variations in occurrence and efficiencies. Variations in occurrence and rate of occurrence between different countries have also been observed, attributed to pharmaceutical use rates, treatment plant efficiencies (Metcalfe et al., 2003a), legislation (i.e., banned use of antibiotics for livestock growth promotion in Switzerland (Wiegel et al., 2004)), demographics, and prescription habits (Zuccato et al., 2006). Common PhACs and EDCs detected in effluents include: bisphenol A, carbamazepine, clofibric acid, diclofenac, estrone, ibuprofen, macrolide antibiotics, naproxen, sulfamethoxazole, trimethoprim and 17β-estradiol. They are detected in WWTP effluents in ng/L to μg/L levels.

2.1.1.1.2 Occurrence in surface and ground water

Municipal WWTP effluents are the primary cause of PhAC and EDC contamination in surface and ground water, as previously discussed. This contamination can be characterized by the detection of "urban" compounds such as caffeine, nicotine, and illegal drugs (i.e., cocaine and its metabolites). After the initial dilution upon discharge into a water body, the proportion of PhAC and EDC remains fairly constant with downstream travel (Lindqvist et al., 2005). Concentration and concentration profiles downstream have been observed to vary, presumably due to sorption and degradation

(see Section 2.1.1.2). Additionally, other sources, such as agricultural run-off, may impact the distribution and concentration of pharmaceuticals found in a given water body, typically contributing to higher levels of pesticides or antibiotics (Hirsch et al., 1999; Metcalfe et al., 2003b). In a US Geological Survey carried out between 1999 and 2000, Kolpin et al. (2002) analyzed 139 US streams (in 30 states) for 95 pharmaceuticals, hormones and organic wastewater contaminants. They detected 80 of the target solutes at least once, found that 50% of the streams contained seven or more PPCPs and EDCs and that 80% of the streams contained some of the target solutes. The contamination and source of contamination of local water bodies needs to be characterized in order to properly assess proper risks and mitigation measures.

Compounds detected in surface water include: NSAIDs such as ibuprofen, naproxen, diclofenac, and acetaminophen, antiepileptics (carbamazepine and primidione), blood lipid regulators (clofibric acid), estrogens (estrone, 17β-estradiol) and EDCs (bisphenol A, nonylphenol). Groundwater appears to be significantly less contaminated than surface water (Hohenblum et al., 2004). Although this may be due to the fact that fewer investigations have been carried out in this area, it is likely due to the fact that most wastewater effluents are discharged into surface waters. Polar compounds, such as clofibric acid, carbamazepine, primidone, and sulfonamide antibiotics, have been found to leach from surface water into groundwater during bank filtration (Heberer, 2002a). Other notable compounds found in groundwater include nonylphenol and bisphenol A (Hohenblum et al., 2004). Concentrations in surface and ground water range from ng/L to μg/L levels however they are generally lower than in wastewater effluents.

2.1.1.1.3 Occurrence in drinking water

Public concern over the detection of PhACs and EDCs in finished drinking water is growing. Few studies discuss the occurrence and impacts of these trace micropollutants, however media outlets have widely reported their occurrence (Canadian Broadcasting Corporation (CBC) 2006, 2001; Canadian Television (CTV), 2003; Anderson et al., 2004). Research into the occurrence of PhACs and EDCs as opposed to synthetic organic contaminants in drinking water is not as widespread for the following reasons: i) these compounds are present at very low levels (ng/L); ii) specific sophisticated (non-routine) analytical methods are required to quantify contamination; iii) analytical methods for trace levels of some of these compounds are in the process of development; iv) cost of the analysis is high; v) only a limited number of analytical laboratories are capable of conducting the analysis; and vi) lack of regulatory monitoring requirements for these compounds.

Concentrations of PhACs and EDCs in finished drinking water can vary significantly as they are a function of the raw water matrix (PhAC and EDC concentration profiles and source water matrix), the treatment technology used in the particular plant, variations in treatment process efficiencies, and other environmental factors. Treatment process efficiencies are discussed in Section 2.1.2. Seasonal effects are also evident from samples collected at water treatment plants (Jasim et al., 2006; Vieno et al., 2006). Ibuprofen and ketoprofen were detected in a Finnish drinking water during winter whereas they were fully eliminated during summer. This was due to increased feed concentrations and lower removal rates during winter (Vieno et al., 2006). Few studies have been published on the

detection of these compounds in drinking water. The results of these studies are summarized in Table 2.3. It should be noted that most monitoring studies have been carried out in Europe where, as a result of denser populations, there is concern over water quality from extensive use of waterways. Common compounds detected include: bisphenol A, clofibric acid, carbamazepine, diazepam, diclofenac, estrone, gemfibrozil, ibuprofen, ketoprofen, sulfamethoxazole, triclosan and tylosin, as shown in Table 2.3. They are detected in the ng/L range.

Table 2.3: Detection of PhACs and EDCs in finished drinking water, reclaimed wastewater and mineral water

Compound	Concentration (ng/L)					Detection Frequency	Type of water	Location	References
	LOQ	Max	Median	Mean	General				
17α-estradiol	0.1	0.3	0.3	0.3		1 of 10	DW	Germany	Kuch and Ballschmiter (2001)
17α-ethynylestradiol		2.4					DW		Heberer (2002a)
	0.05	0.5	0.35	0.35		4 of 10	DW	Germany	Kuch and Ballschmiter (2001)
17β-estradiol	0.1	2.1	0.3	0.7		5 of 10	DW	Germany	Kuch and Ballschmiter (2001)
Acetaminophen (paracetamol)					detected	1 of 2	DW	Louisiana, USA	Boyd et al. (2003)
					detected		DW	Canada	Boyd et al. (2003)
Bezafibrate		27					DW	Germany	Jones et al. (2004)
Bisphenol A					detected	2 of 2	DW	Louisiana, USA	Boyd et al. (2003)
					detected		DW	Canada	Boyd et al. (2003)
	0.02	2	1.1	1.1		10 of 10	DW	Germany	Kuch and Ballschmiter (2001)
	1000	420					DW	USA	Stackelberg et al. (2004)
Caffeine	14	119					DW	USA	Stackelberg et al. (2004)
Carbamazepine	11	258					DW	USA	Stackelberg et al. (2004)
Clofibric acid					detected		DW	UK	Jones et al. (2004)
		170	19	40.08	14 WTPs	12 of 14	DW	Germany	Heberer (2002b)
		270					DW	Germany	Heberer (2002a)
		70					DW	Germany	Jones et al. (2004)
		165					DW	Germany	Jones et al. (2004)
		270					DW	Germany	Jones et al. (2004)
		170					DW	Germany	Jones et al. (2004)
	1.5	5.3			3.2-5.3		DW	Lodi, Italy	Zuccato et al. (2000)
DEET (*N,N*-diethyl-meta toluamide)	160	2110		1310		2 of 6	RWW	USA	Loraine and Pettigrove (2006)
	500	66					DW	USA	Stackelberg et al. (2004)
Diazepam		10					DW	UK	Jones et al. (2004)
	0.02				0.2		DW	Varese, Italy	Zuccato et al. (2000)
	0.02	23.5			19.5-23.5		DW	Lodi, Italy	Zuccato et al. (2000)
Diclofenac		6					DW	Germany	Jones et al. (2004)
Estrone					detected		DW	Ontario, Canada	Boyd et al. (2003)

Compound	Concentration (ng/L)					Detection Frequency	Type of water	Location	References
	LOQ	Max	Median	Mean	General				
Estrone *(con't)*	0.05	0.6	0.4	0.4		4 of 10	DW	Germany	Kuch and Ballschmiter (2001)
	0.1			0.16		5 of 5	DW	Germany	Verstraten et al. (2003)
					detected	2 of 2	DW	Louisiana, USA	Boyd et al. (2003)
Gemfibrozil		70					DW	Canada	Jones et al. (2004)
Ibuprofen					detected		DW	Germany	Heberer (2002a)
		1350		930		2 of 15	DW	USA	Loraine and Pettigrove (2006)
		3					DW	Germany	Jones et al. (2004)
	560	1250		790		3 of 6	RWW	USA	Loraine and Pettigrove (2006)
Naproxen	19600			24600		1 of 6	RWW	USA	Loraine and Pettigrove (2006)
		2600			100-2600		RWW		Ternes et al. (2002)
Nonylphenol	0.05	16	6.6	8		10 of 10	DW	Germany	Kuch and Ballschmiter (2001)
Octylphenol	0.04	4.9	1.8	2		10 of 10	DW	Germany	Kuch and Ballschmiter (2001)
Phenazone					detected		DW	Germany	Heberer (2002a)
		250		150		2 of 2	DW	Germany	Zuhlke et al. (2004)
		400					DW	Germany	Reddersen et al. (2002)
Propyphenazone		80				1 of 2	DW	Germany	Zuhlke et al. (2004)
				120		6	DW	Germany	Reddersen et al. (2002)
Sulfachloropyridazine	13				<LOQ	1	MW	Italy	Perret et al. (2006)
Sulfadimethoxine	8			11		1	MW	Italy	Perret et al. (2006)
Sulfamethizole	7			9		1	MW	Italy	Perret et al. (2006)
Sulfamethoxazole	9	80		46.5		2	MW	Italy	Perret et al. (2006)
Triclosan				734		1 of 15	DW	USA	Loraine and Pettigrove (2006)
	250	2110		1430		3 of 6	RWW	USA	Loraine and Pettigrove (2006)
Tylosin		1.7			0.6-1.7		DW	Lodi, Italy	Zuccato et al. (2000)

LOQ – Level of Quantifiaction, DW – Finished drinking water, MW – Mineral water (bottled), RWW – reclaimed wastewater

2.1.1.2 Fate

The fate of PhACs and EDCs in the aquatic environment varies widely and is not well documented for most compounds. Removal efficiencies in the environment also vary widely, as a function of compound and location. PhACs and EDCs have been deemed "pseudo-persistent" since they are continuously introduced into the environment (Jones et al. 2004; Petrović et al., 2003b). On the other hand, clofibric acid, carbamazepine and diclofenac, among others, are persistent. Mechanisms which may fully or partially remove other PhACs and EDCs are: biotic or abiotic degradation and sorption to sediment and/or natural organic matter (Buser et al., 1998; Bowman et al., 2002; Liu et al., 2005; Tixier et al., 2003; Andreozzi et al., 2003).

2.1.1.3 Effects and risks

The detection of PhACs and EDCs in the environment and concern with potential effects has sparked research to determine effects and potential risks to the aquatic environment and human health. Effects to wildlife have repeatedly been noted at environmental concentrations (Richardson, 2003) yet many effects remain unknown (Andreozzi et al., 2003). Effects caused by EDCs have been significantly more reported than those caused by PPCPs. They have been shown to skew sex ratios, having either androgenic or estrogenic effects, especially in fish. It is speculated that EDCs are also the cause of human health problems such as decreased sperm counts, breast and reproductive tract cancers and early breast development (Snyder et al., 2005; Liu et al., 2005). Effects caused by PhACs are much less widely known. Antibiotics have been listed as compounds of primary concern (in terms of effects and risks) because they have been

shown to cause microbial resistance thus decreasing their effectiveness (Petrović et al., 2003b; Miao et al., 2004). They are also potentially carcinogenic (Miao et al., 2004). Polar compounds are also cause for concern due to their persistence throughout drinking water treatment plants (Petrović et al., 2003b) and their ability to leach into groundwater.

The low concentrations at which these micropollutants are detected raises concern primarily regarding chronic effects (as opposed to acute effects), specifically due to the likelihood of long term exposure. Complete risk assessments are not required for pharmaceuticals (Sanderson et al., 2004) and if they are conducted, only acute toxicity may be determined (Sanderson et al., 2004; Jjemba, 2006). The likelihood of acute toxicity is low, and the lack of information regarding chronic toxicity (Jones et al., 2004) shows that little is known as to the potential chronic effects (Kummerer, 2004). In addition, one should consider that PhACs are detected at sub-clinical levels and that they had to pass acute toxicity level tests as part of the drug approval process, thus it is unlikely they would cause acute toxicity problems. However, studies suggest that effects could be observed at any level in the environment (cell – organ – organism – population – ecosystem) (Sanderson et al., 2004). These effects could be subtle, such as genetic selection, endocrine disruption, and/or genotoxicity, but could lead to altered behaviour, metabolisms, and function in the environment, thus perturbing environmental cycles (Sanderson et al., 2004). A major cause for concern is that these effects may not have been identified yet, but could be subtle and have cumulative and possibly irreversible effects (Bowman et al., 2002).

2.1.2 PhAC and EDC removal performance of drinking water unit operations

The recent detection and concern over PhACs and EDCs in the aquatic environment and finished drinking water has sparked interest regarding the ability of drinking water treatment plants to remove them. Important investigations have been carried out by Westerhoff et al. (2005), Stackelberg et al. (2004), Petrović et al. (2003b), Boyd et al. (2003), and Adams et al. (2002), setting the tone for future investigations. Due to the differences in performance, this discussion will focus on conventional treatment and advanced treatment processes.

2.1.2.1 Conventional treatment

Adams et al. (2002), Petrović et al. (2003a), Vieno et al. (2006), Boyd et al. (2003), and Westerhoff et al. (2005) have studied the removal of target PPCPs, EDCs and organic solutes from drinking water plants via coagulation. From their analysis, it appears that conventional treatment achieves "no significant removal". Vieno et al. (2006) found that removal of ionisable pharmaceuticals was enhanced in the presence of natural organic matter, while non-ionisable pharmaceuticals (i.e., carbamazepine and sulfamethoxazole) were not removed. They concluded that coagulation, in the presence of natural organic matter, would lead to partial removal of ionisable pharmaceuticals, but would be insufficient to meet desired purity levels. Chlorination has shown some removal, however it is not as promising as more advanced oxidants. Westerhoff et al. (2005) found that using a chlorine residual dose of 0.5 to 1.0 mg/L after a 24 hour contact time achieved removals greater than 90% (as a function of source water) for several pharmaceuticals (trimethoprim, sulfamethoxazole, dilantin, triclosan, and erythromycin). While this contact time is large for a clearwell, it is achievable in large distribution systems. Petrović

et al. (2003a) eliminated 43% of compounds after final disinfection in a water treatment plant. It is expected that post disinfection will oxidize some PhACs and EDCs but is likely insufficient for removing all of these emerging contaminants.

2.1.2.2 Tertiary treatment (Advanced technologies)

Adams et al. (2002) showed that at sufficient doses (10 to >20 mg/L) powdered activated carbon (PAC) achieved 51-97% removal (a function of dose). Boyd et al. (2003) showed that at lower doses (2 mg/L), naproxen could not be fully eliminated from Mississippi River water. PAC is typically used for emergency purposes, or for seasonal taste and odour problems, and the PAC doses are generally much higher than 2 mg/L. Additionally, due to the nature of the process, PAC cannot achieve 100% removal, which leads to the question of the viability of PAC for the removal of PhACs and EDCs. Granular activated carbon (GAC), on the other hand, can theoretically achieve 100% removal (until the start of the breakthrough). Petrović et al. (2003b) found that GAC could remove 73% of alkylpolyethoxylates (average feed concentration of 1.5 mg/L) while it could not remove clofibric acid. Poor removal results using GAC have also been shown by Stackelberg et al. (2004) and Vieno et al. (2006). Conversely, Snyder et al. (2007) show that most of the 27 pharmaceuticals and endocrine disruptors they evaluated could be removed by more than 90%. They did, however, notice that more hydrophilic solutes were likely to breakthrough faster than the hydrophobic solutes which were more strongly adsorbed to the GAC. Regeneration was also shown to minimize breakthrough (Snyder et al., 2007). Due to the non-specific nature of activated carbon adsorption, the removal of PhACs, EDCs, and other trace organic contaminants can be significantly

reduced by competition for adsorption sites with NOM, which is present in much higher concentrations.

Similarly to chlorination, removal by ozonation and other advanced oxidation processes (AOPs) have shown more promise than activated carbon, and research into this area is growing rapidly. Boyd et al. (2003) concluded that both chlorination and ozonation were effective in removing PPCPs (clofibric acid, naproxen, ibuprofen, acetaminophen, caffeine, fluoxetine, chlorophene, triclosan) and EDCs (bisphenol A, estrone, 17β-estradiol). Using ozone, Westerhoff et al. (2005) oxidized more than 80% of 62 PPCPs and EDCs, the main exceptions being atrazine and ibuprofen. Removals greater than 95% were also achieved by ozone after 1.3 minutes contact on six antibiotics (Adams et al., 2002). While in general removal is high, certain compounds appear to be oxidized to a lesser extent (i.e., 50% of bezafibrate removed by Ternes et al. (2002)). The major disadvantage of oxidation is the potential creation of by-products, which are currently unidentifiable/undetectable (Westerhoff et al., 2005). These by-products may have more detrimental effects than the target solutes or may become re-activated downstream.

Finally, a number of different membrane separation processes are used in water treatment, some of which achieve high removals of these target compounds. An advantage of membrane filtration over oxidation and adsorption is the absolute retention of target solutes. Membrane processes will be discussed in Section 2.2 and the removal of PhACs and EDCs by membranes is discussed further in Section 2.3.

Tertiary treatment methods, which are currently used in only a fraction of North American water treatment plants, have shown more promise in the removal of target solutes. Adsorption via activated carbon, ozonation and other AOPs and tight membrane filtration processes have shown removals between 50 and 95+%.

2.2 Membrane processes

Pressure-driven membrane processes can be valuable in water and wastewater treatment plants. These include microfiltration (MF), ultrafiltration (UF), nanofiltration, and reverse osmosis. Tables 2.4 and 2.5 highlight important applications in municipal water and wastewater treatment and the major operating parameters and characteristics, respectively. It is important to note that the classification of membranes is not absolute and that there is overlap in characteristics and applications between the types.

Table 2.4: Major applications of membrane processes for water and wastewater treatment

Process	Major Applications
Microfiltration (MF)	Clarification Bacteria removal Pre-treatment to NF/RO
Ultrafiltration (UF)	Organics (particulate, microorganism and colloid) removal Bacteria and virus removal Color removal
Nanofiltration (NF)	Water softening Organics (disinfection by-product precursor) removal
Reverse Osmosis (RO)	Desalination (seawater and brackish water) Wastewater reuse/reclamation Ultrapure water production Low concentration organics removal

With the exception of water reuse operations, the implementation of looser (MF, UF) as opposed to tighter (NF, RO) membrane processes has been more popular in North

American water treatment plants since these membranes are geared towards removal of particulates, bacteria and viruses (UF only) and still operate at a low cost (acceptable cost to the consumer). A smaller number of nanofiltration plants have been built and they were primarily designed for the softening of hard groundwater.

Table 2.5: Operating conditions and characteristics of membrane processes used in water and wastewater treatment

Membrane Type		**MF**	**UF**	**NF**	**RO**
Operating P	*MPa*	0.01 - 0.2	0.05 - 0.5	0.5 - 1.5	0.8 - 10
Flux	*LMH*	15 - 180	15 - 85	8.5 - 34	1 - 26
Molecular Weight Cut Off	*kDa*	>200	10 – 500	0.200 – 5	0.05 – 0.2
Pore size	*nm*	30 - 1200	2 - 100	< 2	< 2
Characteristics		Symmetric macroporous	Asymmetric mesoporous	Asymmetric microporous or TFC	Asymmetric dense or TFC
Separation Mode		Straining	Straining	Straining, Δdiffusion or Δsolubility	Δsolubility, Δdiffusion

Compiled from: Strathmann (2005); Aptel and Buckley, (1996); AWWA (2003); USNRMRL (2003); TFC: thin film composite

2.2.1 Separation mechanisms

Membrane filtration is the selective separation of a solution through a semi-permeable material. The products of the separation are a dilute stream (permeate) and a concentrated stream (retentate), as shown in the figure below.

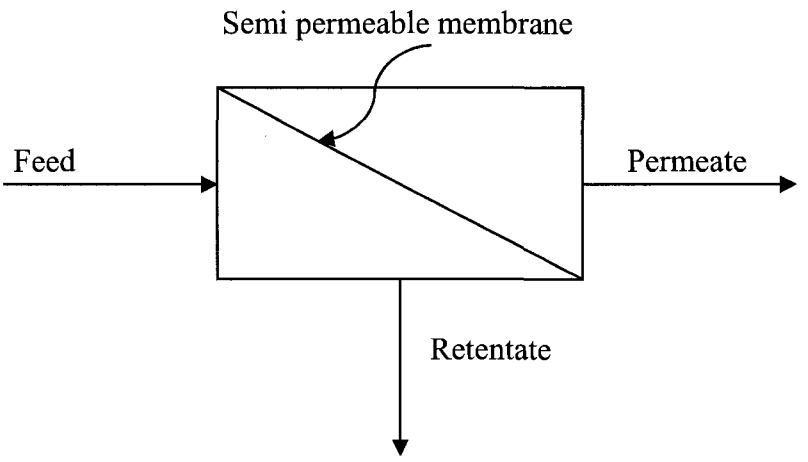


Figure 2.1: Flow diagram of membrane filtration

Pressure driven membranes rely on two principal separation mechanisms, steric exclusion (straining), typical of MF, UF and NF applications, and diffusion/solubility, characteristic of NF and RO membranes. As for properties, there is overlap in terms of the dominant separation mechanism.

2.2.1.1 Steric exclusion

The major separation mechanism of MF and UF membranes is steric exclusion, the absolute retention of compounds based on their size relative to the membrane pore size. Additional mechanisms that may come into play include adsorption and charge repulsion. NF and RO will also evidently reject solutes via size exclusion due to their small pores, however the change in solubility or diffusivity of target solutes also comes into play.

2.2.1.2 Adsorption

Adsorption of solutes onto the membrane is an undesirable removal mechanism, which may lead to concentration of the solute in the permeate stream due to desorption. If the dominant removal mechanism during filtration was adsorption, the membrane would quickly be exhausted, the operational cycles would be shortened and the life could be

considerably reduced. When adsorption is a factor, it is usually noticeable in the beginning of a filtration run, and characterized by high initial removal followed by a constant and lower removal. Charge repulsion, on the other hand, may be beneficial.

2.2.1.3 Charge repulsion

Interactions between the membrane charge and solutes (of the same charge) would ideally improve removals since the retention of the solutes would not rely solely on the relative size (solute and pore). In most cases, UF and MF membranes used for the removal of NOM in drinking water treatment hold slightly negative charges. It is said that NOM also has a negative charge, and therefore the repulsion of this matter by the membrane potentially improves removals and prevents deposition onto the surface.

2.2.2 Microfiltration and ultrafiltration

As previously mentioned (Tables 2.4 and 2.5), MF and UF membranes are used in water treatment for the removal of turbidity causing particulate matter (0.001 – 0.03 μm), color, bacteria and viruses (UF only). Advantages of UF and MF over granular filtration (the competing process) include higher turbidity removal, smaller space requirements, automation and consistent performance since they are independent of feed quality (Crittenden et al., 2005). Disadvantages include lower production rates and greater energy requirements. Due to the advantages of membrane filtration many new plants and plant expansions are incorporating MF and UF, however the majority of North American treatment plants still use deep bed filtration.

In the 1980s, advances in the development of membranes allowed for their introduction into the water treatment market. At this point, significant improvements had been made to membrane materials and filtration operations, rendering this technology economically viable. As well, concerns of microbiological contamination and lower turbidity requirements made MF and UF attractive technologies. Following the Milwaukee cryptosporidium epidemic in 1993, membranes became more popular because they are a more reliable barrier than conventional treatment for protozoa removal and disinfect without using chlorine, which produces harmful disinfection by-products (DBPs). Another advantage of UF over MF is the near complete removal of viruses and somewhat greater NOM removal, further reducing DBP formation. The downfall of the membrane industry is that the lack of regulatory removal requirements associated with one category of membranes has shifted the UF manufacturers to market more porous UF membranes, reducing pressure drop and increasing flux, in order to be more cost-competitive with MF membranes. UF membranes currently have a molecular weight cut off (MWCO) around 100,000 Da and consequently have low NOM removals. Given that the next tighter category of membranes (i.e., NF) are prepared via a different manufacturing method (i.e., thin film composite), tighter commercial and experimental UF membranes have been developed to remove smaller contaminants (Mosqueda-Jimenez et al., 2004a, b).

This section will discuss the characterization, materials and manufacturing methods related to ultrafiltration membranes as well as some key applications.

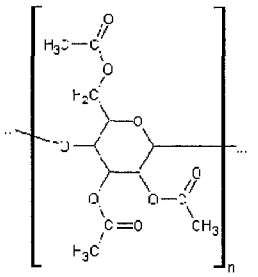
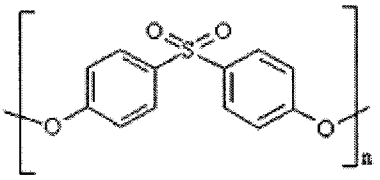
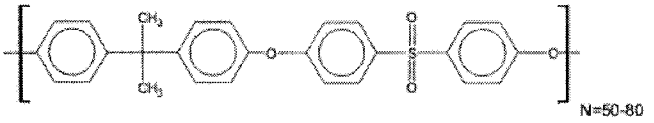
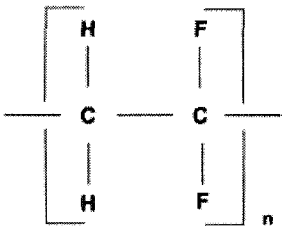
2.2.2.1 Characterization

Membranes may be characterized by their pure water flux (i.e., ideal production rate), retention rating (measured by MWCO), pore size, surface porosity, and pore density as well as material properties such as charge and hydrophobicity. Additional characteristics that should be considered prior to implementation include chemical, mechanical and thermal stability as well as the resistance of the material to disinfectants.

2.2.2.2 Materials and characteristics

Ultrafiltration membranes can be made of various synthetic materials, giving the membranes different properties. The properties of the material used to make the membranes will not necessarily translate to the properties of the membrane. Materials can be inorganic, such as ceramics, or organic (polymeric). Inorganic membranes are typically used in the food or pharmaceutical industry and in industries where their high thermal and chemical resistance is required. Their main disadvantage is that they are brittle. Polymeric membranes, on the other hand, are more widely used, but have lower thermal and chemical stability. Typical polymers used include cellulose acetate (CA), polyamides (PA), polyalcrylonitrile (PAN), polysulfone (PS), poly(ether sulfone), polytetrafluorethylene (PTFE), polyvinylidene fluoride (PVDF), polyethylene (PE), polycarbonate (PC) and isotactic polypropylene (PP). Table 2.6 highlights some important polymers used for water treatment membranes, their characteristics and applications.

Table 2.6: Properties of select polymers used in UF membranes for water treatment

Polymer	Properties	Applications
Cellulose Acetate (CA) 	• T_m =230°C • resistant to oxidants • hydrophillic • sensitive to acid/base, temperature, biological activity	• desalination • softening • disinfection • clarification
Poly(ether sulfone) (PES) 	• T_g = 225 °C (PES), T_g=190°C (PS) • good thermal, chemical and mechanical stability • good pore formation • high adsorption capacity	• UF • Support for TFC
and Polysulfone (PS) 		
Polyvinyldienefluoride (PVDF) 	• T_g = -35 °C • good thermal, chemical and mechanical stability • hydrophobic	• UF

T_g: Glass transition temperature; T_m: Melting temperature

Polymers selected for membranes can either be crystalline or amorphous. The distinction between these parameters is via the glass transition temperature, T_g, or the melting temperature, T_m, of a material. T_m is the point at which the crystalline properties of a material are lost and T_g is the distinction between amorphous or glassy materials, and below which the material becomes very brittle. The glass transition temperature may also

be used to characterize the rigidity of a polymer, such that the larger the T_g, the more rigid. Polymers used to produce UF membranes are more amorphous (as opposed to crystalline) since they allow for ease of development during phase inversion (i.e., tailoring the membrane to have a specific pore size and structure). Polysulfone and poly(ether sulfone) are one of the more popular amorphous polymers to prepare UF membranes (Nunes and Peinemann, 2001) primarily because they can withstand a wide range of pH (both low and high), they resist chlorine concentrations higher than levels in water and wastewater treatment applications, they can form membranes with a wide range of MWCO and pore sizes, and have an acceptable thermal stability (Anselme and Jacobs, 1996).

2.2.2.3 Manufacturing

Membranes may be produced via methods including:

- sintering: powders of a specific size and grade are compressed and heated until they merge to form to a porous structure,
- track etching: a two step process: a beam of ions is directed to the membrane during the tracking phase which breaks the polymeric structure and these holes are then etched to a given size in chemical baths (etching phase),
- stretching: a dense polymeric layer is stretched to enlarge the pores,
- thin film coating: a supporting polymeric layer is coated with a thin membrane film which is then gelated, yielding a thin selective and generally denser layer,
- phase inversion: a polymer/solvent solution is cast to the desired nominal thickness and then immersed in a non-solvent, precipitating the polymer into an asymetric porous structure, and

- thermal inversion: a polymer/solvent solution is cast to the desired nominal thickness and cooled at such a rate that there is a differential cooling rate across the thickness of the membrane, generally forming a skinned membranes.

Polymeric ultrafiltration membranes are typically produced via phase inversion. In phase inversion, a solution of base polymer (the polymer which will become the membrane), a solvent, and possibly one or more additives are cast into a thin 100-300 μm sheet. When the cast solution is immersed into a gelation bath, the relative affinity of the solvent and polymer to the bath solution (non-solvent) will determine the properties and structure of the membrane. The mechanism of diffusion between the solvent and the non-solvent is essentially what forms the membrane. The membrane solution/gelation bath interface polymerizes first, creating a dense polymeric layer (Figure 2.2b). Layers below polymerize slower (Figure 2.2c, d), the rate being a function of the relative diffusion of solvent out and non-solvent in. These (lower) supporting layers contain less polymer and are therefore more porous, creating an asymmetric membrane. Figure 2.2 illustrates the polymerization of the cast membrane film during the gelation process.

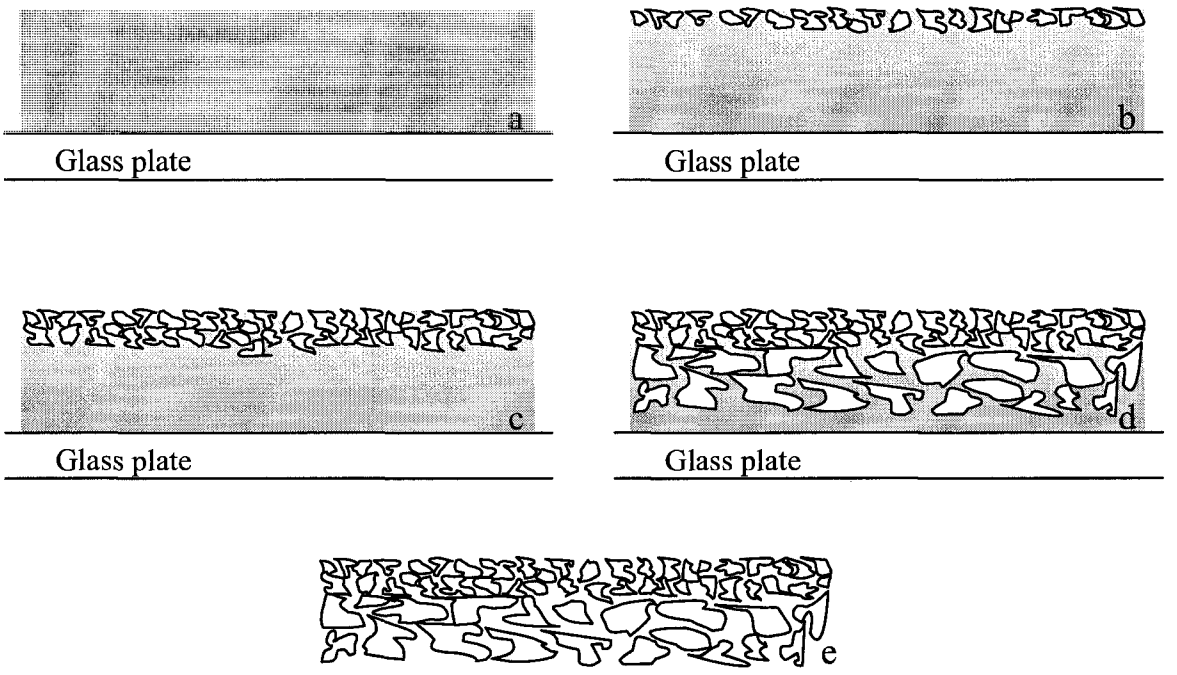


Figure 2.2: Polymerization of cast membrane solution
a) uniformly mixed polymer and solvent solution is cast over a clean glass plate; **b)** as the glass plate and cast polymeric solution are placed in the gelation bath, the polymer at the solution-bath interface polymerizes quickly, **c), d)** as the solvent leaves the polymer/solvent mixture and is replaced by the non-solvent, a more porous structure is formed (there is less polymer), **e)** polymeric membrane separates from the glass plate.

Properties of the solvent, non-solvent, polymer as well as ambient conditions will impact the final membrane characteristics (i.e., asymmetric, pore structure, pore size, etc.).

2.2.3 Membrane surface modification

The modification of membrane surfaces allows for selective tailoring of membranes for a given application. Methods can include:

- Plasma modification
- Reactive ligand deposition
- Reactive gas exposure
- Sulfonation
- Vapour deposition
- Ion beam enhanced deposition
- Ion doping
- Surface modifying macromolecules

A relatively new method of membrane modification is the addition of surface modifying macromolecules into the casting solution, developed by our research group in the 1990s. The advantage of this method is that it is a single-step manufacturing process; other surface modifying procedures require multiple steps.

2.2.3.1 Surface modifying macromolecules

Surface modifying macromolecules are surface-active polymeric additives that can alter the surface properties of a polymeric membrane without altering the property of the supporting material. Pham (1995) and Tang et al. (1996) have discussed at length the theory behind SMM preparation. When SMMs are added to the casting solution, it is expected that during casting, and given a certain pre-gelation time (time before the solution is immersed in the gelation bath), these additives will rise to the solution-air interface. This occurs because the SMMs have a lower surface free energy than the base polymer used. Figure 2.3 illustrates the theorized rise of these additives for a given pre-gelation time.

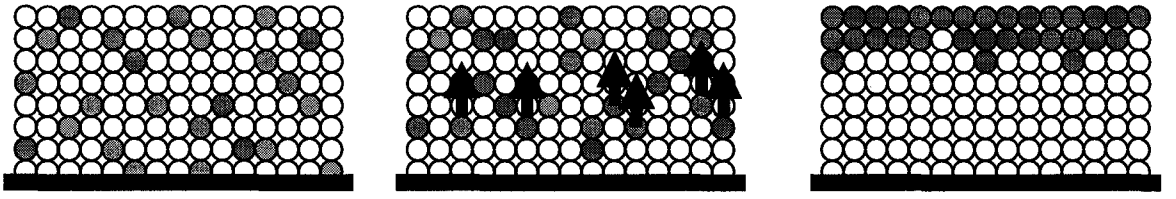


Figure 2.3: Rise of SMMs in cast membrane film before gelation (phase inversion method)
At time **t = 0**, the cast solution is a uniform mix of SMMs (dark circles), polymer and solvent (white circles); after casting (**t > 0**), the SMMs will rise in the solution to the air-solution interface; at **t = ∞**, all the SMMs will have reached the surface. (Adapted from Fang, 1997)

The theoretical structure of SMMs consists of a main body which is capped by end-groups. These end groups are expected to rise to the polymer-air interface giving the membrane new surface properties. Many different hydrophobic SMMs have been created and evaluated using poly(ether sulfone) membranes. Membrane making parameters studied include: polymer and SMM concentrations, pre-gelation time, migration time, drying time, evaporation temperature and kinetics of migration (Suk et al., 2002a, b; Mosqueda-Jimenez et al., 2004a, b, 2006; Nguyen et al., 2007). Recently, more hydrophilic SMMs (LSMMs) have been evaluated (Rana et al., 2005; Nguyen et al., 2007), specifically as additives to hydrophobic materials typically used in water treatment with the aim of improving flux and reducing membrane fouling potential during the filtration of raw drinking water (Nguyen et al., 2007).

2.2.3.2 Application of SMMs

The use of SMMs in pervaporation, membrane distillation, ultrafiltration and the biomedical field has been researched, with varying degrees of success.

The development of pervaporation PES membranes using SMMs has been conducted by Pham (1995), Mahmud (1996), Fang (1997) and Minnery (2000). They found that the modification of PES membranes did not result in better separation of chloroform from water. By varying the evaporation period, Fang (1997) did however find that the addition of SMMs could help change the structure of the membrane. Mahmud et al. (2001) showed that their PES membranes were water selective in the separation of chloroform and water, however the impact of the SMM could not be determined.

Recently, Mosqueda-Jimenez et al. (2004a, b, c, 2006) examined the effect of hydrophobic SMM addition and membrane manufacturing conditions on PES ultrafiltration membrane characteristics and in a drinking water treatment application. They hypothesized that adding the SMM would make the membrane very hydrophobic, like Teflon, and foulants would not stick to it within water treatment applications. They found that while the addition of SMMs decreased the pore size and increased the surface porosity, the migration that occurred did not change the hydrophobicity as quantified by contact angle measurements. The general performance of SMM blended membranes compared to the unmodified membranes was only slightly better, with minor improvements in total organic carbon (TOC) removal likely due to the slight decrease in flux.

The development of LSMMs for drinking water treatment has been examined (Rana et al., 2005; Nguyen et al., 2007) since the use of hydrophobic SMMs was not very successful. Rana et al. (2005) found that with increasing concentrations of LSMMs, the static contact angle of the membrane decreased (by up to 11° for 12% wt LSMM). Nguyen et al. (2007) also showed decrease in contact angle (by up to 8°) but found there was no clear effect of SMM concentration on advancing contact angle. The slight decrease in contact angle was found to beneficially impact the membrane performance (lower flux reduction, stronger membranes, less NOM fouling than control PES membranes). Subsequent tests showed that the best PES-LSMM membrane was not as hydrophobic as many commercial membranes yet performed well (Dang et al., 2006).

The experimental membrane was quite a bit tighter (MWCO ~ 60 kDa) than conventional membranes yet it had a slighter lower normalized flux reduction.

These recent improvements in membrane modification, via LSMM addition, open doors for the development of other applications.

2.3 Review of membrane performance for removal of PhACs and EDCs from drinking water

The performance of commercial membranes for the removal of PhACs and EDCs from drinking water has been evaluated by many.

2.3.1 Commercially available membranes

Over two dozen commercially available membranes have been tested for the removal of PhACs and EDCs from drinking water. A summary of the membranes tested and some of their key characteristics are listed in Table 2.7.

It is important to note that, at this point, only commercially available membrane have been evaluated and that these test membranes have generally been NF and RO, with a select few tests on looser UF and MF membranes. Removals achieved are presented in Table 2.8.

Table 2.7: Characteristics of commercial membranes tested for the removal of PhACs and EDCs from drinking water

Membrane (Manufacturer)	MWCO (Da)	Material	Contact Angle	Reference
Tight ultrafiltration				
GM (Desal/Osmonics)	8000 ± 1000	PA on sulfonated PES TFC	46±2.1[1,2], 58[3]	1, 2, 3
PES 10k (Milipore)	10000	PES	-	3
PES 5k (Milipore)	5000	PES	-	3
PW (Desal)	10000	PES	66	3
Nanofiltration				
ESNA (Hydranautics)	600 ± 200	Aromatic PA TFC	57±1.8	1, 2
NE 1812-70 (Saehan)		PA on PS support		9
NE 4040-90 (Saehan)		PA on PS support		9
NF-200 (Dow/Filmtec)	300	PA TFC	30.3	7, 8
NF-270 (Dow/Filmtec)		Semi-Aromatic Piperazine based PA on PS support		4, 5, 6
NF-90 (Dow/Filmtec)	200	Semi-Aromatic Piperazine based PA on PS support	63.2	4, 5, 7, 6, 8
RF (Saehan)	200 ~ 500	PA TFC	43	3
TFC-S (Koch)	200	PA on PS support	30-45	10, 8, 11, 12
TFC-SR2 (Koch)	400	PA on PS support	55.3[7], 10-20[15]	7, 10, 8, 11, 12, 15
Nanofiltration/Reverse osmosis				
TFC-SR1 (Koch)		PA on PS support	10-20	10, 11, 12
TFC-ULP (Koch)		PA on PS support	30-45	10, 11, 12
Ultra low pressure reverse osmosis (ULPRO)				
XLE (Dow/Filmtec)	100[7, 8], <200[13]	PA TFC	66.3	7, 13, 8
Reverse osmosis				
CTA (Koch)	100	CTA		8
ACM-4 (Trisep)		PA-urea TFC	30-45	10, 11, 12
D2731 (Barnstead)		CA (low pressure)		14
Re 4040-BLN (Dow/Filmtec)		PA on PS support		9
SC-3100 (Toray)	200-300	CA (low pressure)		13
TFC-HR (Koch)	100	PA TFC	35	7, 8
TS-80 (Trisep)		PA-urea TFC	30-45	10, 11, 12
X-20 (Trisep)		PA-urea TFC	30-45	10, 11, 12
XN-40 (Trisep)		PA-urea TFC	30-45	10, 11, 12

References: [1] (Yoon et al., 2006), [2](Yoon et al., 2004), [3] (Park and Cho, 2005), [4] (Nghiem et al., 2005a), [5] (Nghiem et al., (2005b), [6](Nghiem et al 2004b), [7](Xu et al., 2005), [8](Drewes et al., 2005), [9] (Shah et al., 2005), [10](Nghiem et al., 2004a), [11](Nghiem et al., 2002a), [12](Nghiem et al 2002b), [13](Kimura et al., 2004), [14](Adams et al., 2002) and [15](Nghiem et al., 2002c)

Abbreviations: PA: Polyamide, PES: Poly(ether sulfone), TFC: Thin Film Composite, CA: Cellulose Acetate, PS: Polysulfone, CTA: Cellulose Triacetate.

Table 2.8: Reported removals and adsorption of PhACs and EDCs on commercial membranes

Membrane	Target Solutes	Retention	Adsorption	Scale	Ref
Tight ultrafiltration					
GM (SC)	Group 1	**<40%** except triclosan (87%), oxybenzone (77%), progesterone (56%);	>50% solute recovery (14 of 25 solutes)	B	1
GM (SC)	17β-Estradiol, Fluoranthene	**95%+** in absence of NOM (fluoranthene). Without NOM, removal decreases for 17β-estradiol (60-90% to 10-20%)	Fluoranthene: 15 to 25%; not adsorbed in presence of NOM	B	2
GM (XF)	Ibuprofen	**~98-99%** (no NOM) (electrostatic repulsion)			3
Nanofiltration					
NF-270 (XF, PF)	BPA, NP, Tertbutylphenol	**~45%** BPA , **~50%** tertbutylphenol (NOM/DI water); **~55%** BPA , **~65%** tertbutylphenol (NOM/NaCl/DI); At pH = 11, **>90%** BPA (above results are at pH = 6)	NP strongly adsorbs	B	4
NF-270 (XF, PF)	Sulfamethoxazole, CBZ, IB	**~96%, ~84%** and **~99%,** respectively	No adsorption	B	5
NF-270 (XF)	Estradiol, Estrone, Testosterone, Progesterone	Initially 100% (due to adsorption); decreases until equilibrium is achieved	Initially contributes to removal		6
NF-200 (SW)	Group 3	**>89%**; For negatively charged solutes, **93.5% ± 2.3%** (DI water), **97.7 ± 1.0%** (EfOM)	Adsorption clogs pores and enhances steric and charge exclusion	P	7
NF-200 (FS, SW)	Group 5	**>89%** for ionic pharmaceutical residues and pesticides			8
NF-90 (XF, PF)	BPA, NP, and Tertbutylphenol	**>90%** BPA and tertbutylphenol (NOM/DI water)	NP strongly adsorbs	B	4
NF-90 (XF, PF)	Sulfamethoxazole, CBZ, IB	**100%, 96%** and **100%,** respectively	No adsorption	B	5
NF-90 (SW)	Group 3	**>95%**; For negatively charged solutes, **97.1 ± 1.4%** (DI water), **99.3 ± 0.3%** (EfOM)	Adsorption clogs pores and enhances steric and charge exclusion	P	7
NF-90 (XF)	Estradiol, Estrone, Testosterone, Progesterone	Initially 100% (due to adsorption); decreases until equilibrium is achieved	Initially contributes to removal		6
NF-90 (FS, SW)	Group 5	**>95%** for ionic pharmaceutical residues and pesticides			8

Membrane	Target Solutes	Retention	Adsorption	Scale	Ref
ESNA (SC)	Group 1	**44-93%** except naproxen (not removed)	100% solute recovery for 8 of 25; solutes with $\log K_{OW}$>2.8 <40% solute recovery (except GEM and IB)	B	1
ESNA (SC)	17β-Estradiol, Fluoranthene	Increase from **15** and **77%** (DI water) to **70** and **95%** (with NOM) (17β-estradiol, fluoranthene, respectively)	Fluoranthene 10 - 20%; not adsorbed in presence of NOM	B	2
RF (XF)	Ibuprofen	**>90%**			3
TFC-S (XF, SC)	Estrone, Estradiol	**~78%** and **~82%**, respectively		B	10
TFC-S (SC)	Estrone	**98.7%**			12
TFC-SR2 (SW)	Group 3	**41.2 ± 15.6%** (DI water), **32.6 ± 23.1%** (EfOM); For diclofenac, increased by 11.5% with EfOM	Adsorption clogs pores and enhances steric and charge exclusion	P	7
TFC-SR2 (XF, SC)	Estrone, Estradiol	**13%** at equilibrium (estrone)	Retention decreases as adsorption decreases	B	10
TFC-SR2 (XFSC)	Estrone	Initially high (adsorption); decreases to about **55%**	Initially high (45%), decreases to ~10%	B	11
TFC-SR2 (SC)	Estrone	**97.6%**			12
Nanofiltration/Reverse osmosis					
TFC-ULP (XF, SC)	Estrone	**~90%**; not affected by diffusion	Retention decreases as adsorption decreases	B	10
ACM-4 (SC)	Estrone	**99.1%**			12
ACM-4 (XF, SC)	Estrone	**~90%**; not affected by diffusion			10
TFC-SR1 (SC)	Estrone	**98.3%**			12
TFC-SR1 (XF, SC)	Estrone, Estradiol	**34%** at equilibrium (estrone)	Retention function of adsorption	B	10
TFC-ULP (SC)	Estrone	**98.7%**			12
TS-80 (SC)	Estrone	**98.8%**			12
TS-80 (XF, SC)	Estrone	**~90%**; not affected by diffusion		B	10
XN-40 (SC)	Estrone	**81.6%**			12
XN-40 (XF, SC)	Estrone, Estradiol	**43%** at equilibrium (estrone)	Retention decreases as adsorption decreases	B	10

Membrane	Target Solutes	Retention	Adsorption	Scale	Ref
Ultra low pressure reverse osmosis					
XLE [(SW)]	Group 3	**> 95%**; For negatively charged compounds, **93.5% ±1.0%** (DI water), **97.2 ±0.6%** (EfOM)	Adsorption clogs pores and enhances steric and charge exclusion	P	7
XLE [(FS)]	Group 4	**57-91%**, Dominant mechanism is size exclusion, solutes with high dipole moment are poorly rejected		B	13
XLE [(FS, SW)]	Group 5	**>95%**			8
Reverse Osmosis					
CTA [(FS, SW)]	Group 5	Fouling led to high concentrations in permeate			8
D2731	Antibiotics	**90.2%** (DD water), **90.3%** (MRW);		P?	14
SC-3100 [(XF)]	Group 4	**0-85%**, Dominant mechanism is size exclusion, rejection function of polarity		B	13
TFC-HR [(SW)]	Group 3	**> 95%**; For negatively charged compounds, **95.8% ± 2.8%** (DI water), **98.6 ± 0.5%** (EfOM)	Adsorption clogs pores and enhances steric and charge exclusion	P	7
TCF-HR [(FS, SW)]	Group 5	**> 95%**			8
X-20 [(XF, SC)]	Estrone	**~95%** (natural water), **~88%** (secondary effluent), **~85%** (electrolyte); not affected by diffusion		B	10
X-20 [(XFSC)]	Estrone	Dominant mechanism is size exclusion (diffusion)	No breakthrough	B	11
X-20 [(SC)]	Estrone	**98.8%**			12

References: [1](Yoon et al., 2006), [2](Yoon et al., 2004), [3](Park and Cho, 2005), [4](Nghiem et al., 2005a), 5 (Nghiem et al., 2005b), [6](Nghiem et al 2004b), [7](Xu et al., 2005), [8](Drewes et al., 2005), [10](Nghiem et al., 2004a), [11](Nghiem et al., 2002a), [12](Nghiem et al 2002b), [13](Kimura et al., 2004) and [14](Adams et al., 2002);
Abbreviations: SC: Dead-End Stirred cell, XF: Cross-Flow, PF: Plate and Frame, FS: Flat sheet bench scale, XFSC: cross-flow stirred cell, P: Pilot scale, B: Bench scale, DI: Deionized water, EfOM: Effluent organic matter, NP: Nonylphenol
Antibiotics: Carbadox, Sulfachlorpyridazine, Sulfadimethoxine, Sulfamerazine, Sulfamethazine, Sulfathiazole, Trimethoprim;
Group 1: GEM, Triclosan, Estradiol, IB, Progesterone, Oxybenzone, Ethynylestradiol, Testosterone, Naproxen, Estrone, Erythromycin-H_2O, Diazepam, Androstenedione, Atrazine, Diantin, CBZ, Estriol, DEET, TCEP, Trimethoprim, Sulfamethoxazole, Diclofenac, Meprobamate, Acetaminophen, Pentoxfylline, Caffeine, Iopromide;
Group 3: IB, Diclofenac, Ketoprofen, Naproxen, GEM, Mecoprop, Primidone, Bromoform, Chloroform;
Group 4: 2-Naphthol, 4-Phenylphenol, Pheancetine, Caffeine, NAC standard, Primidone, BPA, Isopropylantipyrine, CBZ, Sulfamethoxazole, 17β-Estradiol;
Group 5: *Hydrophilic ionic:* IB, Diclofenac, Ketoprofen, Naproxen, GEM, Mecoprop, Propyphenazone, Dichloprop, 2,4 dihdroxybenzoic acid, 2-Naphthalenesulfonic acid, 1,5-Naphthalenedisulfonic acid, glutaric acid, acetic acid; *Hydrophilic non-ionic:* Primidone, Phenacetine, Caffeine, Tris(2-chloroethyl)-phosphate, Tris(2-Chloroisopropyl)-phosphate, sucrose, glucose, urea; *Hydrophobic non-ionic:* Bromoform, Chloroform, Trichloroethyelene, 17β-Estradiol, Estriol, Testosterone, 2-Naphthol, CBZ, Napthalene;

The role of membrane, solute and water matrix characteristics in removing these solutes is presented in the following section. Additionally, general trends seen from the results compiled in Table 2.8 as well as more detailed results will be discussed in the following subsections.

2.3.2 Effect of solute and water matrix characteristics in removal

From the results presented above, it is obvious that no one membrane is capable of removing all target solutes. Solute and water matrix effects will impact the removal and removal mechanisms during membrane filtration.

2.3.2.1 Effect of solute properties on removal mechanisms

PhACs and EDCs are terms used to identify a wide range of compounds with generally low molecular weight. The variability in structures and properties of these compounds makes it difficult to generally predict their removal during any operation. A key property found to influence removals in membrane filtration is the octanol-water partition coefficient (log K_{OW}): the affinity of a compound to the water or organic phase. It has been shown that compounds with higher log K_{OW}, such as estrogens and EDCs, have a higher tendency to adsorb to membranes. Additionally, the hydrophobicity of estrogens and EDCs lends to interactions with NOM present in source water, which is also generally hydrophobic (see Section 2.3.2.2). The charge of a target solute may also influence removals, especially if the membrane is similarly charged.

2.3.2.1.1 Adsorption

Adsorption of these compounds onto the membrane generally occurs at the beginning of filtration (Nghiem et al., 2005a, 2004a, b; Yoon et al., 2004; Nghiem and Schafer, 2002)

yielding false retention results. It is generally irreversible (Nghiem and Schafer, 2002). This removal mechanism is quick and is not the major removal mechanism in the process (Nghiem et al., 2004b). Adsorption onto the surface can lead to cake formation, decreasing the pore size and thereby increasing the removal (Xu et al., 2005; Yoon et al., 2004; Nghiem et al., 2004a; Park and Cho, 2005). The fouling cake layer can also have adverse effects, helping in the transport of compounds across the membrane and thereby decreasing rejection (Drewes et al., 2005). This is expected since once compounds adsorb to pore walls or the pore surface, they can essentially be "carried" through the pores by the force of the permeating solution. Nghiem and Schafer (2002) and Nghiem et al. (2002c) carried out batch tests on membranes to characterize the adsorption process. Their experiments yielded distinct breakthrough curves typical of adsorption.

2.3.2.1.2 Charge repulsion

The charge of a given solute is largely function of the solution pH and the solutes' dissociation constant (pK). If a given solute holds the same charge as the membrane surface, the surface and solute will repel each other. This means that the separation will not necessarily rely on the relative size of the solute and pore for removal. Charge repulsion has been shown to be the dominant removal mechanism for some PhACs and EDCs. Nghiem et al. (2005b) found that, at a pH of 8, ibuprofen (MW: 206.3 g/mol, pK_{a1} = 4.4 to 5.2) and sulfamethoxazole (MW: 253.3 g/mol, pK_{a1} = 1.7 to 2.1, pK_{a2} = 5.6 to 5.7) were rejected at higher rates than carbamazepine (MW: 236.3 g/mol, pK_{a1}: 2 to 2.45). They found the dominant removal mechanism for the first two compounds was charge repulsion, and that carbamazepine was removed solely due to size exclusion since it was neutrally charged at the given pH. Drewes et al. (2005) state that by changing the

pH of a solution to exceed the pK of a solute, the charge of a target compound can be changed to enhance rejection

2.3.2.2 Effect of water matrix

As mentioned above, both the natural organic matter and pH of source water can influence removals. In drinking water treatment, NOM has generally been found to enhance the removals of EDCs, especially during the sedimentation step (Bowman et al., 2002). This is attributed to the hydrophobicity (high log K_{OW}) of both EDCs and NOM, which allows them to bind together and settle during flocculation/sedimentation. Favourable and unfavourable effects of NOM have also been shown in membrane filtration (Nghiem et al., 2004a).

During filtration, NOM naturally forms a foulant layer on the surface of the membrane. This layer is beneficial to the removal of EDCs since it decreases the pore size (Xu et al., 2005; Yoon et al., 2004; Nghiem et al., 2004a). During the fouling process, NOM may also adsorb to the membrane surface along with EDCs or foul alone and act as a sorbent to EDCs. Conversely, Drewes et al. (2005) showed that NOM hindered the rejection of target solutes (i.e., estrogens (Nghiem et al., 2004a)) by enhancing their transport through the membrane. In addition, the accumulation of a foulant layer on a membrane may alter the charges experienced by solute molecules as they approach the membrane surface.

2.3.2.3 Effects of membrane properties

From the review of recent research, it is clear that no one membrane is capable of removing all of the target solutes. Solute, water matrix and membrane properties govern the removal of the target compounds.

2.3.2.3.1 Membrane classifications

As discussed in Section 2.2, there are four different membrane types based on pore size: microfiltration, ultrafiltration, nanofiltration and reverse osmosis, ranked in decreasing pore size. As the membrane pore size decreases the necessary operating pressure increases and the flux decreases, which increase the system capital and operating costs. Market competition in drinking water treatment means that loose UF membranes compete with MF membranes; tight UF membranes are designed to compete with NF membranes whereas NF membranes try to compete with RO membranes. Due to the size of PhACs and EDCs, it is not expected MF and UF membranes can remove them. Removals using NF and/or RO membranes range from 0 to 95+% (Table 2.8).

In a study comparing a tight UF membrane (**GM**: MWCO 8000 Da, sulfonated PES) to an NF membrane (**ESNA**: MWCO 600 Da, aromatic PA), Yoon et al. (2004) showed that in the absence of NOM, greater than 95% 17β-estradiol and fluoranthene was removed by both membranes. Note that the molecular weights of both of these compounds are significantly smaller (i.e., 272.39 g/mol and 202.26 g/mol, respectively) than the membrane MWCOs meaning that mechanisms other than size exclusion dominated. Yoon et al. (2006) used the same membranes to remove various pharmaceuticals and PCPs. Both membranes achieved greater removals of PCPs than pharmaceuticals, and

removal rates were similar for both membranes (for pharmaceuticals <40% (GM) and 4 to 44% (ESNA)). If the membrane pore size played a significant role, ESNA would have performed better than GM. This was not the case, and thus the membrane material properties are more likely influential in removal.

As expected, tighter membranes lead to higher target contaminant removal; reverse osmosis systems, which have membrane MWCOs in the same range as the size of EDCs and PhACs, remove many of these emerging contaminants to non-detectable levels. Nanofiltration membranes, given their larger pore sizes, are not quite as effective but achieve higher than expected removals.

2.3.2.3.2 Membrane materials

The primary materials of the commercial tight-UF, NF and RO membranes listed in Table 2.7 were polyamide (PA), cellulose acetate (CA) and polysulfone (PS). Additionally, in the case of TFC membranes, the supporting materials generally consist of PS or PES. PA membranes have shown high removal rates for hormone mimicking compounds (Xu et al., 2005) with size exclusion as the primary removal mechanism (Kimura et al., 2004). Charge repulsion is the primary removal mechanism for the removal of pesticides and other micropollutants using CA (Yoon et al., 2004). To date, no research has involved the development and synthesis of a membrane designed specifically for this application.

Currently, no one commercial membrane has proven effective to remove all PhACs and EDCs. Membrane tailoring may prove to be more effective in the development of a solution for the removal of PhACs and EDCs from drinking water.

2.4 Summary, objective and hypothesis

The widespread occurrence of PhACs and EDCs in the aquatic environment is primarily due to wastewater effluents. Reported effects to aquatic biota are increasing and not favourable, however little is know as to the potential effects of these low-level contaminants to humans. The detection of PhACs and EDCs in finished drinking water demonstrates that most existing treatment plants do not effectively remove these compounds.

Studies have shown that conventional treatment, consisting of coagulation/flocculation/sedimentation, deep bed filtration and chlorine disinfection achieve little or no removal of target solutes. More advanced processes such as adsorption, oxidation and membrane filtration have shown more promising (yet variable) results. Although advanced technologies may, alone or in combination, achieve desired removals, North American treatment facilities are typically not equipped with them. Additionally, it has been found that removals achieved are compound and process specific and are also function of the source water matrix.

In general, NF and RO membranes appeared to remove many solutes while looser membranes such as loose-NF and UF were not as effective. This is expected since PhACs and EDCs are small, typically ranging in size from 200 to 400 Da (120 to 850 Da). The

characteristics of the source water, namely the presence of NOM, and the solute and membrane characteristics play key roles in the removals achieved.

The objective of this thesis is to develop charged poly(ethersulfone)-based ultrafiltration membranes via the addition of surface modifying macromolecules. By modifying the membrane surface without compromising flux, these membranes would be tailored for the removal of pharmaceutically active compounds and endocrine disrupting compounds during drinking water treatment while remaining economically viable for North American treatment facilities.

It is hypothesised charged SMMs (CSMM) incorporated into PES based membranes would migrate to the surface thus creating a charged surface. The membrane charge would then aid in the removal of target PhACs and EDCs by repelling the solutes (charge repulsion) without compromising flux. Allowing a pre-gelation time during which the CSMMs may migrate to the surface is presumed to create a greater surface modification. It is expected that membranes prepared without pre-gelation time, but with varying polymer quantities exhibit similar trends when incorporating the same CSMM. Increasing the concentration of base polymer (PES) is presumed to create a denser (less porous) membrane but also presumed to inhibit the migration of the CSMMs due to the increased quantity of polymer.

CHAPTER 3

MATERIALS AND METHODS

3.1 Overview

The overall objective of this thesis was to develop and evaluate a number of different experimental ultrafiltration membranes for the removal of PhACs and EDCs. The approach followed was to manufacture tight poly(ether sulfone) ultrafiltration membranes incorporating tailor-made charged surface modifying additives so as to create charged membranes. These membranes may therefore be able to remove the target compounds through charge repulsion or other mechanisms. This research project was carried out in two stages. In the preparatory stage, the membrane filtration system was modified from a serial configuration to a parallel configuration and all plastic components were replaced with stainless steel. Analytical methods were also established. In the testing stage, membranes were prepared, characterized and tested for the removal of target compounds at mg/L levels in ultrapure lab grade (MQ) water.

3.2 Chemicals and reagents

Novel membranes were prepared using poly(ether sulfone) (PES) (Victrex 4100P, ICI Advanced Materials, Billingham, UK, MW ~17-19 kDa) as the base polymer, 1-methyl-2-pyrrolidone (NMP) (+99.5%, Fluka, VWR) as the solvent and different tailor-made additives. CSMMs, listed below (Table 3.1), were synthesized in-house by Dr. Dipak Rana. The procedure followed in the preparation of the CSMMs has been modified from that outlined by Rana et al. (2006) in that charged hydrobenzene sulfonate (HBS) and naphthol disulfonate (NDS) groups were end-capped onto the di-ethyleneglycol (DEG),

poly(ethylene glycol) (PEG) or poly(propylene glycol) (PPG) mid-segments to produce charged polymers. A detailed description of the synthesis procedure, as well as the procedure to determine glass transition temperature (from Dr. Rana) is presented in Appendix A. The expected structures of these CSMMs are also presented in Appendix A. It is expected that, based on the glass transition temperatures, the CSMMs are increasingly rigid following: CSMM-NDS>CSMM-PEG_{200}>CSMM-PEG_{400}>CSMM-PPG. A major hypothesis posed regarding rigidity is that the more rigid the CSMM, the less it will be able to migrate. This is proposed because a more rigid, and therefore less mobile molecule, will have difficulty (or take longer) rising to the surface, especially at higher PES concentrations, where the solution viscosity is increased.

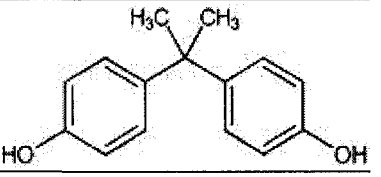
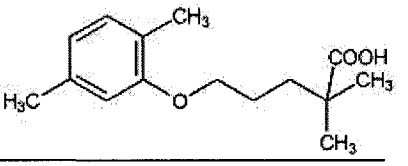
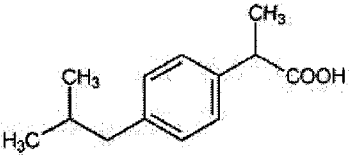
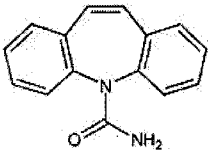
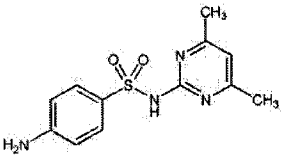
Table 3.1: Properties and molecular formula of CSMMs

ID	SMM structure	MW of mid-segment (Da)	T_g (°C)
CSMM-NDS	MDI-DEG-NBS		> 280
CSMM-PEG_{200}	MDI-PEG_{200}-HBS	200	68.50
CSMM-PEG_{400}	MDI-PEG_{400}-HBS	400	13.44
CSMM-PPG	MDI-PPG-HBS	425	-11.56

MDI: Methyl-diisocyanate, T_g: Glass transition temperature

Four pharmaceuticals, sulfamethazine (SMZ) (+99%), carbamazepine (CBZ), gemfibrozil (GEM) and ibuprofen (IB) (98%) (Sigma-Aldrich, St.Louis, MO) and one endocrine disrupting compound, bisphenol A (BPA) (+99%) (Sigma-Aldrich, St.Louis, MO) were selected as representative PhACs and EDCs for the screening phase. Table 3.2 lists their properties. They were selected based on their occurrence in Ontario (Tabe, 2006) and the fact that they represent a wide range of properties, especially covering the range of octanol water (log K_{OW}) partition coefficients of PhACs and EDCs.

Table 3.2: Properties of selected target solutes

Compound (ID)	MW g/mol	log Kow	pK	Solubility mg/L	Structure
Bisphenol A (BPA)	228.29	3.32; 3.40[a]	n/a	120-300[a]	
Gemfibrozil (GEM)	250.33	4.39; 4.77	4.7 - 4.8	n/a	
Ibuprofen (IB)	206.28	3.14 - 4.5	4.4 - 4.9; 5.2	49; Relatively insoluble in water[a]	
Carbamazepine (CBZ)	236.27	2.18 - 2.93	<2 - 2.45; 7	17.7, 18; Practically insoluble in water[a]	
Sulfamethazine (SMZ)	278.33	0.28	7.4 ±0.2; 2.65 ±0.2	430; 1500 (29°C)[a]; 1920 (37°C)[a]; increases w/ pH[a]	

pK: dissociation concstant, [a] Merck index. Solute properties were compiled from an extensive literature review

For the molecular weight cut off determination, sucrose, various sizes of poly(ethylene glycol) and poly(ethylene oxide) (PEO) were used as the test solutes, as shown in the following table (Table 3.3). The range of MW covered, from 300 Da to 100 kDa, was selected in order to achieve a high removal distribution to make MWCO and pore characteristic predictions more accurate. The solutes included some with molecular weights lower than normally used in characterizing UF membranes; they were included because the objective of the study was to prepare tight UF membranes that could possibly

remove the target compounds via size exclusion and their molecular weights are below 300 g/mol.

Table 3.3: Average molecular size (Da), purity and source of MWCO solutes

Compound (ID)	Average Size	Size Range	Source
Sucrose	342	99.9% purity	Aldrich
Poly(ethylene glycol) (PEG)	400	380-420	BDH
	1,000	950-1,050	Aldrich
	1,500		BDH
	4,000		BDH
	6,000		Fisher
	8,000	7,000-9,000	BDH
	14,000		Aldrich
	35,000		Fluka
Poly(ethylene oxide) (PEO)	100,000		Aldrich

Hydrochloric acid (0.0001 M) and silver wire (+99.9%) (Ø 1.5 mm, Aldrich, St. Louis, MO) were used to make the electrodes for streaming potential measurements. Potassium hydroxide and hydrochloric acid were used to adjust the pH during the streaming potential measurements. Potassium chloride (+99%, Sigma-Aldrich, St.Louis, MO) was used to make the electrolyte solution for streaming potential tests.

Reagents for the low temperature TOC Analyzer were made using sodium persulfate (+98%, Alfa Aesar, Ward Hill, MA) and 85% *o*-phosphoric acid (Fisher Scientific), which was also used for the high temperature TOC Analyzer. Unless otherwise specified all solutions, test waters and standards were prepared using distilled water purified by a Milli-Q Water System (CDOFO1205, Milipore, Bedford, MA), denoted as MQ water. The Milli-Q Water System purification process consists of a synthetic activated carbon

cartridge, followed by a mixed bed ion exchange resin cartridge, an organic scavenger (ion exchange) cartridge, and a membrane filter capsule. Due to water flow problems, and increasing system pressure, the original membrane filter was replaced by a larger capsule filter (CCS-020-C1B, Advantec, AMD Manufacturing, Inc., Mississauga, ON), doubling the membrane surface area and thereby decreasing the system pressure and increasing production rates. The feed to this system was distilled water.

3.3 Preparatory stage

3.3.1 System modifications

The original experimental set-up consisted of three 316 stainless steel (316-SS) ultrafiltration cells in series, as shown in Figure 3.1. The cross-flow UF cells were manufactured in-house (Department of Mechanical Engineering Machine Shop and the Department of Chemical Engineering Machine Shop, University of Ottawa) according to designs described in the literature (Sourirajan and Matsuura, 1985). A 20 L polyethylene carboy (Nalgene) was used as a feed tank and Nalgene (polyethylene) tubing was used for the feed, permeate and retentate lines. A diaphragm pump (Hydracell Model M-03, Wanner Engineering, Inc., Minneapolis, MN) was employed to pump the feed solution at 1.1 L/min and 50 psi, as monitored by a rotameter (GF-5341-2516, Gilmont Instruments) and pressure gauges (Cole Parmer). The flow and pressure were adjusted by recycling part of the feed directly back into the feed tank and by a back-pressure valve located after the UF cells. The system was designed to run in recycle mode, with both retentate and permeate returning to the feed tank.

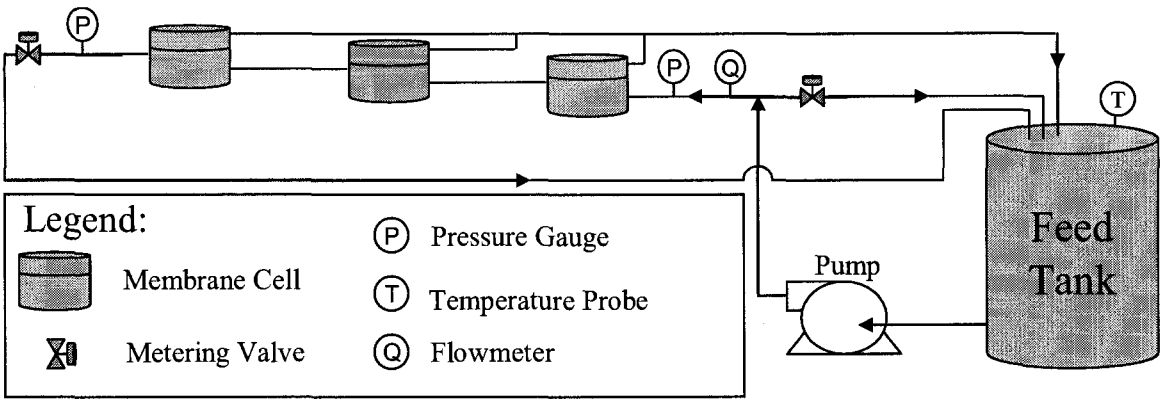


Figure 3.1: Original lab-scale membrane filtration set-up

Due to the nature of the target compounds, and the anticipated working concentration range, concern was raised with regards to loss onto the apparatus via adsorption. Adsorption onto the apparatus was expected and if unmonitored, could have lead to false performance results of the test membranes. In order to minimize adsorption of these organic compounds, it was decided that the system be refurbished using stainless steel and the feed tank be replaced by a 10 L glass carboy. Additionally, 48 hour single-solute adsorption tests were carried out on the system to establish a baseline.

The existing three-cell ultrafiltration apparatus was configured in series. Although this configuration is used within the research group (Mosqueda-Jimenez (2003), Nguyen (2005)), there were concerns that the feed concentration to each cell may vary too much (high removals would lead to progressively higher feed concentrations from the first to the sixth cell). A parallel configuration would allow for a consistent feed concentration (the same for each cell) and for stage cuts to be established. Additionally three cells were to be added to the filtration apparatus in order to screen more membranes per run. Figure 3.2 illustrates the design of the refurbished parallel system.

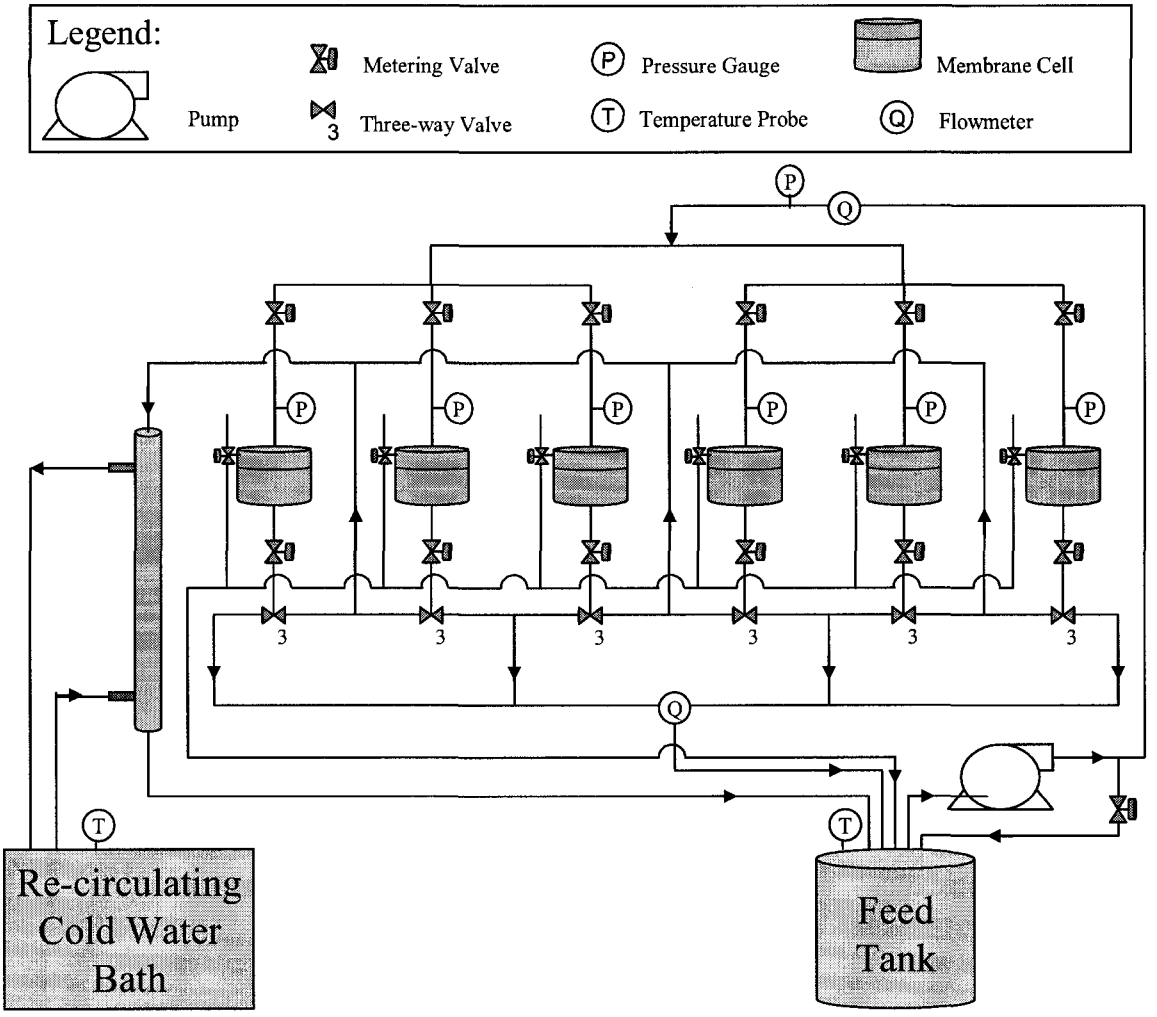


Figure 3.2: Parallel lab-scale membrane filtration system (experimental set-up)

The design of the system illustrated in Figure 3.2 was based on a cost and feasibility analysis of various options (Appendix B). As illustrated in Figure 3.2, the feed from a 10L borosilicate glass carboy (Pyrex) is partly recycled via a metering valve to help adjust the flow and pressure. Next, the line is split into two headers which each feed three UF cells. These two headers were implemented to minimize head loss along the header and ensure a more similar pressure and flow through each cell. The two headers are approximately 30 cm from the main header. The header outlet lines (feeding the membrane cells) are approximately 10 cm apart.

Metering valves (Swagelok: SS-6L and SS-4L, Ottawa Fluid System Technologies, Ottawa, ON) placed before and after each cell were used to control pressure, monitored by pressure gauges (Swagelok: PGI-63C-PG300-LBG1, Ottawa Fluid System Technologies, Ottawa, ON) before each cell. Flow was monitored via one common rotameter (GF-8341-2516, Gilmont Instruments (Barnant Company), Barrington, IL). Although both valves impacted pressure and flow, the feed-side valve primarily controlled the flowrate through the cell and the pressure was mainly controlled using the retentate-side valve (this set the back-pressure). Three-way valves (Swagelok: SS-43GXS4, Ottawa Fluid System Technologies, Ottawa, ON) (denoted by the number 3 in Figure 3.2) were used on the retentate side of the cells to recycle the retentate back to the feed tank (through the heat exchanger) or to measure the flowrate through the common rotameter (when flow measurements were taken). The system included a common rotameter for all the cells to reduce costs and avoid measurement errors (that may have arisen from using multiple rotameters). The lines to the rotameter were designed to minimize head loss and flow restrictions (Westgate, 2008). Three-way valves (Swagelok: SS-41GXS2, Ottawa Fluid System Technologies, Ottawa, ON) on the permeate lines (not shown in Figure 3.2 to avoid overcrowding the diagram) enabled sampling or recycling back to the feed tank. All the parts used in the construction of the filtration system were made of 316-SS with the exception of the inner casing of the rotameter and the feed tank, both made from borosilicate glass, the pump diaphragm made from polypropylene and the membrane cell O-rings, which were wrapped in Teflon tape. Tubing on the feed side of the cells and through the heat exchanger to the feed tank was 3/8". On the retentate side, tubing was reduced to 1/4" to minimize costs; permeate lines were 1/8" The system

was primed using approximately 0.75 meters of head (water) or using a vacuum pump (Little Giant (model # 13154), Gelman Instrument Company, Ann Arbour, Michigan).

During a trial run of the parallel system, it was noted that the temperature of the feed tank increased significantly – approximately 9°C in 24 hours (see Section 4.1.2). To minimize this temperature variation, a shell and tube heat exchanger was built using 3/8'' stainless steel tubing encased in a 2.5'' stainless steel tube and incorporated into the system (as shown in Figure 3.2). A circulating refrigerated water bath (Haake G/D1, Haake, Berlin, Germany) was used to circulate cold water counter-currently in the shell side of the heat exchanger. The cold water bath was maintained at approximately 15°C in order to maintain a constant feed temperature (21 ± 1°C).

3.3.2 Analytical methods

3.3.2.1 Instruments

Due to the lack of access to analytical equipment to measure the concentration of mixtures of PhACs and EDCs at ng/L or µg/L levels, the experimental approach was to evaluate the membranes by conducting a series of tests using mg/L levels of individual PhACs and EDCs. The target solutes could then be individually analyzed using a TOC Analyzer.

Two TOC Analyzers were used to analyze organic compound concentrations; a high temperature TOC Analyzer (Phoenix 9000, Teledyne-Tekmar, Cincinnati, OH) for molecular weight cut off samples (containing PEG, PEO or sucrose at concentrations ranging from 1 to 200 mg Carbon/L (mg C/L)) and a low temperature TOC Analyzer

(Phoenix 8000, Tekmar-Dorhman, Cincinnati, OH) for target solute samples (containing SMZ, CBZ, GEM, IB or BPA at concentrations ranging from 1 to 20 mg C/L). The use of mg C/L as opposed to mg/L was selected based on the detection method of the TOC Analyzer – the analyzer can only detect carbon within the target compound structure and the concentrations used were in the lower limit of the analyzer. The high temperature TOC Analyzer uses a catalytic oven operated at 750F to oxidize organics to CO_2 which in turn is measured by a non-dispersive infrared (NDIR) detector (Standard Method 5310B, Standard Methods, 1989). The low temperature TOC Analyzer oxidizes samples using a wet chemical method: simultaneous persulfate oxidation and UV irradiation of the sample produces CO_2 which is detected and measured in real time by a NDIR detector (Standard Method 5310C, Standard Methods, 1989).

Both MWCO and solute filtration test samples were collected in 40mL amber borosilicate vials. If insufficient sample was collected, MQ dilution water was added to ensure sufficient sample for analysis (25 mL for MWCO, 35 mL for solute filtration tests). In the event of dilution, concentration results were adjusted accordingly.

Vials used to collect samples were cleaned using Chromerge ©; a mixture of chromic and sulphuric acid. The cleaning procedure was as follows: firstly, the vials were soaked in dilute lab-grade soap solution (Contrex, Deacon Labs, Inc., University of Ottawa Chemistry Store, Ottawa, ON) for at least two hours, triple rinsed with distilled water, soaked in Chromerge © for at least one hour and finally triple rinsed with distilled water and once with MQ water. The vials were dried in an oven at 105°C. Other glassware was

washed following the same procedure using dilute phosphoric acid (1%) for at least 24 hours.

3.3.2.1 Concentration range determination

In order to prepare the test protocol and determine working concentration ranges, the selected target solutes (SMZ, CBZ, GEM, IB, BPA) were dissolved in MQ water at various concentrations to determine their solubility and analyzed via the UV-persulfate based TOC Analyzer. Based on the limitations of the TOC Analyzer, and the solubility of the target solutes, a feed concentration of 10 mg C/L (ppm C) was selected. All compounds dissolved well within 4 to 48 h in MQ water at 20 mg/L C with the exception of gemfibrozil. Gemfibrozil was not found to dissolve in the working range, even with the addition of a solvent (i.e., methanol) or heat and therefore had to be eliminated as a target solute. For ease of analysis, individual calibration curves were prepared for each target solute. Table 3.4 lists the relative concentration of 10 mg C/L for each of the solutes.

Table 3.4: 10 mg C/L equivalent concentrations for target solutes

Compound	Concentration (mg/L)
Sulfamethazine	19.31
Carbamazepine	13.11
Bisphenol A	12.67
Ibuprofen	13.21

3.4 Membrane preparation

Membranes were prepared by dissolving the CSMM followed by the base polymer, in this case PES, into the solvent, NMP. The characteristics of the CSMMs tested are listed

in Table 3.1. For each CSMM, three different types of membranes were prepared at the following conditions: 18% PES, no pre-gelation time (PES18-0), 18% PES, three minutes pre-gelation time (PES18-3) and 20% PES, no pre-gelation time (PES20-0). In each variation, three percent (weight basis) CSMM was used and the percent solvent changed from 79% to 77% when 20% PES was used. Controls (without CSMMs) for the three different PES content/pre-gelation time conditions were also tested. The order in which the membranes were made and tested was randomized (Table 3.5). The pre-gelation time of three (3) minutes was selected after the control membrane prepared with five (5) minute pre-gelation time failed to produce promising permeabilities (see Section 4.1.3). This was followed by tests using three and one and a half (1.5) minute pre-gelation times for both a control and a CSMM-blended PES membrane. The three minute pre-gelation time appeared to be the most promising for the target application and was thus selected for the remaining tests (see Section 4.1.3).

Table 3.5: Composition of membranes and order of preparation

Test Order	CSMM	%PES	%NMP	%CSMM	Pre-Gelation Time *min*
1	none	18	82	0	0
2	none	20	80	0	0
3	none	18	82	0	3
4	NDS	18	79	3	5
5	PPG	18	79	3	0
6	NDS	18	79	3	1.5
7	none	18	79	0	1.5
8	NDS	18	79	3	3
9	none	18	79	0	3
10	PEG_{400}	18	79	3	0
11	NDS	18	79	3	0
12	PPG	20	77	3	0
13	PEG_{200}	18	79	3	0
14	PEG_{200}	20	77	3	0
15	PEG_{200}	18	79	3	3
16	PPG	18	79	3	3
17	NDS	20	77	3	0
18	PEG_{400}	18	79	3	3
19	PEG_{400}	20	77	3	0
20	none	*NF270 (Dow/Filmtec) commercial membrane*			

For each membrane, 80 g of casting solution were prepared according to the following procedure. NMP was weighed using a digital analytical scale (R200D, Sartorius) in 100 mL glass bottles and the pre-weighed CSMM added through a funnel. The bottle was then sealed by wrapping the threads with Teflon tape, capping the bottle with a Teflon lined cap and sealing the cap with electrical tape. The solution was then mixed in an environmental orbital shaker (G24, New Brunswick Scientific Co., Inc., Edison, NJ) at 640 rpm and 50°C until the CSMM was completely dissolved, typically 4 to 24 hours. Once the CSMM was dissolved, the pre-weighed PES was added to the solution via a funnel and the bottle was re-sealed and placed back into the shaker until completely

dissolved, typically 6 to 24 hours. It was crucial to dissolve the CSMM prior to the PES since the CSMMs could not be dissolved if added simultaneously with the PES. If the solution contained impurities or agglomerations of undissolved PES (visible to the naked eye), it was filtered through 5.0 μm Teflon PTFE 47-mm discs (Cat# LSWP04700, Millipore, Bedford, MA) using a stainless steel pressure filter (XX4004700, Millipore, Bedford, MA) under nitrogen gas at 69 to 276 kPa gauge (10 to 40 psig). After filtration, the solution was left in a desiccator for a minimum of 2 to 4 hours to degas (remove air bubbles). Prior to casting, solutions were placed in the refrigerator (4°C) for at least 1 hour to increase their viscosity. Each solution produced six to ten membrane sheets.

Membranes were cast via the phase inversion technique (Matsuura, 1994). A clean glass plate, 20.3 x 30.5 cm (8x12"), was placed on a level surface in a fume hood and a copper casting bar (knife) was placed at one extremity of the plate. Solution was poured on the plate next to the casting bar (the casting bar creates a 250 μm gap between the glass and the bar by its end supports) and the casting bar was dragged swiftly over the solution to create a 12.7 x 20.3 cm (5x8") film with a nominal thickness of 250 μm. The pre-gelation time refers to the time between this step and the next step: the immersion of the glass plate (with the solution film) into a cold water bath (4.0 ± 0.2°C) to harden the membrane. When the membrane was formed and had peeled off the glass plate, it was stored in a cold water bath (4°C, in the refrigerator) until used. Between membranes, the glass plate was cleaned with a dilute solution of lab grade detergent (Contrex ©), rinsed with distilled water and rinsed again with boiling distilled water. A light box was used to examine the membrane sheets for defects (pinholes, wrinkles and impurities). Membrane

coupons were cut from the membrane sheets in areas free from defects. Typically one or two coupons could be obtained per sheet.

3.5 Membrane characterization

Membrane evaluation was carried out in two phases: a characterization phase and an applicability phase. In the characterization phase, prepared membranes were characterized through filtration/permeation tests consisting of pure water permeability (PWP) and molecular weight cut off. Within the characterization phase, membrane hydrophilicity (contact angle analysis) and charge (zeta potential) were also evaluated. Finally in the applicability phase, filtration tests consisting of mg/L-level solute filtration tests (SFTs) were carried out to assess membrane performance.

3.5.1 Membrane characterization via filtration tests

Pure water permeability, molecular weight cut off and single-solute removal (solute filtration tests) were determined for each membrane (in triplicate) and a commercial NF membrane (NF270, Dow/Filmtec) as a reference. Membrane coupons (average filtration area: 20 cm^2) were selected from the cast sheets and backed with 2.5 μm cellulosic filter paper (grade 42, Whatman) as a support. The selected membranes were placed in the cells and the three tests were performed sequentially (on the same coupons) as described below.

3.5.1.1 Pure water permeability

The purpose of PWP was to determine the steady state flux of the membrane (filtering MQ water), its ideal production rate. Flux, J, is defined as the flow of permeate (product water) per effective area (Equation 3.1) and is typically reported in LMH ($L/m^2/h$):

$$J = \frac{Q_{permeate}}{A_{membrane}} = \frac{\dot{M}_{permeate}}{A_{membrane}\rho_{permeate}} \qquad 3.1$$

Where J is the flux (L/m^{2}h), $Q_{permeate}$ is the permeate flowrate (L/h), $A_{membrane}$ is the membrane area (m^2), $M_{permeate}$ is the mass flowrate of permeate (g/min), $\rho_{permeate}$ is the density of the permeate (kg/m^3), taken as the density of water (assumption of a dilute solution) at the appropriate temperature. To account for temperature or pressure effects, pure water flux may be expressed as specific flux, J_{sp}, at a specific temperature, typically 20°C, or as normalized standard flux (NSF), the latter accounting for pressure effects. The following expressions are typically used to account for temperature and pressure effects (Equations 3.2 and 3.3).

$$J_{sp,20^oC} = J_T\left(\frac{\mu_T}{\mu_{sp,20^oC}}\right) \qquad 3.2$$

Where $J_{sp,20^oC}$ is the specific flux at 20°C, J_T is the measured flux at temperature T and μ_T and $\mu_{sp,20^oC}$ are the permeate viscosities at temperatures T and 20°C, respectively.

$$NSF = \frac{J}{\Delta P} \qquad 3.3$$

Where NSF is the normalized standard flux, typically expressed in (L/m^2/h/bar), J is the measured flux (LMH) and ΔP is the trans-membrane pressure (bar).

The preceding expressions were applied to the results of the following test protocol. Using MQ water, the membranes were first pre-compacted at 551.6 kPa (80 psi) for one hour and subsequently the flux was measured for 50 hours at 344.7 kPa (50 psi). At each sample time, cell pressure, retentate flow and feed tank temperature were measured. Permeability was calculated by recording the mass of water collected over a given period

of time (typically two to five minutes) at given intervals (time of 5, 15, 30, 60 min for precompaction; 5, 15, 30, 60, 120, 240, 360 min, 22, 24, 28, 46, 48, 50 h for pure water permeability) and dividing it by the membrane area, density at the corresponding feed tank temperature and by the operating pressure. On a test run, a comparison was made between measuring the mass versus volume collected and the methods were found to be interchangeable (± 1% error) however the mass based method was chosen for accuracy. This was especially applicable for membranes with low permeability where volumetric measurements were virtually impossible. Once the PWP test was completed, MWCO was determined using the same membrane coupons by switching the feed from MQ water to a number of different solutes.

3.5.1.2 Molecular weight cut off

The molecular weight cut off test characterizes the size of solute which is removed at the 90% level by the membrane. It is typically determined with non-reactive, uniformly sized compounds that are theoretically not affected by adsorption, charge repulsion or other mechanisms since the removal mechanism is assumed to be solely size exclusion. To determine MWCO, solutions of macrosolutes with uniform sizes are filtered and their removal is measured. By plotting removal versus the size of solute, a sieving curve can be used to estimate the size of compound removed at 90%. Michaels (1980) determined that the log-normal probability function accurately described sieving curves for UF membranes. It is important to note that the MWCO is not an absolute measure since it is dependent on the membrane pore size distribution. Assuming a standard distribution of pores, and therefore a standard distribution of removal, one can determine MWCO based on the assumption that the solute separation, f, of a solute with a known size, d_s, follows

a log-normal distribution (Singh et al., 1998). By plotting the probability of removal, f, as a function of the logarithm of the solute size, a straight line is generated. The extrapolation (or interpolation) of this line leads to the estimates of MWCO (at f of 90%), mean pore size (at f of 50%) and pore size distribution (using f of 84.13% and 50%), assuming a geometric distribution. It is also possible to determine the surface porosity (S_p), and pore density (N). It is important to generate removals which cover a wide range in order to ensure better prediction. Selecting a wide range of size of macrosolutes is therefore an important factor in accurate MWCO determination. Singh et al. (1998) developed a series of correlations (see Appendix C) for these parameters based on the filtration of PEG and PEO.

The following test protocol was used to determine MWCO, pore size, surface porosity, pore density and pore size distribution. Stock solutions of desired molecular weight solutes (Table 3.3) were prepared with MQ water and diluted in the feed tank to a volume of 8 L and concentration ranging from 100 to 200 mg C/L. The system was run in recycle mode for one hour (i.e., permeate and retentate are returned to the feed tank) after which permeate from each cell was collected. The feed tank was sampled in duplicate and each permeate sample was collected over a given period of time (5 - 15 minutes). The mass of permeate collected enabled the determination of permeability and the sample collected was diluted to an acceptable volume for analysis using the high temperature TOC Analyzer to determine removal. Once the solute filtration portion of the MWCO test was performed, a rinsing/cleaning step was performed. For twenty minutes, the system was run in flow-through using MQ water. This step ensured the solute was sufficiently

flushed from the system. After the twenty minute flow-through, the system was run in recycle for an additional forty minutes. Permeability was then measured to ensure there was no reduction due to fouling during the solute run and/or that the cleaning run was successful. On average, five solutes were tested, in order of increasing molecular size (generally 1 kDa, 8 kDa, 14 kDa, 35 kDa and 100 kDa). Many of the smaller molecular weight solutes secured for this test (Table 3.3) were not used because most membranes had much larger pores.

3.5.2 Contact angle

Membrane hydrophilicity was assessed by measuring contact angle using the sessile drop method. The sessile drop method is based on the principle of three-phase equilibrium that occurs at the solid-liquid-air interface of a liquid droplet on the test surface. Membranes were dried for five days between layers of tissue paper and then cut into 1.5 x 6 cm strips and affixed to frosted microslides (2.5 x 7.5 cm) (FisherFinest, Fisher Scientific, USA) using electrical tape. Electrical tape was used to minimize the glare from the camera when measuring/viewing the liquid droplet at the membrane surface (Westgate, 2008). Advancing contact angle was measured using a VCA Optima XE Surface Analysis System (AST Products, Inc., Billerica, MA). A 2.0 μL droplet of water was deposited onto the membrane and 0.25 μL drops were added until the droplet/membrane interface increased. Between each addition, the contact angle was measured and the advancing contact angle was recorded as the left and right angle average of the droplet before the interface increased. For each membrane, triplicate coupons were tested and at least three measurements were made per coupon. It should be noted that there was variability from location to location on any given membrane (Westgate, 2008).

3.5.3 Zeta potential

The membrane charge was assessed by measuring the streaming potential between the feed and permeate sides when filtering an electrolyte solution at known pH and temperature. The experimental set-up for the streaming potential measurement is shown in Figure 3.3 below. This set-up was developed by Huyen Dang, PhD Candidate at the University of Ottawa, and was based on the system described by Syzmczyk et al. (1998).

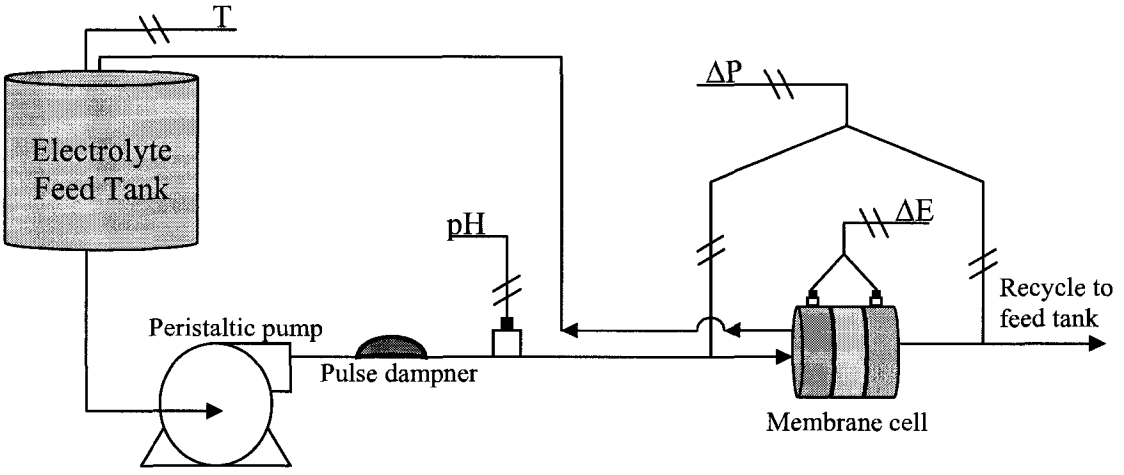


Figure 3.3: Experimental set-up for streaming potential determination
(T: Temperature probe, ΔP: Transmembrane pressure, ΔE: Streaming potential measurement, pH: pH probe)

Silver/silver chloride (Ag/AgCl) electrodes were prepared via the following method. Aligator clips were soldered onto a 1.5 V battery. The silver electrode (Ø 1.5 mm, +99.99%, Aldrich, St. Louis MO) was attached to the positive side of the battery and a thin silver reference electrode was attached to the negative side. Both electrodes were immersed in a 0.0001 M HCl solution for 24 h (so that the chloride could deposit on the electrode). The electrodes were stored in a 0.1 M KCl solution between runs. In order to measure streaming potential, a membrane coupon (20 cm^2) was inserted into the membrane cell. A 0.001 M solution of potassium chloride (KCl) was sequentially filtered

at five increasing pressures ranging from 1 to 30 kPa (10 to 300 mbar) through the cell. Temperature and pH were monitored on the feed side of the membrane and adjusted using ice and hot water baths, and hydrochloric acid (0.1 M HCl) and potassium hydroxide (0.1 M KOH) solutions, respectively. The difference in current (streaming potential) between the silver chloride electrodes, placed on the feed and permeate sides of the membrane, was measured. By collecting the streaming potential at given pressures, a plot of streaming potential versus pressure was generated. Using linear regression, the slope of the best line of fit was used to calculate the variation in streaming potential with pressure ($\Delta E/\Delta P$). The zeta potential can then be determined using the Helmholtz-Smoluchowski equation (Nystrom et al., 1994):

$$\varsigma = \frac{\Delta E}{\Delta P} * \frac{\eta \kappa}{\varepsilon_o \varepsilon_r} \qquad 3.4$$

Where ΔE is the variation in streaming potential (mV), ΔP is the variation in transmembrane pressure (mbar), η is the permeate viscosity, κ is the solution conductivity, ε_o is the vacuum permittivity and ε_i is the dielectric constant of the media. It should be noted that a system baseline (calibration) was established by measuring the charge of a known commercial membrane prior to testing the novel membranes.

3.6 Applicability evaluation

Following the MWCO filtration test, four solute filtration tests were carried out. The purpose of these tests was to determine the capacity for removal of target solutes. Removal is defined as:

$$\text{Removal}\,(\%) = \frac{C_{feed} - C_{permeate}}{C_{feed}} * 100\% \qquad 3.5$$

Where C_{feed} and $C_{permeate}$ are the feed and permeate concentrations (mg/L). The test protocol for the solute filtration tests was as follows. Ten mg C/L solutions of each solute (i.e., sulfamethazine, carbamazepine, bisphenol A and ibuprofen) were prepared. The protocol consisted of sequentially filtering a single solute solution for four hours followed by a 30 minute rinse/cleaning run and then proceeding to the solution of the next solute. For each solute, permeate samples were collected continuously to determine removal, permeability and breakthrough (where applicable). Every half hour, the feed was sampled and the cell pressures, retentate flows and feed tank temperature were recorded. When membranes with high flux, (i.e., >2 mL permeate/min) were tested, permeate samples were collected continuously for the first one or two hours and then samples were collected periodically (every half hour) for the final two or three hours in order to ensure sufficient feed solution remained in the feed tank. Collected samples were analyzed using the UV-persulfate TOC Analyzer. The 30 min rinsing/cleaning run used MQ water in flow through for 20 min and the final 10 min were run in recycle. Rinse water was occasionally sampled to characterize any residuals. The concentration of these results was found to be less than 1% of the feed concentration and therefore the cleaning method was deemed acceptable. Permeate flowrate, cell pressure, retentate flows and temperature were recorded at the end of the rinsing run. It should be noted that the 20 minute long flow-through rinsing step of this cells-in-parallel system (for both the SFT and MWCO tests) was conducted at the normal operating flowrate (i.e., ~6 L/min), creating a very large demand for MQ water. This demand was much larger than that for earlier cells-in-series system, and a large supply of MQ water had to be collected *a priori*.

CHAPTER 4

RESULTS AND DISCUSSION

This chapter will discuss briefly the system characterization and establishment of membrane casting conditions using CSMM-NDS blended membranes. The effect of CSMM addition to charge, hydrophilicity, flux, MWCO, surface porosity, and pore size distribution will be assessed. Finally, the PhAC and EDC removal performance of the novel membranes will be evaluated.

4.1 System characterization

The system was first characterized to determine baseline losses in the system and potential temperature variations. Additionally, CSMM-NDS modified and control PES based membranes were tested using various pre-gelation times to determine optimal casting conditions. The results of these tests are presented in this section.

4.1.1 Single solute adsorption results

Figure 4.1 illustrates the variation of BPA and IB in the system without the membrane coupons during single-solute runs. For these runs, no membranes were placed in the system and the retentate and permeate streams were recycled to the feed tank. The entire system is made of 316-SS with a few exceptions: the inner casing of the rotameters and the feed tank are made of glass, the pump's diaphragm constructed of polypropylene and the O-rings used to seal the membranes in the cells were wrapped in Teflon tape. As discussed in Section 3.3.1, maximizing the use of 316-SS was undertaken to minimize adsorption losses. Based on mass balances, 10.82 mg BPA and 27.32 mg IB,

respectively, adsorb to the system over the course of the characterization tests. This represents 89.1 and 74.7 percent of mass of these solutes within the system. SMZ and CBZ were not found to adsorb onto the system (see Appendix D). Additionally, BPA appears to saturate the system after approximately 24 hours, whereas the system does not appear to be saturated with IB within the 48 hour test. These relative orders of compound adsorption results were expected, since solutes with higher log K_{OW} have higher sorption tendencies. The log K_{OW} of BPA and IB are 3.4 and 3.97 (IB ranges from 3.15-4.5), respectively, thus it was expected that the quantity of IB adsorbed to the system be higher. The log K_{OW} of SMZ and CBZ are 0.28 and 2.56 (CBZ ranges from 2.18-2.93), respectively. Kimura et al. (2004) found that 17β-estradiol partially adsorbed to their stainless steel filtration apparatus, whereas all other solutes with lower log K_{OW} (including BPA) did not. This somewhat confirms the results obtained here, where solutes with high log K_{OW} adsorb and less lipophilic compounds do not. Additionally, Kimura et al. (2004) evaluated the Henry's law constants for their target solutes and found that volatilization would not be a major loss mechanism. The adsorption results were used as a baseline for the assessment of adsorption of the target solutes onto the membranes.

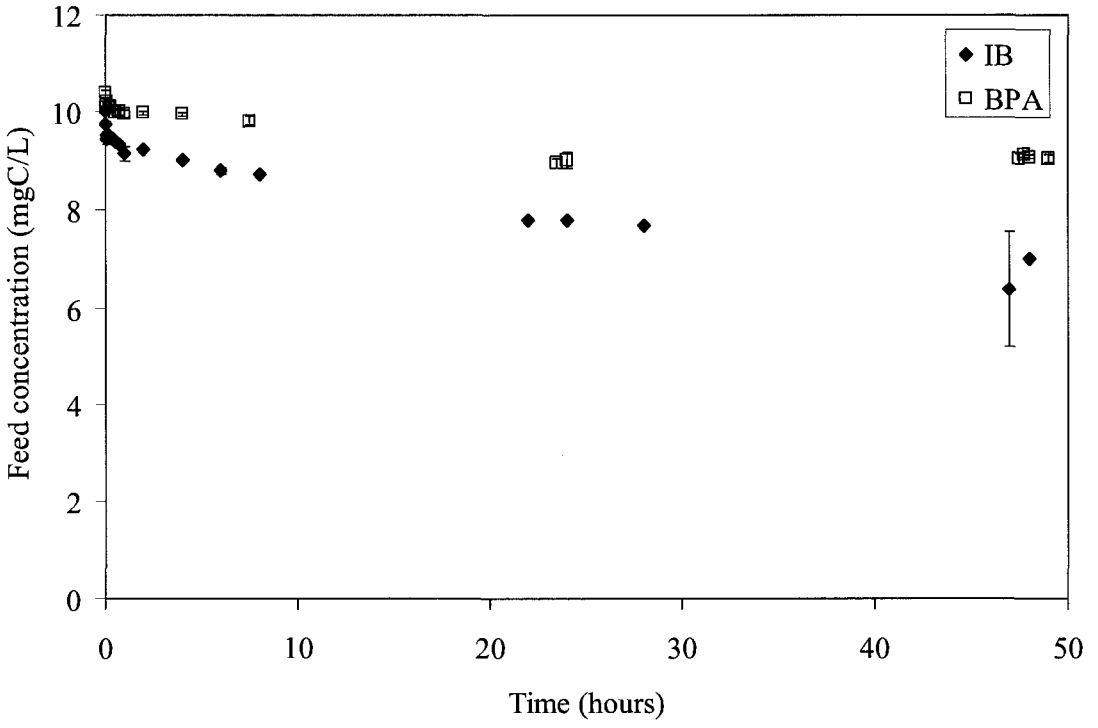


Figure 4.1: Temporal variation of IB and BPA feed concentration during single-solute system characterization

4.1.2 Temperature variation

Commercial membrane coupons (NF270, Dow/Filmtec) were used to determine operating conditions of the test system prior to the filtration experiments. Two tests were carried out: Test #1 consisted of one hour pre-compaction at 551.6 kPa (80 psi) followed by three hours of filtration at 344.7 kPa (50 psi) (the system was inadvertently shut off overnight); Test #2 consisted of 24 hour filtration at 344.7 kPa (50 psi) on the following day (and using the same membrane coupons as in Test #1). During these tests, significant temperature increases were noticed, as shown in Figure 4.2. An increase in temperature was anticipated, since Mosqueda-Jimenez (2003) had encountered similar problems with a cell-in-series version of the filtration system, however the magnitude of the increase

was not known for the cells-in-parallel system constructed for this study. In order to maintain a constant temperature, different cooling methods were investigated. A single pass counter-current shell and tube heat exchanger was built similar to the one used by Mosqueda-Jimenez (2003). A Haake G/D1 re-circulating cold water bath was used to feed cold water in the shell-side while the test fluid circulated in the tube side, maintaining the temperature at approximately 21 ± 1°C.

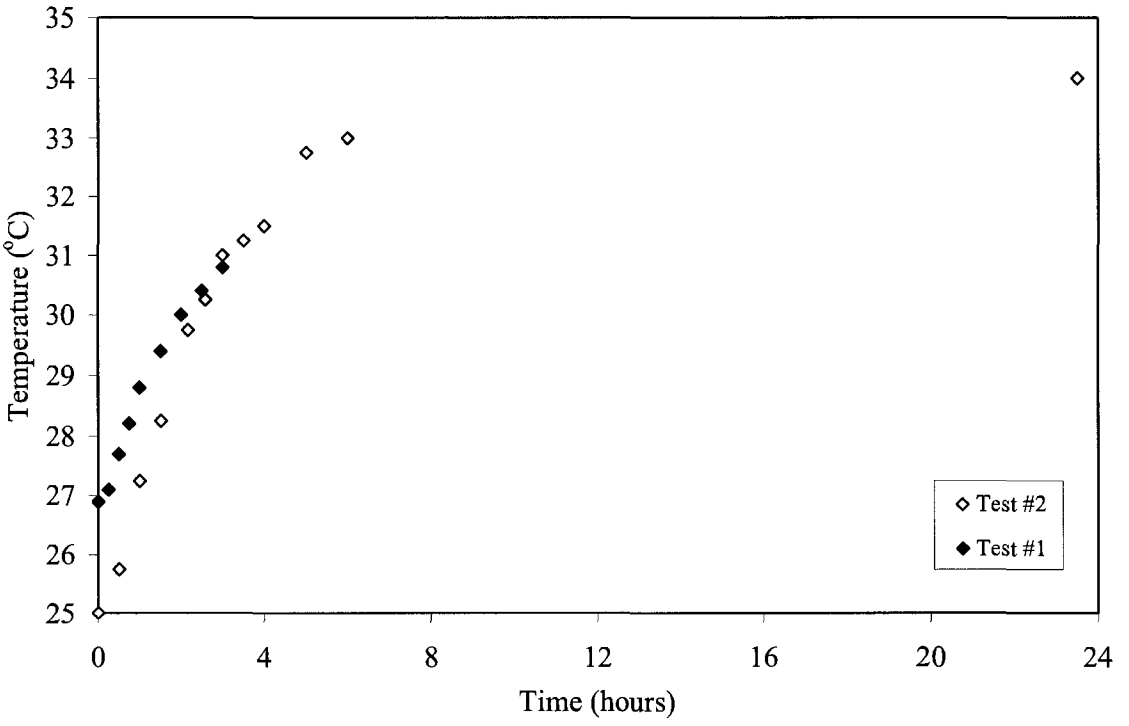


Figure 4.2: Temperature increase during filtration tests using NF-270 (Dow/Filmtec)

4.1.3 Determination of optimal pre-gelation time

Previous research has shown the effect of pre-gelation time on surface modification using SMMs can be variable, primarily depending on other factors (i.e., environmental conditions during migration and gelation, membrane composition, SMM characteristics, etc.). Based on previous experience, primarily Mosqueda-Jimenez (2003), a pre-gelation

time of five minutes was selected. Previously, as little as three minutes was shown to be sufficient for effects to be noticeable. By increasing the pre-gelation time to five minutes, with these new SMMs, it was assumed that the migration would be more pronounced, and that the additional time may produce tighter membranes (which would aid in the removal of the target solutes). Initial tests with CSMM-NDS at a five minute pre-gelation time appeared promising; however the control membrane at the same condition (PES18-5) was extremely tight, resulting in such a low flux that no assessments could be carried out. This caused a dilemma since the five minute membrane incorporating the CSMM performed well in terms of production rate, however there was no benchmark against which it could be compared. In order to be able to produce accurate comparisons, new pre-gelation times of 1.5 and 3 minutes were evaluated using the same CSMM.

Figures 4.3 and 4.4 illustrate the effect of pre-gelation time on normalized standard flux and molecular weight cut off, respectively. The control PES membranes show the expected decreasing flux with increasing migration, as the membranes become tighter. The increasing membrane tightness is likely a function of the environmental conditions at which the membranes were cast, with relative humidity (air moisture) precipitating a thin selective layer before gelation. Air moisture may also come into play with the migration of the CSMMs, as their predicted hydrophilicity would draw them up to the air/solution interface by the attraction to the humidity. The CSMM-NDS appears to have an inverse effect on flux with pre-gelation time when compared to the control membrane; it is significantly increasing flux, especially with five minute migration. It also appears to have an opposite effect on MWCO. The increase in MWCO with pre-gelation time for

the modified membrane correlates to the increase in flux, which is expected. From these preliminary results of NSF and MWCO, the pre-gelation time for all the test membranes was reduced to three minutes. This time was selected as there was a minor improvement in flux (of the modified membranes) for both the 1.5 and 3 minute migration as well as a similar increase in MWCO for both pre-gelation times. In order to ensure a maximum rise of the CSMMs, three minutes was selected. Although the difference in flux and MWCO between the two appears insignificant, it was hoped that other CSMMs may show more distinct differences at this pre-gelation time. The effect of pre-gelation time on the CSMM-NDS charge and contact angle are presented in Appendix E.

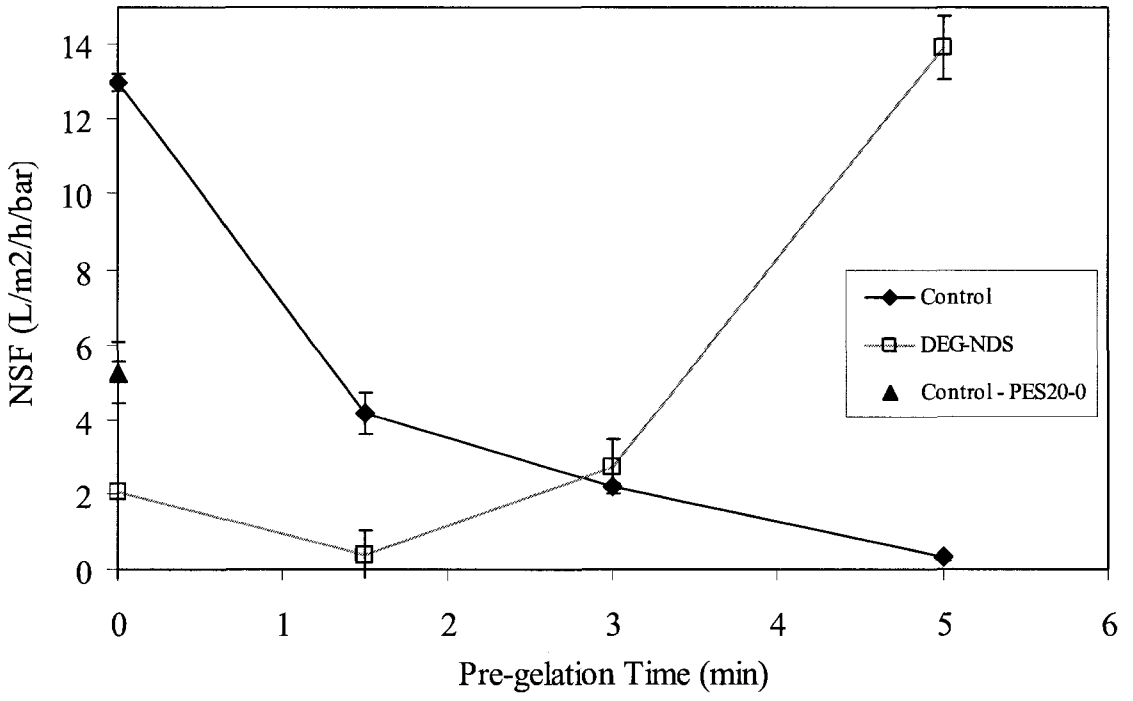


Figure 4.3: Effect of pre-gelation time on flux for modified (using CSMM-DEG-NDS) and unmodified (control) membranes with 18% PES

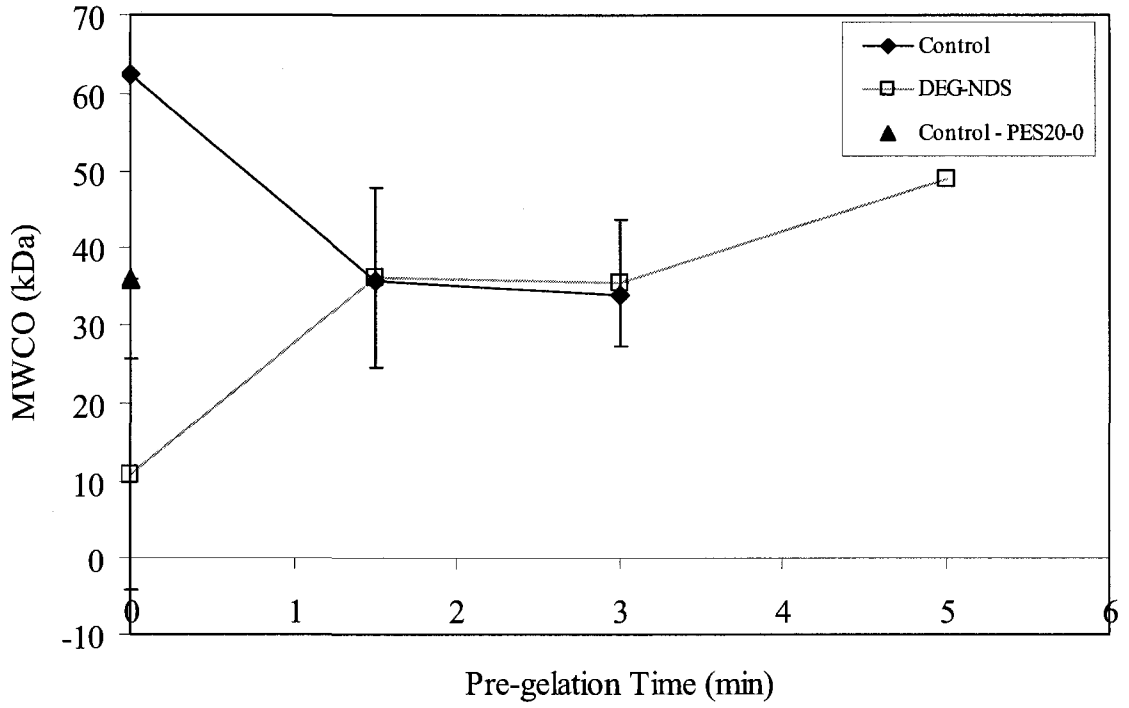


Figure 4.4: Effect of pre-gelation time on MWCO for modified (using CSMM-DEG-NDS) and unmodified (control) membranes with 18% PES

It should be noted that the CSMM used in the determination of the optimal pre-gelation time could not be cast at PES20-0. The casting solutions were also difficult to work with and exhibited high variability. For this reason, a discussion on the impact of this CSMM on membrane characteristics is presented in Appendix E as opposed to the following sub-sections.

4.2 Impact of CSMMs and casting conditions on membrane characteristics

This section will assess the impact of three CSMMs (CSMM-PEG_{200}, CSMM-PEG_{400} and CSMM-PPG) when compared to the control (no CSMM in the membrane) for three casting conditions, 18% PES (PES18-0), 18% PES with three minute migration (PES18-3) and 20% PES (PES20-0). The discussion presented in this section will not focus on the

fourth CSMM (CSMM-NDS) since it does not have the same end-group and proved difficult to cast; a discussion on this CSMM is presented in Appendix E. In order to measure the impact of the CSMMs, hydrophilicity and membrane charge were evaluated. Additionally, characteristics including flux, MWCO, surface porosity and pore size distribution are compared for the different membranes and casting conditions. Finally, correlations between the properties are assessed.

4.2.1 Hydrophilicity

The hydrophilicity of the experimental membranes developed in this study was quantified via the advancing contact angle (Section 3.5.2). It was expected that the membranes prepared without pre-gelation time (PES18-0 and PES20-0 conditions) achieve similar contact angles and that these angles be different (higher or lower – unknown in which direction because of the new properties of the CSMMs) than the PES18-3 condition. This was anticipated since the pre-gelation time is expected to allow the CSMMs to rise to the surface, ensuring a higher concentration and thus a greater surface modification. This trend was not found. The contact angle results are discussed below.

Figure 4.5 represents the advancing contact angle of the modified and unmodified membranes at each of the casting conditions, with the error bars representing one standard deviation. All of the contact angles range between 50 and 80°, indicating that the membranes are hydrophilic (i.e., wettable, since their contact angle < 90°). Note that in the legends of this figure (and subsequent figures) CSMM-PEG_{200}, CSMM-PEG_{400} and CSMM-PPG will be denoted as PEG_{200}, PEG_{400} and PPG, respectively, for simplicity.

At PES18-0, the contact angles of CSMM-PEG_{200} and CSMM-PPG are similar to the control ($61.2 \pm 4.4^{\circ}$, $62.0 \pm 2.9^{\circ}$ and $63.2 \pm 3.5^{\circ}$, respectively), whereas the addition of CSMM-PEG_{400} decreases hydrophilicity by approximately 17% (contact angle of $73.9 \pm 3.0^{\circ}$). As shown by Figure 4.5, a decrease in hydrophilicity of all the modified membranes with respect to the control is seen at both PES18-3 and PES20-0 casting conditions, although the angle increase is statistically insignificant for the PES18-3 condition. It was expected the CSMMs make the membranes more hydrophilic. This is clearly not seen, and may be explained by the drying technique used. Since the membranes were completely dried prior to measurement, the pores were filled with air. The hydrophobicity of air in the pores would increase the contact angle (Matsuura, 2008), as shown in Figure 4.5 (with the exception of CSMM-PPG at PES18-0). This is consistent with the high surface porosity of the modified membranes cast at the PES18-3 and PES20-0 conditions (Table 4.1), such that the more porous membranes have increased contact angles. The CSMMs used for this project were developed specifically for it, and therefore there are no prior results against which the CSMM-modified membranes can be compared.

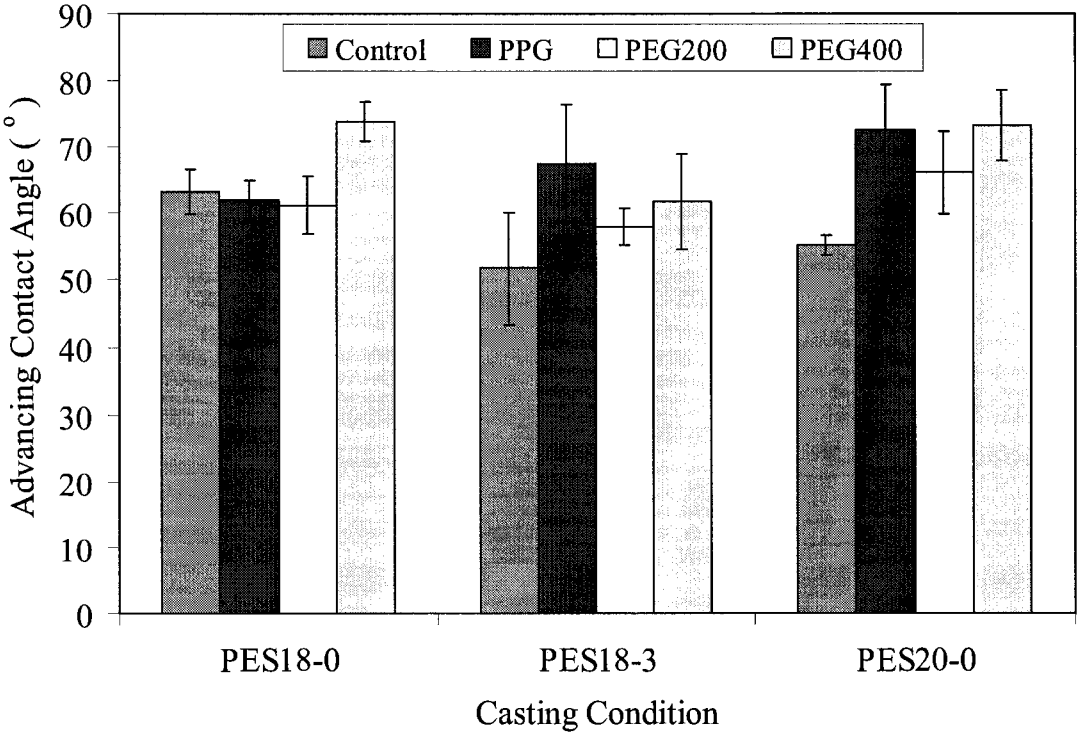


Figure 4.5: Advancing contact angle of CSMM-modified and unmodified membranes at three different casting conditions

Despite the lack of background on these specific CSMMs, both trends (no change and change in contact angle) have been observed for other SMM-blended PES membranes without pre-gelation time: Suk et al. (2002a, b) and Mosqueda-Jimenez et al. (2004a) did not observe changes in contact angle with the addition of hydrophobic SMMs while Rana et al. (2005) and Nguyen et al. (2007) found decreases in contact angle using 3% wt of an LSMM (i.e., making the membrane more hydrophilic). The variability of results shown in the literature may be attributed to differences in SMM properties (i.e., use of hydrophobic SMMs versus hydrophilic SMMs) however may also lie in the differences of membrane manufacturing (i.e., the hydrophobic membranes were heat-treated prior to gelation). Rana et al. (2005) and Nguyen et al. (2007) both prepared membranes similar to those prepared here; the difference between their LSMMs and these CSMMs is that their

SMMs were not end-capped with HBS (theirs were PEG end-capped LSMMs, these are CSMMs). In comparison, the CSMMs appear to have increased hydrophobicity while the LSMMs have increased hydrophilicity. The difference in effect could therefore be attributed to the HBS end-cap on the CSMMs.

The largest decrease in hydrophilicity was seen for the modified membranes at the PES20-0 casting condition, which was not the expected effect of these CSMMs at this condition. There is little CSMM migration to the surface of the membranes cast at the PES18-0 condition (based on the contact angle results), so there was even less CSMM migration expected for those cast at PES20-0 given their higher polymer concentration (and presumably higher viscosity) casting solution. It is interesting to note that the increase in contact angle at this casting condition follows the size of the PEG/PPG used in the CSMM (i.e., PEG_{200}<PEG_{400}<PPG). Nguyen (2005) has also shown this trend with LSMMs (MDI-PEG using either PEG_{200}, PEG_{400} or PEG_{600}) blended into 18% PES membranes. Despite the molecular weight trend, the increase in hydrophobicity is statistically similar for all three CSMMs, which could be attributed to the CSMMs having the same end groups and/or having similar mid-segments. It could also be attributed to the variability of the measurements at the surface due to localized modifications, as shown by Ho (1997). The increase in contact angle could also be related to the rigidity of the CSMM. Rigidity can be characterized by the glass transition temperature and a plot of contact angle versus glass transition temperature is presented in Figure 4.6. The glass transition data was supplied by Rana (2008). From this figure, it can be shown that only with pre-gelation time or increased PES concentration is the contact angle a function of

rigidity. Accordingly, it can be concluded that migration does occur at these conditions, but that the quantity of migration is a function of the CSMM mobility in the solution. It appears as though mobility increases with increasing PES concentration or pre-gelation time, however to confirm this it would be necessary to investigate more CSMMs and casting conditions in order to increase the number of data points. It should be noted that it is presumed the increase in contact angle is a result of CSMM migration to the surface however it would have been interesting to measure the contact angle of the permeate-side of the membrane to confirm the change was only seen at the surface. The downfall of this method is the increased roughness which would have lead to highly variable results. It is recommended this characterization be investigated for the future development of these membranes and other modified membranes.

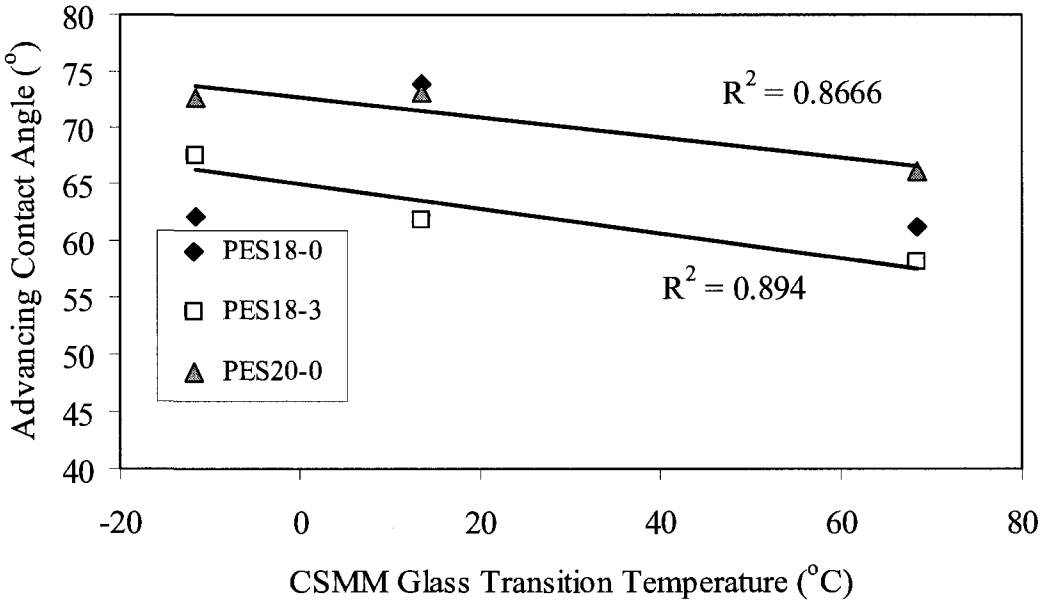


Figure 4.6: Effect of CSMM rigidity on advancing contact angle (regressions for PES18-3 and PES20-0)

Casting conditions do not appear to have a significant effect on the hydrophilicity of the membranes: variations in contact angle for a given CSMM-blended membrane at

different casting conditions are within the standard deviations (Figure 4.5). It should be noted that the manufacturer reports the VCA Optima has a repeatability of 1° and an accuracy of 0.5°; the wide confidence limits in Figure 4.5 indicate that the high accuracy was clearly not experienced. This is attributed to the heterogeneity of the membrane and the difficulty of preparing membranes with completely uniform surfaces. Additionally, the large confidence limit of contact angles for some types of membranes is fairly common in small-scale membrane making (Dang et al., 2006).

The contact angle of the control membrane cast at the PES18-0 condition (63.2 ± 3.5°) is lower than those reported elsewhere. For an 18% PES membranes (cast with a 250 μm nominal thickness), Nguyen et al. (2007) reports a contact angle of 79°, however the instrument and drying technique used were both different, both potentially contributing to the variation. Rana et al. (2005) report a contact angle of 68.1 ± 1.1° for a 20% PES membrane which is significantly higher than the 55.2 ± 1.5° reported here. The variation in this case may be due to the instrument, a much larger sessile drop and the gelation bath temperature: Rana et al. (2005) kept the gelation bath at ambient temperature whereas the membranes tested in this report were precipitated at 4°C.

The differences between contact angle values reported in this and other studies that manufactured their membranes under apparently identical conditions may also be caused by some other yet undetermined factor. Such factors are more likely to be consistent within one study and the objective of this study is to determine the impact of using the CSMMs rather than how well the controls compare with those in other studies.

Contact angle can be impacted by various factors, including surface porosity and surface roughness (Chan, 1994). Decreasing surface porosity is expected to increase the advancing contact angle owing to less adsorption of water into the pores whereas increasing roughness is expected to increase the advancing contact angle. As discussed in Section 4.2.3.1, the addition of CSMMs has increased surface porosity for the membranes cast at the PES18-3 and PES20-0 conditions (CSMM-PPG, CSMM-PEG_{400}) whereas it has decreased surface porosity for those cast at the PES18-0 conditions (and PES20-0 with CSMM-PEG_{200}). It was therefore expected that the contact angle may decrease at PES18-3 and PES20-0 and may increase at PES18-0, however the effect was the opposite. Higher surface roughness has also been attributed to larger contact angles (Chan, 1994, Dreilich et al., 1996, Andrade, 1985), as shown by Dang et al. (2006), which may also explain the higher contact angles observed for some of the modified membranes. These trends show that the CSMMs have migrated to the surface and that, for the PES20-0 casting condition, they generally produce less hydrophilic membranes than the unmodified membranes.

4.2.2 Charge

Membrane charge (zeta potential) was quantified by filtering an electrolyte (0.001M KCl) solution through the membrane and measuring the streaming potential at various (low) pressures, as described in Section 3.5.3. The Helmholtz-Smoluchowski equation was used to calculate the charge (Nystrom et al., 1994).

It should first be noted that a few problems were encountered while evaluating membrane charge. Firstly, the system design did not include a support structure for the membranes

being tested; the feed pressure ruptured the membranes at approximately 150 mbar which led to many failed experiments. The membrane failures could be an indication of poor mechanical strength when compared to a commercial membrane tested without problems in the same apparatus. In order to ensure the charge could be accurately evaluated without breaking the membranes, two superimposed Teflon mesh spacers were used as support material. With these supports, the experimental membranes did not rupture, however the feed pressure was also kept lower (<300 mbar) in order to prevent further failures. Streaming potential was therefore recorded at increasing pressures, beginning around 5 to 20 mbar. Generally, the first few pressure points (between 5 and 20 mbar) yielded unreliable results (i.e., not yet at steady-state) and these were discarded. A change in slope (slope of streaming potential with pressure) was noted in some cases at pressures ranging from 50 mbar to 150 mbar. The pressure at which the slope change occurred could not necessarily be predicted and for most membranes the operating pressures ranged from 20 mbar to 100 mbar. The change of slope problem was also not encountered for all membranes. In order to compare the membranes properly, the slope was selected in the lower pressure range (in some cases, maximum pressures reached were less than 100 mbar). The change in slope effect has also been observed by Nystrom et al. (1994). They attribute the slope variation to the flow through different pore sizes at the given pressures: at low pressures, flow is through the larger pores, which give a more real estimate of the charge since the pores act as a channel where flow cannot be disturbed. At higher pressures, flow passes through the smaller pores, which may disturb the flow and alter the actual charge, negating some of the assumptions used to quantify

charge. It is recommended that further work be carried out with this streaming potential apparatus to refine and improve accuracy of measurements and the method used.

Figure 4.7 illustrates the membrane charge for each of the membranes at the three casting conditions. It is difficult to compare the charge results obtained with those published in the literature since there are inherent variations between in-house manufacturing methods, especially with the gelation bath temperature (many reported are at ambient temperature), the use of various backing materials, the concentration of PES and the solvent used (i.e., NMP, Dimethylacetate (DMAC)). Additionally, the conditions under which the streaming potential is measured yield varied results. Generally, zeta potentials reported for commercial PES membranes vary between -13 mV and -90 mV and are measured around pH 6 to 7 using KCl or NaCl as the electrolyte (in the same concentration range used here). In comparison to these commercial membranes, the control and modified membranes tested here show lower charges. The control membranes here show a decrease in charge with increasing PES concentration, and also their -4 to -10 mV charge does not compare well to the charge of -20 mV (at pH 7) measured by Boussu et al. (2006) for a 32% PES membrane prepared on a backing material. The difference in pH between the values reported here and those reported by Boussu et al. cannot account for the discrepancy of the values. Irrespective of the differences between this work and published results, comparison of the charge results for the different membranes may yield information about the effects of the CSMM addition and the different CSMMs developed.

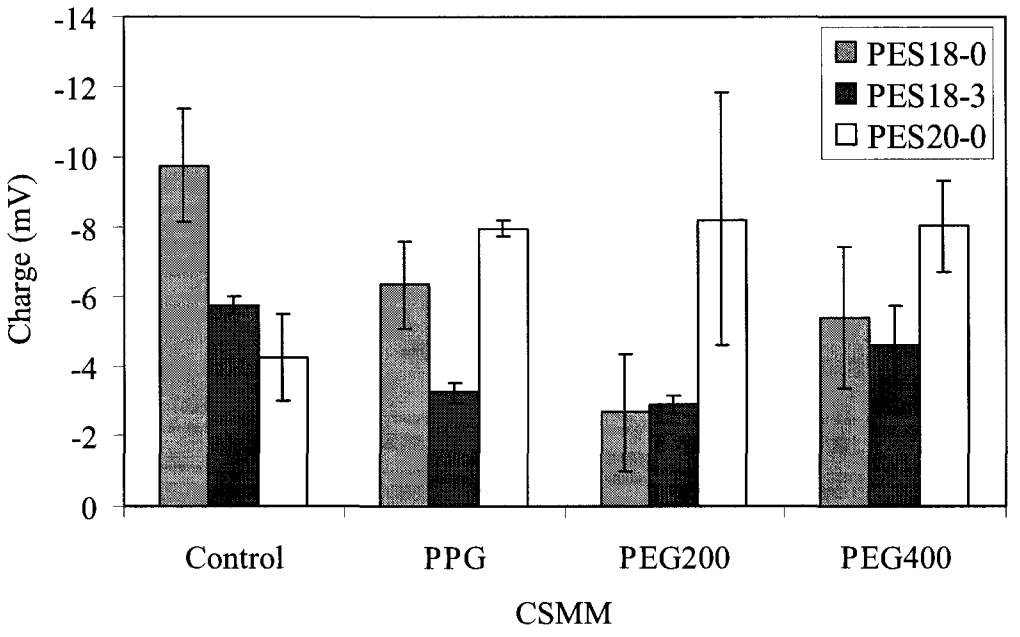


Figure 4.7: Charge of modified and control membranes as a function of CSMM and casting condition

From Figure 4.7, it is apparent that the charge of modified membranes for each casting condition is similar (i.e., there is not much change with respect to the CSMMs), since the CSMMs all hold the same end group, they should all hypothetically hold a similar charge (i.e., not magnitudes of order difference). It was expected that the different mid-segments impact the rise of the CSMMs to the surface and potentially vary the surface characteristics (i.e., charge) however this does not appear to be the case. The lack of charge variability at the three casting conditions for each modified membrane does correspond to the results obtained via contact angle analysis. It was also expected that the greatest CSMM migration and therefore highest change in charge would be achieved by the PES18-3 casting condition, because of the expected lower viscosity associated with the lower polymer concentration, and with the pre-gelation time. However this was not

the case: the modified membranes had the highest charge (and change in charge) at the PES20-0 casting condition, which had more polymer (20% PES versus 18% PES) and no pre-gelation time. In fact for both CSMM-PPG and CSMM-PEG_{400}, the pre-gelation time led to the least charge of the three casting conditions. It is also interesting to note that the charge of the control membrane decreases with casting conditions PES18-0 > PES18-3 > PES20-0, which resembles the trend seen with flux and pore size (probability density function) (Sections 4.2.3.1 and 4.2.3.2). Additionally, the charge of the modified membranes is less than the control for both the PES18-0 and PES18-3 conditions, however is greater than the control at the PES20-0 condition. Again, this correlates to the trends seen with other membrane properties (flux (Section 4.2.3.1) and contact angle (Section 4.2.1)), especially with the membranes cast at PES20-0 behaving differently than the membranes cast at PES18-0 and PES18-3 conditions. It may be that at 18% PES, the CSMMs are at equilibrium in the casting solution, whereas at 20% PES, the need for the CSMMs to reach the lower surface free energy is greater because of the higher polymer concentration (and a new equilibrium is necessary), and thus a more marked effect is seen at this condition.

As for contact angle, the effect of CSMM rigidity on charge should yield information as to the migration and effect of the CSMM on the membrane. Figure 4.8 shows the variation in charge with CSMM glass transition temperature for the modified membranes. Conversely to the trend with contact angle, charge correlates linearly to rigidity for the casting conditions without pre-gelation time. It was expected the effect of CSMMs be comparable on both charge and contact angle, however this does not appear to be the

case, as shown in Figure 4.9 by the lack of trend between the change (with respect to the control at each casting condition) in charge and contact angle. Figure 4.8 clearly shows linear trends for both the PES20-0 and PES18-0 conditions, however the trends are different in that for PES20-0, the charge appears to be statistically independent of T_g whereas for PES18-0, charge increases (more negative) with increasing T_g. This may result from CSMM rigidity, as increased rigidity may interfere with its ability to migrate. CSMM-PEG_{200} shows the most change in the more viscous casting solution (PES20-0) whereas in the less viscous solution, this CSMM decreases charge. At the lower PES concentration (PES18-0), CSMM-PEG_{200} may be evenly distributed, and a sufficient amount of the CSMM is able to migrate in comparison to the other CSMMs (the other two are less rigid, more mobile, and therefore may not reach the solution-air interface as quickly because they are already at semi-equilibrium). A discussion of the differences between the correlations found in Figure 4.6 and Figure 4.8 is found in Section 4.2.2.1.

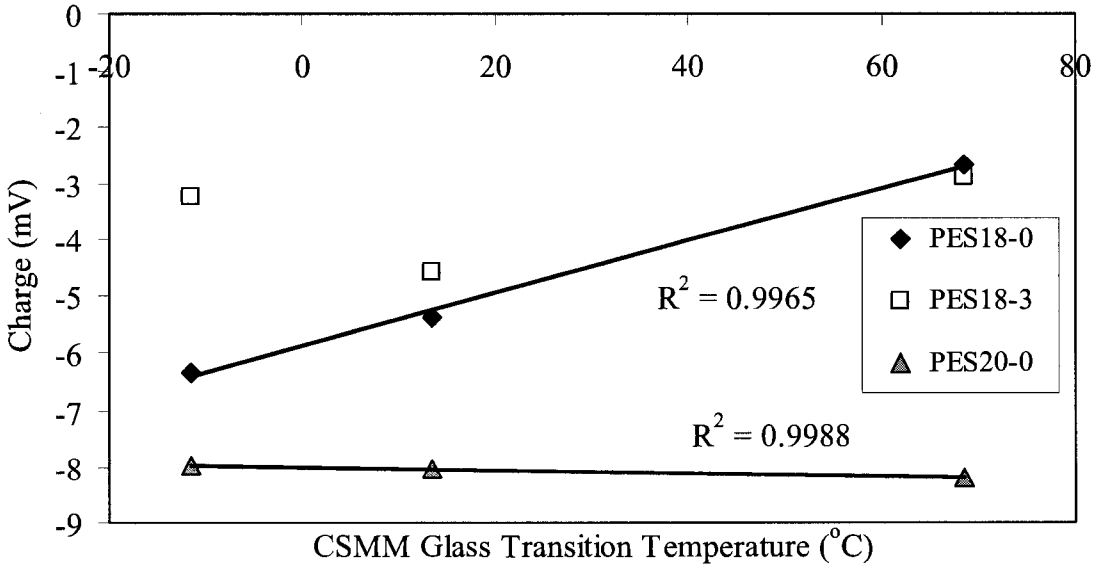


Figure 4.8: Effect of CSMM rigidity on modified membrane charge

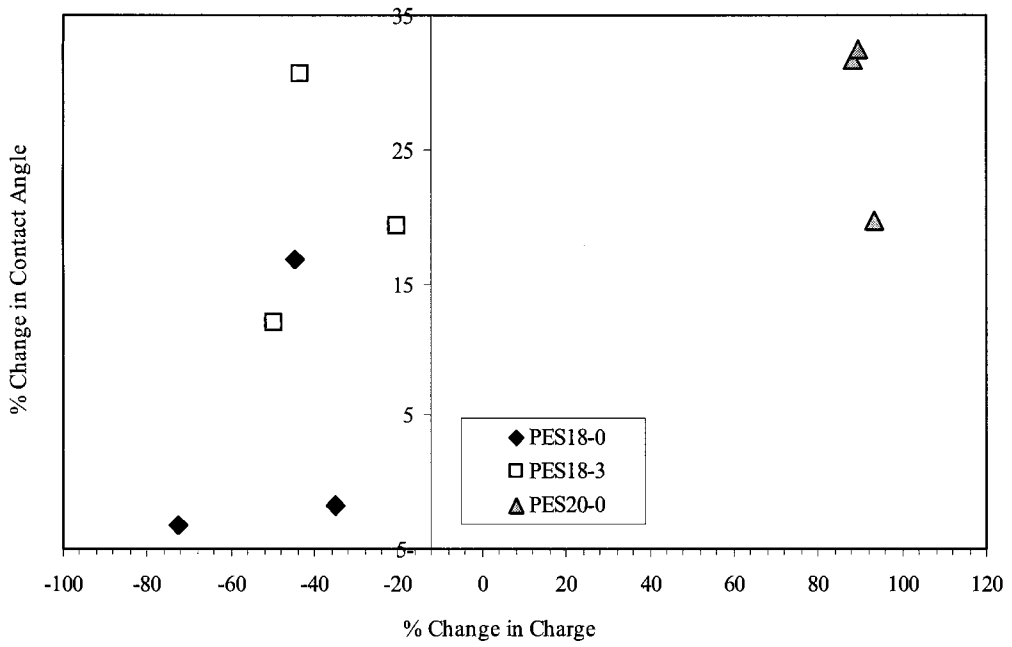


Figure 4.9: Change in charge and contact angle for CSMM-modified membranes at three casting conditions

Figure 4.10 illustrates the percentage change in charge from the PES18-0 casting condition for each of the modified and unmodified membranes. From this figure, the membranes containing CSMM-PPG and CSMM-PEG_{400} behave similarly: both decrease in charge with pre-gelation time and increase in charge with an increase in PES concentration (when compared to the PES18-0 condition). The decrease in charge seen at PES18-3 is also characteristic of the control membrane however this membrane also sees a decrease in charge with increasing PES concentration, which was not seen in the modified membranes. The similar behaviour of CSMM-PPG and CSMM-PEG_{400} may be attributed to the similar size (size based on molecular weight: 425 Da for PPG, 400 Da for PEG_{400} versus 200 Da for PEG_{200}) of the mid-segment of the CSMM. It is interesting to note that the change in charge with respect to the PES18-0 casting condition is increasingly positive (charge becomes less negative) in the following order: Control <

CSMM-PPG < CSMM-PEG_{400} < CSMM-PEG_{200}. This trend follows that of rigidity for the modified membranes, with PPG being the least rigid and PEG_{200} being the most, based on the glass transition temperature (Table 3.1). From this, one could conclude that increased rigidity yields more visible effects on membrane charge. It is also interesting to see the two-fold increase in charge in the case of CSMM-PEG_{200} at 20% PES. This may be due to the interactions between the polymer (PES) and the CSMM at the given solution conditions, resulting in more end-groups orientated at the surface, and thus a higher charge. CSMM-PEG_{200} is the least flexible CSMM, and therefore expected to be the least mobile in the more viscous solution (i.e., 20% PES) however it appears that the CSMM rigidity is aiding the orientation of the charged end-groups to the surface. Finally, the proportion of change for each modified membrane (Figure 4.10) shows that the effect of the CSMM is the same for each casting condition, but the magnitude of change, with respect to the control, is a function of the CSMM itself, likely from the rigidity or magnitude of charge. It would be interesting to measure the CSMM and PES charges to quantify this hypothesis.

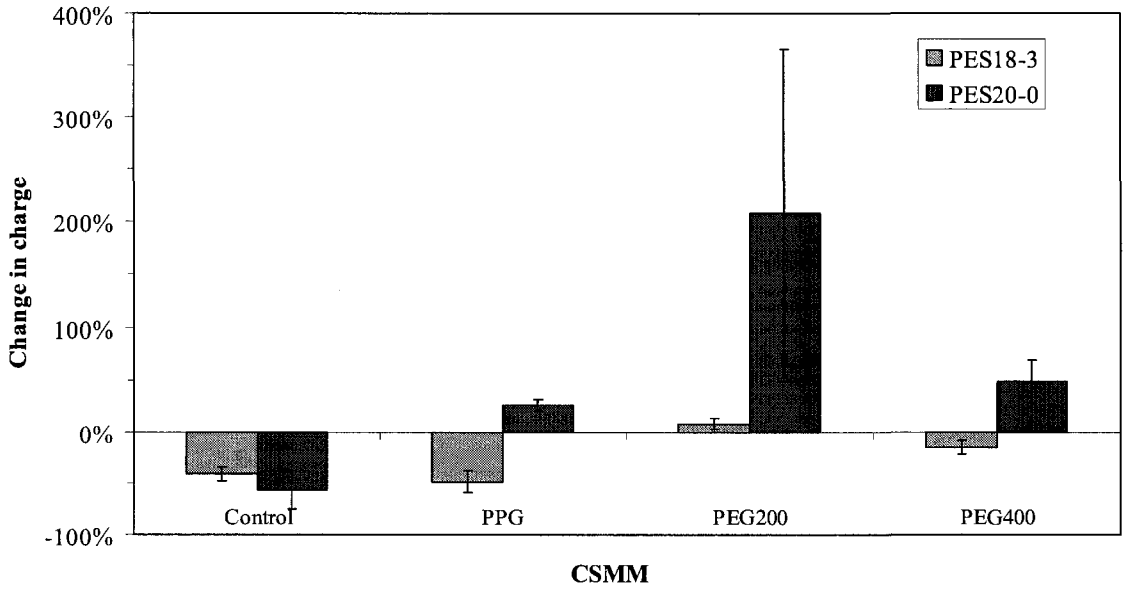


Figure 4.10: Percentage change with respect to the PES18-0 casting condition for each of the modified and unmodified membranes (i.e., PES18-3 PPG compared to PES18-0 PPG)

4.2.2.1 Effect of CSMMs on hydrophilicity and charge

Figure 4.11 shows a linear trend when comparing the charge and contact angle of all the modified and unmodified membranes. The increase in hydrophilicity with decreasing charge is expected. There is no distinct trend when comparing any given CSMM or the control membranes, however the general trend of decrease in contact angle with charge is clear.

It is also interesting to compare the correlations found when comparing charge and contact angle to rigidity. In Figure 4.8, correlations were found for charge and rigidity at the casting conditions without pre-gelation time (i.e., PES18-0 and PES20-0). Conversely, Figure 4.6 shows a clear trend of contact angle and rigidity for the casting condition with pre-gelation time and with increased PES content (i.e., PES18-3 and

PES20-0, respectively). It is interesting that the trends in Figures 4.6 and 4.8 are for different casting conditions (i.e., PES18-0 has no trend with contact angle; the trends for PES20-0 do not match up). The discrepancy between the trends for PES20-0 casting condition could be due to the high variability experienced with both characterization tests. Surface porosity and pore size distribution could also come into play as variables. As will be shown in subsequent sections, the surface porosity and pore size distribution of the modified membranes cast at the PES18-3 condition are the most constant, and therefore any variation in advancing contact angle from water adsorption in the pores, air in the pores or from surface roughness could virtually be eliminated (the surface porosity and pore size distribution is constant); the trend seen here is therefore a result of the CSMM and not membrane morphology – this is not certain for the other two casting conditions.

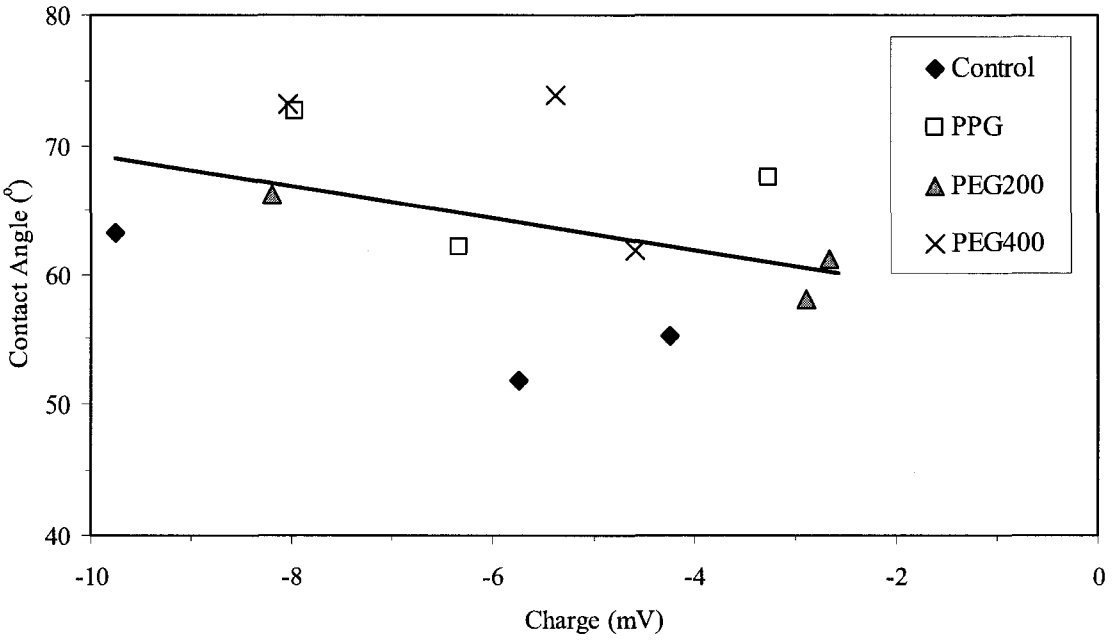


Figure 4.11: Variation in contact angle and charge for modified and unmodified membranes prepared at three casting conditions (PES18-0, PES18-3 and PES20-0) (linear trend is seen when all the data points are combined)

4.2.3 Membrane performance and characteristics

All flux and MWCO tests were carried out in triplicate. From the data, significant outliers were removed using the Dixon method, reducing all tests to duplicates. The procedures followed are detailed in Chapter 3. In summary, the flux was determined by the filtration of MQ water (in recycle) for two sets of membrane coupons (in triplicate) over 50 hours (following one hour of pre-compaction). The NSF was measured at 50 hours, when the membrane flux was constant. Following flux determination, probe solutes were filtered consecutively (with increasing MW) and their removal assessed in order to characterize the membrane MWCO, surface porosity and pore size distribution. Details on the development of the MWCO results are presented in Appendix C. This section will discuss the impact of CSMMs and the casting conditions on performance (as normalized standard flux measured at 50 h) and on membrane characteristics such as MWCO, surface porosity and pore size distribution.

4.2.3.1 NSF, MWCO and surface porosity

Figure 4.12 illustrates the effect of casting conditions and the impact of CSMMs on the normalized standard flux. The NSF of the control membranes is not comparable to work previously done by Nguyen et al. (2007) as they report a PWP that is four times higher than that obtained here. It is hard to pinpoint the flux discrepancy with Nguyen et al. (2007) since MWCO is comparable (as is the manufacturing technique). On the other hand, Dang et al. (2006) found a flux of 28 $L/m^2/h$, which is approximately half that reported here. This value is much closer to the one found here, and the method used is the same.

At PES18-0, the addition of 3% weight CSMM significantly decreased the flux. This is likely because the increase in total polymer created a denser and therefore less porous membrane, which did not allow as much permeation. The three minute pre-gelation time increased the flux of the CSMM blended membranes by three to four times. This indicates that despite the increase in polymer mass within the casting solution, the CSMM appears to have increased the surface porosity and is therefore increasing the flow through the membrane. This is confirmed by the correlation of contact angle and surface porosity (Figure 4.13), showing that the CSMMs have directly impacted surface porosity and therefore flux. It should be noted that a linear correlation is inferred due to the error of each measurement, allowing the linear trend to be traced within the error bars of each point. For the membranes cast at the PES20-0 condition, the effect of CSMM addition was not consistent: the flux was expected to decrease, similarly to those cast at the PES18-0 condition. The higher polymer concentration in the PES20-0 casting solution would yield a casting solution with higher viscosity which would hinder CSMM migration. This was only found with the CSMM-PEG_{200} (at PES20-0) membrane. The CSMM-PEG_{400} and CSMM-PPG membranes (at PES20-0) both showed flux increases of 165% and 285%, respectively. The explanation for this effect may lie in the relative properties of these CSMMs (specifically the size and rigidity of CSMM-PEG_{200} versus CSMM-PEG_{400} and CSMM-PPG). Larger pores and/or increased surface porosity increased the flux, and may have been due to lower rigidity of the larger CSMMs (i.e., CSMM-PPG and CSMM-PEG_{400} versus CSMM-PEG_{200}). Since no correlation of flux and charge is evident, especially for CSMM-PEG_{200}, it is likely that the change in flux is due to the change in membrane morphology.

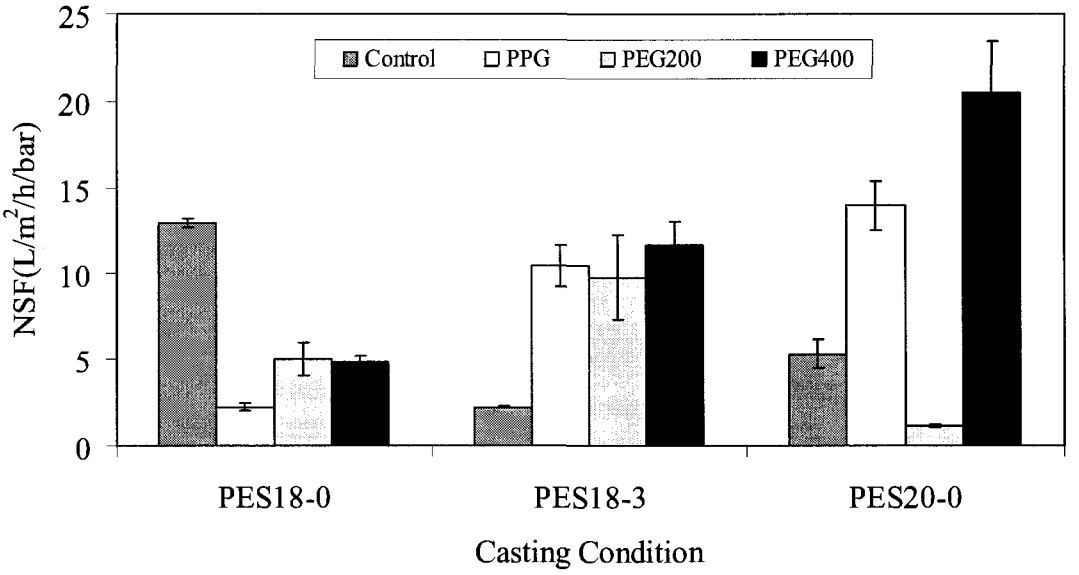


Figure 4.12: Effect of casting condition and CSMM on normalized standard flux

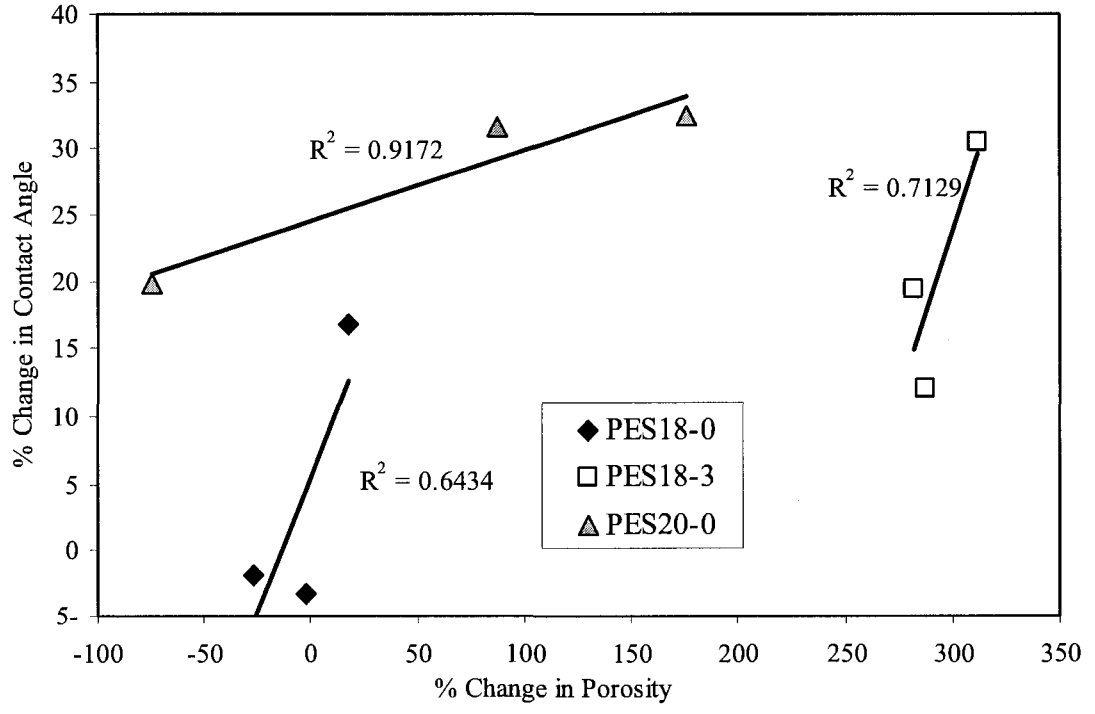


Figure 4.13: Change in surface porosity and contact angle of CSMM modified membranes from control membranes

The effect of these casting conditions and CSMMs on flux may also be explained by the impact on the molecular weight cut off (Figure 4.14). The CSMM blended membranes cast at PES18-0 had smaller MWCOs with respect to the control whereas the three minute pre-gelation time increased the MWCO. These trends correlate to those seen with the flux; however the proportion of change is not the same. For example, at the PES18-0 condition, the MWCO of the CSMM-PPG membrane is almost twice that of the CSMM-PEG_{400} membrane, however the flux of the CSMM-PPG membrane is half that of the CSMM-PEG_{400} membrane. Finally, at the PES20-0 condition, the membranes behave unexpectedly in that the flux increases with decreasing MWCO (i.e., for MWCO, CSMM-PEG_{200} > CSMM-PPG > CSMM-PEG_{400}, whereas for flux CSMM-PEG_{200} < CSMM-PPG < CSMM-PEG_{400}). However, such a deviation makes the membranes more promising for the removal of PhACs and EDCs; the CSMM-PEG_{400} membrane cast at PES20-0 is the most promising as it has the lowest MWCO and highest NSF. It is also important to remember that MWCO is a key characteristic of UF membranes, in order to define retention of larger solutes. For the removal of PhACs and EDCs, it is apparent that the MWCO of the experimental UF membranes is too large since the target solutes are significantly smaller, i.e., 200 to 300 Da. For this reason it is imperative the UF membranes tailored in this project have additional properties (i.e., charge) which might facilitate the removal via charge repulsion.

Based on earlier work by our group, it was expected that both having a pre-gelation time and increasing the PES concentration to 20% would lead to membranes with smaller MWCOs (Mosqueda-Jimenez, 2003). This pattern was followed by the control

membranes; the membranes with additives had different patterns which appeared to be dependent on the casting conditions. The deviation of the modified membranes from the expected trend may also be associated with the type of SMM (i.e., charged versus hydrophobic), and many other environmental factors.

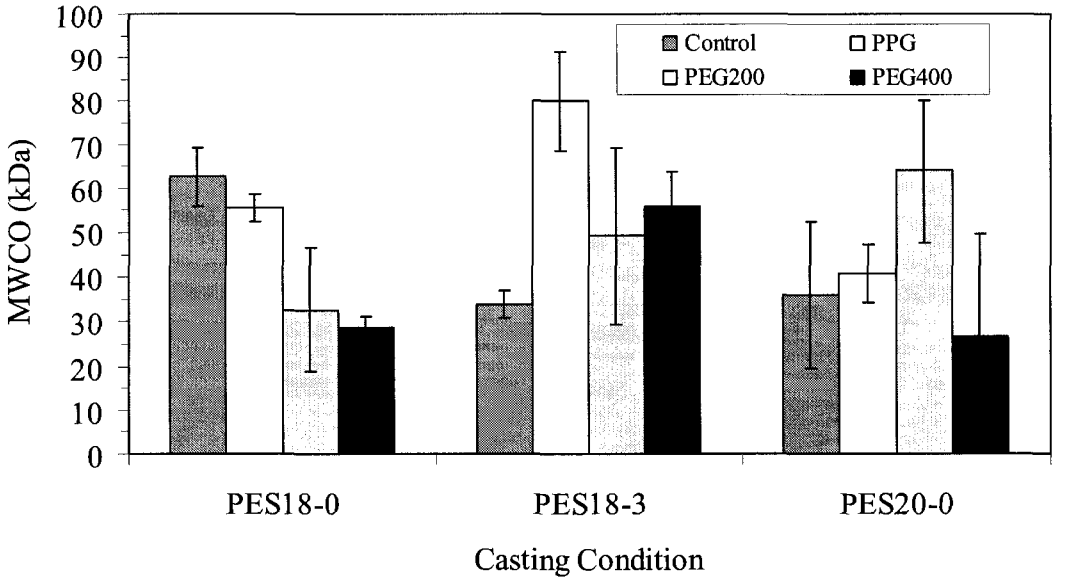


Figure 4.14: Effect of casting condition and CSMM on molecular weight cut off

The effect of the casting conditions and the three CSMMs on the flux and MWCO are summarized in Figure 4.15. Generally, the addition of 3% weight CSMM at 18% PES decreased both the flux and MWCO with respect to the control. Given the three minute pre-gelation time, the effect of the CSMMs was the opposite, increasing both flux and MWCO. For the PES20-0 condition, a similar trend to the PES18-0 was expected. However the addition of CSMM-PEG_{400} and CSMM-PPG translated in increases in flux and decreases in MWCO, whereas the addition of CSMM-PEG_{200} had the opposite effect,

decreasing flux and increasing MWCO. Since there is no clear pattern, the casting condition seems to be critical.

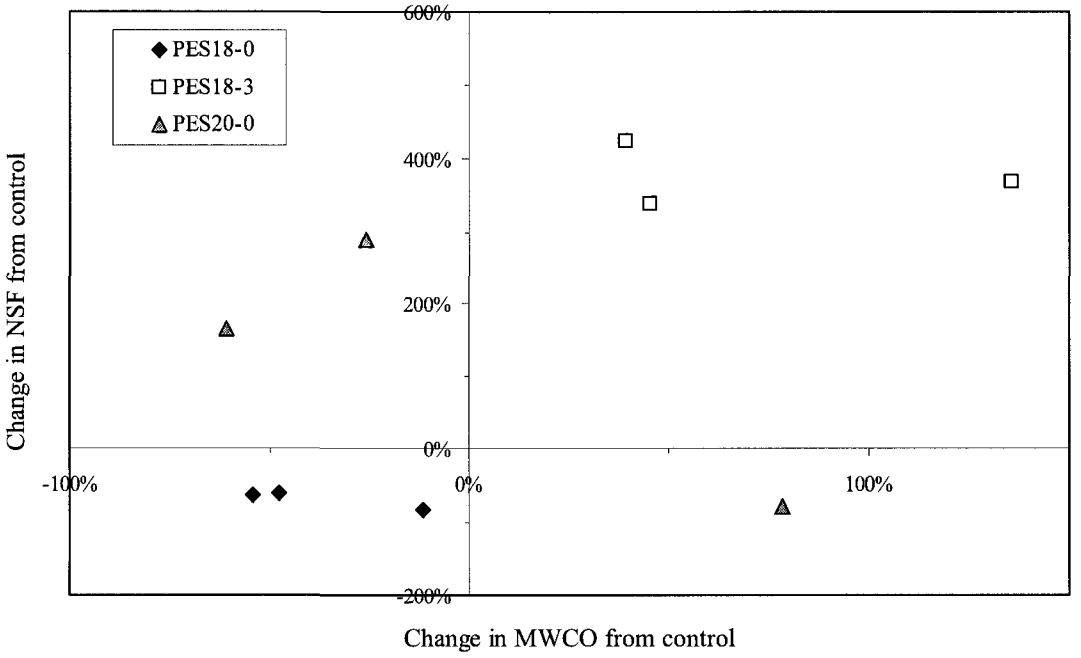


Figure 4.15: Change in MWCO and NSF with respect to controls

As discussed above, it was expected that a larger MWCO result in larger fluxes (larger pores allowing more fluid to flow through) however the surface porosity (or total pore area) of the membrane must also be accounted for. The difference lies in that a given level of surface porosity of a membrane may arise from a smaller number of larger pores (i.e., larger MWCO). Membrane porosities are presented in Table 4.1. In general, the addition of CSMMs has increased surface porosity (exception: CSMM-PEG_{200} at PES20-0). The increase is most significant at the PES18-3 conditions, indicating that the pre-gelation time has a significant effect on membrane surface porosity. Unfortunately, denser membranes were not examined with pre-gelation time. It is recommended that in future studies CSMM-blended membranes with increased PES content (i.e., 20% PES or

more) be tested with pre-gelation time. The increased PES content may decrease pore size, but the pre-gelation time will improve surface porosity, thus achieving tight ultrafiltration membranes with high flux.

Table 4.1: Porosities of CSMM modified and unmodified membranes at three casting conditions

CSMM	Casting Condition		
	PES18-0	**PES18-3**	**PES20-0**
Control	1.60%	1.22%	2.28%
CSMM-PPG	1.18%	5.05%	4.28%
CSMM-PEG_{200}	1.57%	4.74%	0.58%
CSMM-PEG_{400}	1.89%	4.68%	6.31%

As shown below (Figure 4.16), the surface porosity of the membranes correlates well with the flux for the modified membranes.

Comparing the change in surface porosity to the change in flux from the modified membranes to the control, Figure 4.16 shows the expected linear trend. This is clearly different than what was observed when comparing the change in MWCO and flux and confirms the effect of surface porosity on flux. It is interesting to note, however, the quantity of change for each condition. In the case of the membranes prepared with a three minute pre-gelation time, the increase in surface porosity and flux is significant, approximately 300% and 400%, respectively, and similar for the three CSMMs. The effect on the membranes cast at the PES18-0 condition is also consistent for all three CSMMs, with a similar surface porosity to the control (-26% to 17%) and a decrease in flux (-83% to -61%). A decrease in flux is generally unexpected for more hydrophobic surfaces, however some studies report the opposite trend (decrease in flux for more hydrophilic surfaces) (Nguyen et al., 2007; Amy et al., 2001), which correlates somewhat

with the slight decrease in contact angle for two of these membranes (with respect to the control).

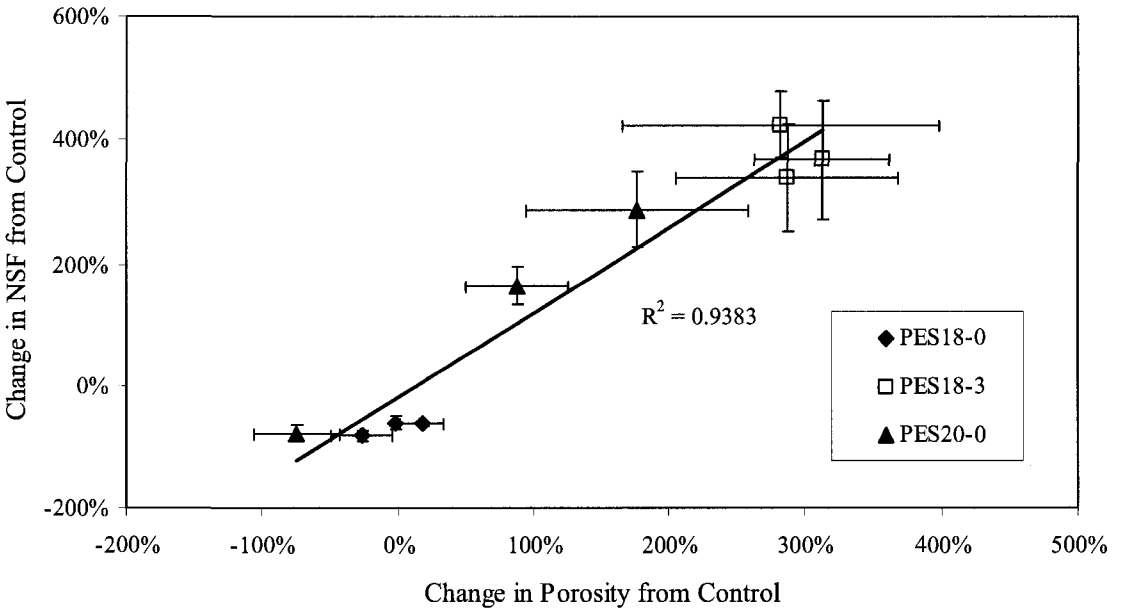


Figure 4.16: Comparison of the change in surface porosity and flux in CSMM-blended membranes with respect to control membranes

Dissimilarity in membrane characteristics for the three CSMM-modified membranes is clearly seen with the PES20-0 condition – the change in surface porosity and flux is not consistent for the three modified membranes (Figure 4.16). It is interesting that this effect is seen only for the membranes with 20% PES, however consistent with other results (i.e., the CSMM modified membranes all behave differently at the PES20-0 condition, as for charge). One would expect that this may be because with 20% PES, the solution is more viscous, and therefore migration of the CSMMs is hindered in comparison to only 18% PES in solution, however, based on results of contact angle and charge, it appears the effects of migration are more pronounced at this condition. Again, the decrease in flux for the modified PES20-0/CSMM-PEG_{200} membranes correlates with the increase of

hydrophilicity whereas the increase in flux corresponds to the membranes which showed an increase in hydrophobicity, as shown in Figure 4.17 by the change in contact angle and change in surface porosity (which is correlated to flux). Additionally, there is a linear trend between MWCO and surface porosity for the PES20-0 cast CSMM-membranes, as shown in Figure 4.18. The decrease in MWCO with increase in surface porosity was unexpected; however it is important to remember that the MWCO is not function of surface porosity but of the pore size distribution.

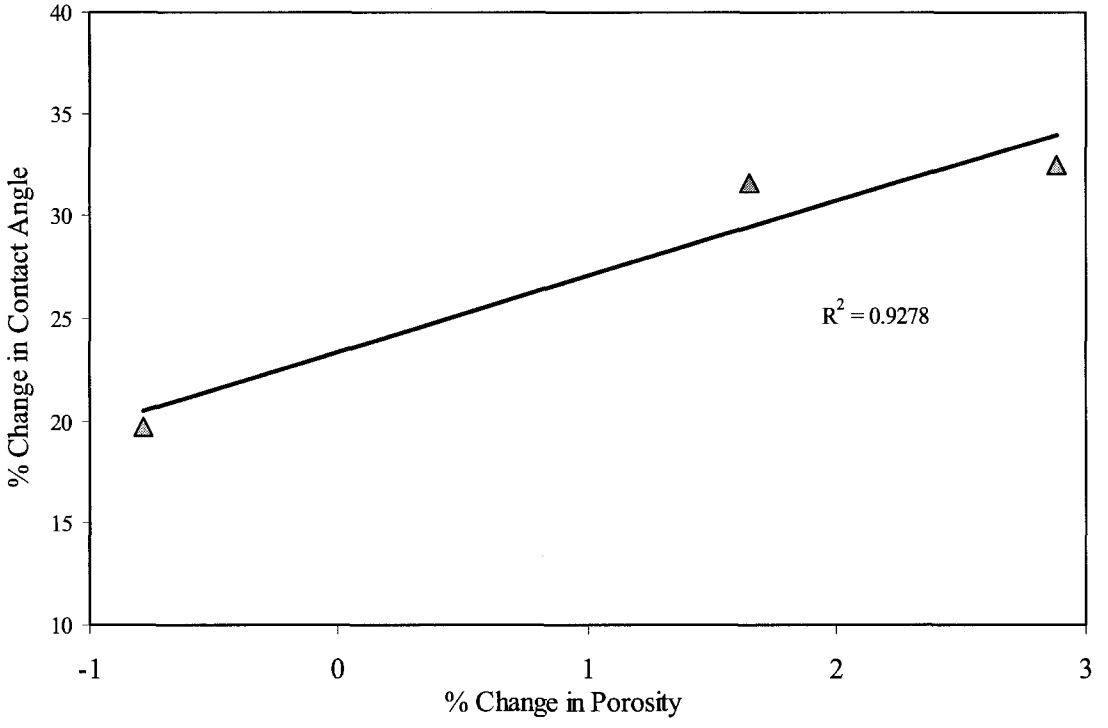


Figure 4.17: Change in surface porosity and contact angle with respect to the control PES20-0 membrane for CSMM-modified membranes made at PES20-0

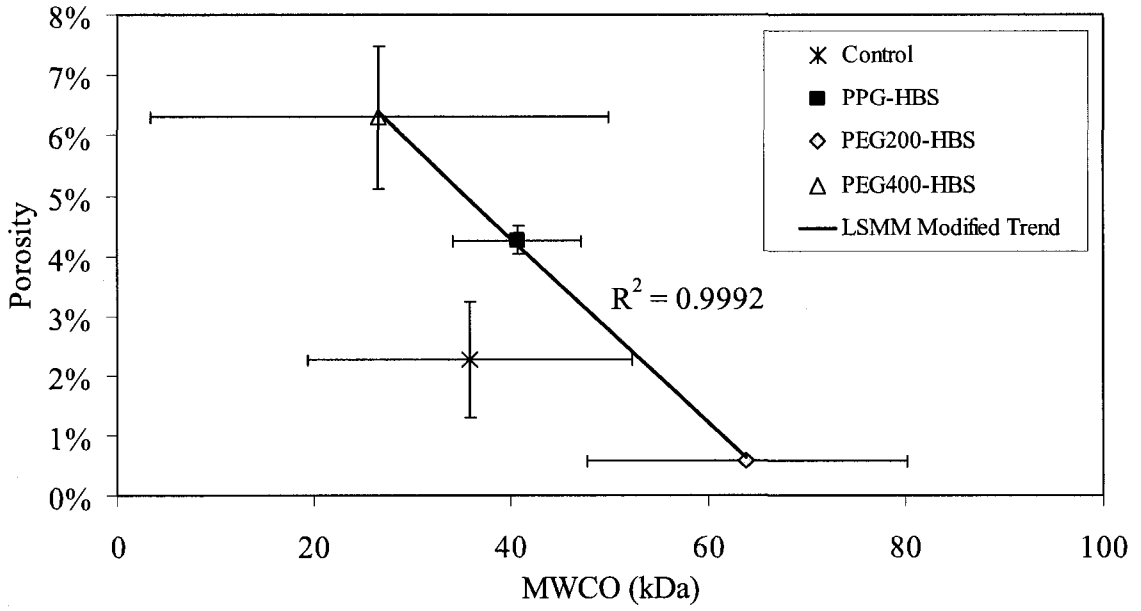


Figure 4.18: Variation in surface porosity with MWCO for CSMM-modified and unmodified membranes cast at PES20-0 (correlation for modified membranes only)

4.2.3.2 Pore size distribution

The pore size distribution is determined from the solute tests (that were also used to determine the MWCO). Mathematical development details of the hydrated pore model used are presented in Appendix C. Figure 4.19 shows the pore size distribution (probability density function of the solute diameter) of the modified and unmodified membranes for each of the casting conditions. At both the PES18-0 and PES18-3 casting conditions, the three CSMM-modified membranes deviate from the unmodified membranes, however the deviation for both casting conditions is different. In the first case (i.e., PES18-0), the addition of CSMM tightened the pores, and also reduced the distribution whereas with the pre-gelation time (i.e., PES18-3), the CSMM addition increased the pore size and the breadth of the distribution with respect to the control. An interesting observation is that for the PES18-0 casting condition, CSMM-PEG_{200} did not

behave exactly as CSMM-PPG and CSMM-PEG_{400}, creating a pore size distribution that is in between that of the modified and unmodified membranes. Also, the pore size was significantly reduced with the pre-gelation time for the control membrane (i.e., control in Figure 4.19a versus 4.19b). The pre-gelation time effect on pore size distribution for the PES18-3 CSMM membranes is variable; using CSMM-PPG, the mode pore size doubled and the distribution widened significantly, whereas with CSMM-PEG_{200} and CSMM-PEG_{400}, the pore size and distribution did not change significantly. The largest variation between the CSMM-modified membranes is at the 20% PES condition (Figure 4.19c). In this case, the pore size and distribution increase as follows: Control < CSMM-PEG_{400} < CSMM-PEG_{200} < CSMM-PPG. It is interesting that the pore size distribution follows this pattern, differing from those seen in flux, MWCO and surface porosity.

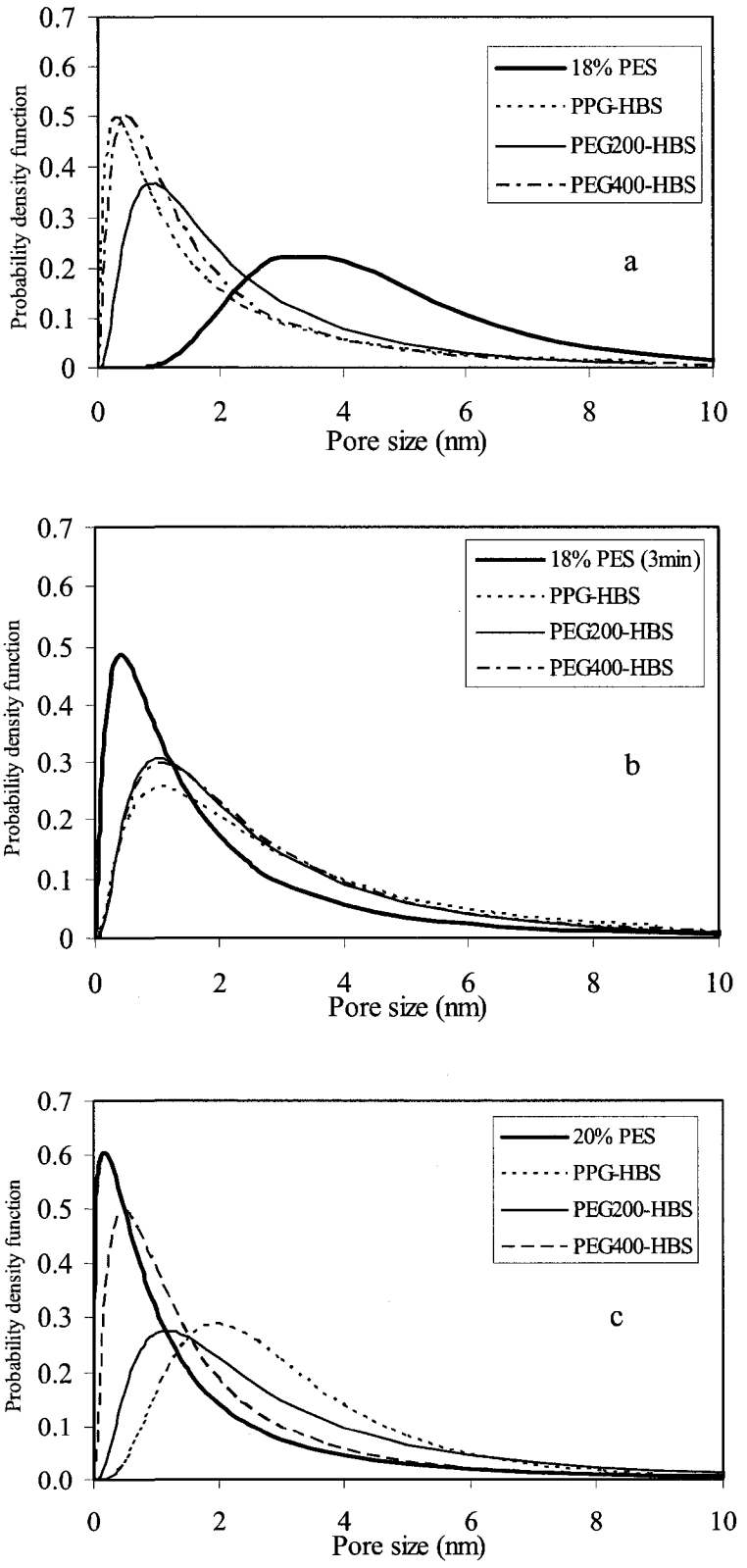


Figure 4.19: Pore size distribution of modified and unmodified membranes as a function of casting conditions (18%PES, 18%PES (3min) and 20%PES represent unmodified membranes) (**a:** PES18-0, **b:** PES18-3, **c:** PES20-0)

When comparing the three casting conditions for each CSMM and the control (Figure 4.20), the control behaves as expected, with pore size decreasing from PES18-0> PES18-3>PES20-0 (Figure 4.20a). This is not the case for the modified membranes, where three separate trends are observed. For the membranes with the CSMM-PPG additive, the membrane cast at the PES18-0 condition has the smallest pore size, and narrowest distribution, followed by the PES18-3 and PES20-0 conditions (Figure 4.20b). For this CSMM, the pre-gelation time and increase in PES concentration (to 20% PES in the casting solution) have similar effects – the breadth of the distribution increases, as does the mode pore size. On the other hand, for the membranes prepared with CSMM-PEG_{200}, the difference in pore size and distribution between the three casting conditions is minimal (Figure 4.20c), therefore the effect of PES concentration and pre-gelation time may be negligible. Finally, the membranes cast at PES18-0 and PES20-0 conditions with CSMM-PEG_{400} have almost identical pore size distribution for the conditions, while the pre-gelation time increased the pore size and distribution (Figure 4.20d).

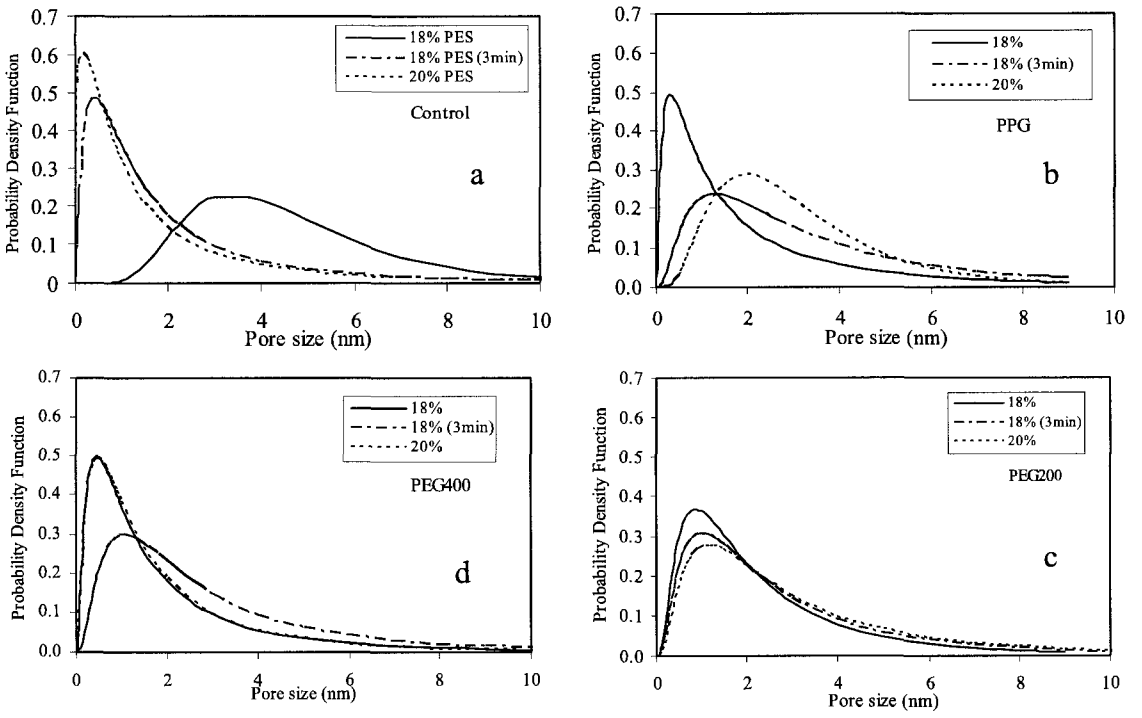


Figure 4.20: Pore size distribution variation with casting condition for each CSMM (**a:** Control, **b:** CSMM-PPG, **c:** CSMM-PEG_{200}, **d:** CSMM-PEG_{400})

In summary the impact of CSMM addition on the pore size distribution was very dependent on the CSMM itself and the casting conditions. Only the CSMM-PEG_{200} was not impacted by the casting conditions and the impact of the casting conditions for the modified membranes was quite different from the controls.

4.2.3.3 Impact of charge and hydrophilicity on flux

In order to better assess the effect of CSMMs, the flux and hydrophilicity of modified membranes are compared (Figure 4.21). As discussed previously, it is generally expected that a more hydrophilic surface yield higher flux, however this is not always the case. In this case, the pattern is not statistically significant for the PES18-0 and PES18-3 conditions. A clear decrease in flux with increased hydrophilicity is seen with the PES20-

0 condition, again corresponding to the results of Nguyen et al. (2007). The high contact angle variability on the membranes cast at PES18-0 and PES18-3 is possibly the cause of the scatter in the data (see Appendix G for the figures which include the standard deviation): by improving the accuracy of contact angle measurement technique, the expected trends may become more distinct.

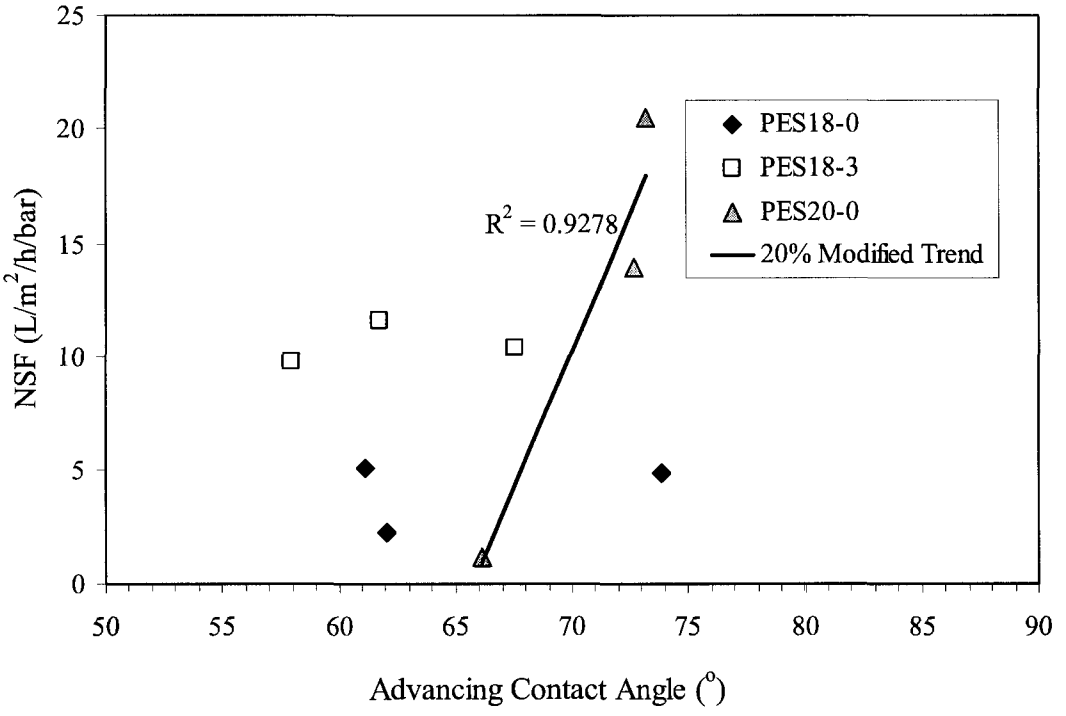


Figure 4.21: Comparison of advancing contact angle and NSF at three casting conditions for CSMM modified membranes

The relationship between flux and charge for the modified membranes is illustrated in Figure 4.22 and yields more distinct trends than the correlations between flux and hydrophilicity, however these trends are not consistent for the three casting conditions. This indicates that charge does not significantly impact flux: flux is more likely influenced by the surface porosity (as shown previously).

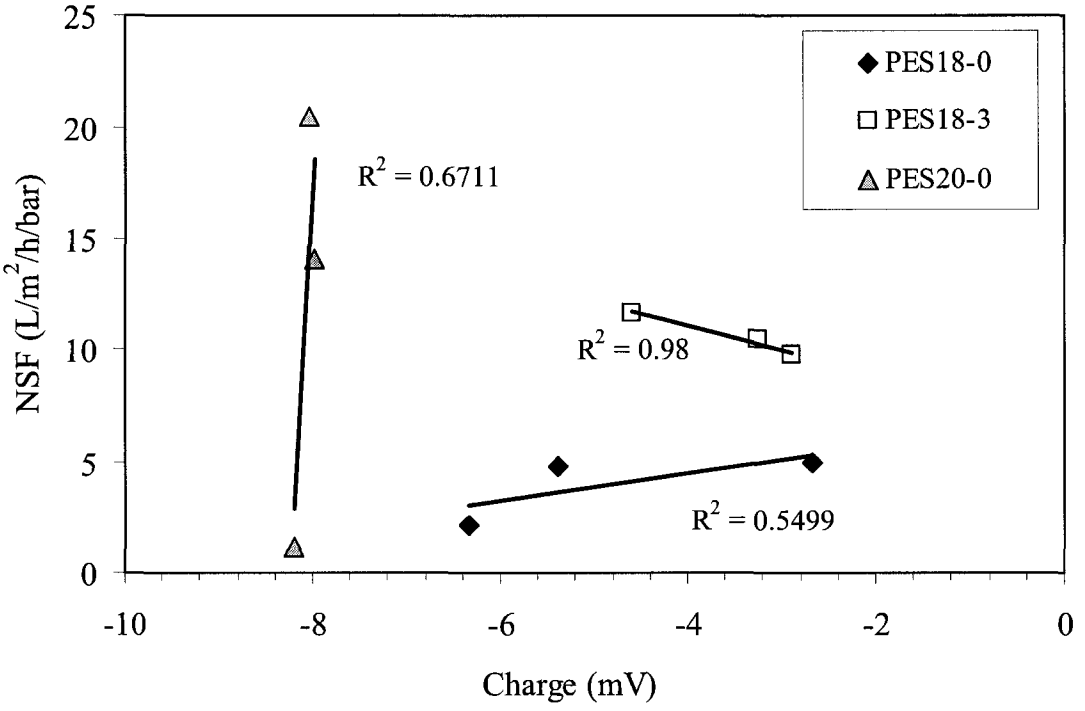


Figure 4.22: Comparison of charge and NSF at three casting conditions for CSMM modified membranes

When comparing the flux with charge and contact angle as a function of the CSMMs (as opposed to casting conditions) positive and negative linear trends are found with contact angle (Figure 4.23). From Figure 4.23 one can conclude that CSMM-PPG behaves similarly to the control whereas CSMM-PEG_{200} behaves in an opposite manner. Both CSMM-PPG and the control increase in flux with increasing hydrophobicity, a trend generally not expected whereas CSMM-PEG_{200} decreases in flux with increasing hydrophobicity. Unfortunately, the data is inconclusive for CSMM-PEG_{400}, which may be due to the high error associated with the contact angle test. Based on these results, it could be assumed that the PPG mid-segment behaves similarly to PES, or is inhibited by it whereas the PEG_{200} mid-segment changes the base-polymers' effect on flux. This could be attributed to the relative rigidity of the two CSMMs. If this were the case, the CSMM-

PEG_{400} should behave somewhere in the middle, however it is not clear at this point whether or not it does. Again it is recommended to carry out additionally studies with more casting conditions and CSMMs in hopes of confirming the trends with more data points.

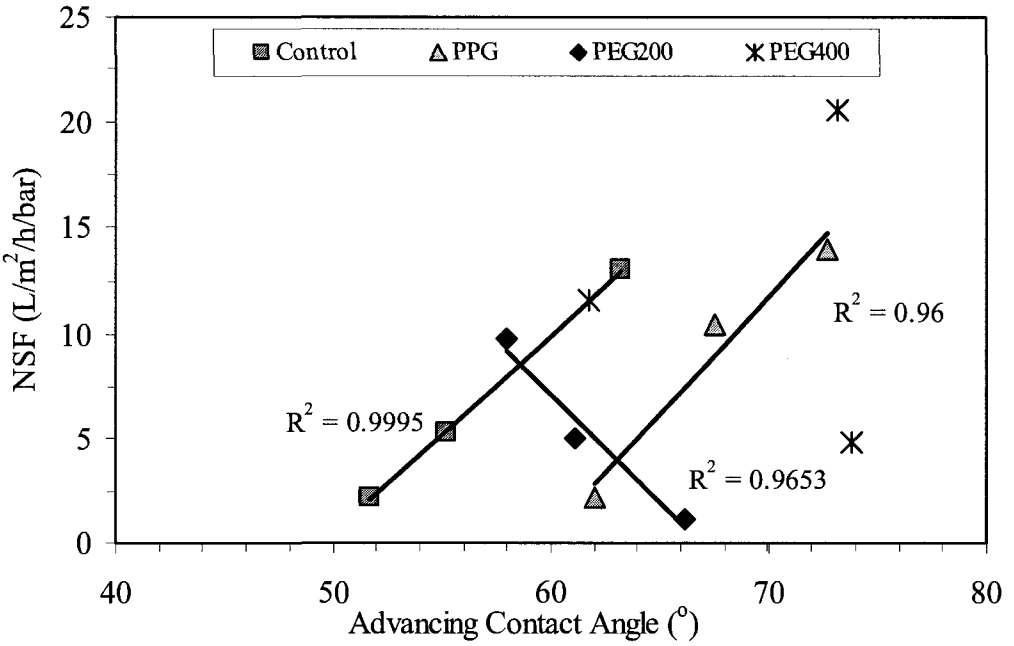


Figure 4.23: Effect of hydrophilicity on flux for modified and unmodified membranes

4.3 Performance of CSMM blended membranes on removal of PhACs and EDC

4.3.1 Removal of PhACs and EDC

The removal of three target PhACs (SMZ, CBZ and IB) and one EDC (BPA) was assessed via the filtration of 10 mg C/L solutions over the course of four hours. The solutes were tested in order of increasing log K_{OW} (Table 3.2): SMZ, CBZ, BPA followed by IB. Prior to each solute test, the system was flushed with MQ water.

Figure 4.24 presents the removals for two coupons of the membranes cast at the PES18-0 condition using CSMM-PEG_{200}. While there are differences in the removals between the two coupons, the order of the compound removal (maximum to minimum) remains the same. Initially, the target solutes are partially removed; however after approximately one hour of filtration, the target solutes are no longer significantly removed. This trend is characteristic of all membranes tested and their removal graphs are presented in Appendix H. It does, however, differ significantly from the trend seen with the NF270 (Dow/Filmtec) commercial thin-film composite nanofiltration membrane (Figure 4.25), where removal only decreases slightly. It should be noted that the two points obtained for the NF270 are due to the lower flux (and therefore less sample collected when compared to the previous membrane). A longer filtration test could yield more information into the validity of these high removal rates. Few studies have published removal rates specifically for NF270; Nghiem et al. (2004a) found the removal of BPA to be between 45 and 55% by filtering solutions containing NOM while in another study (2004b) they found CBZ and IB removed at approximately 84 and 99%, respectively. The initial results achieved here and those published by Nghiem et al. (2004a, b) show that this commercial thin-film composite nanofiltration membrane significantly outperforms the experimental tight ultrafiltration membranes developed in this study. The higher removals of the NF270 are not surprising given that it has a significantly smaller MWCO (i.e., 200 Da) than experimental membranes (i.e., MWCO >10,000 Da). For comparison purposes, and to examine correlations between removal and the different modified membranes and properties, the initial removal of each membrane will be compared.

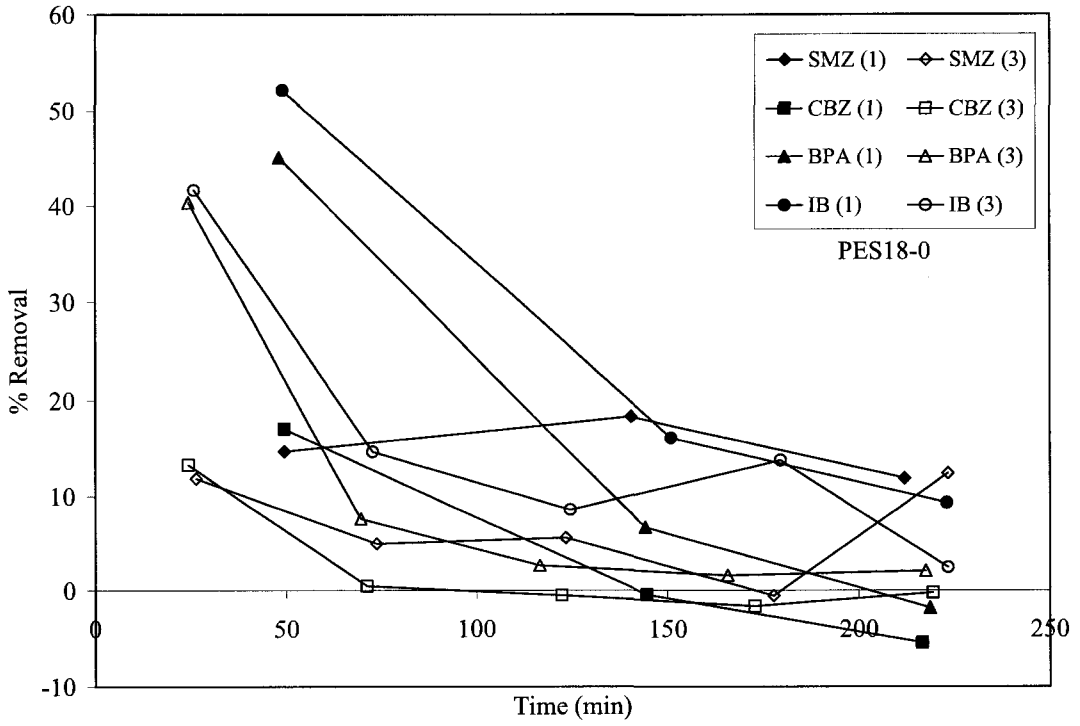


Figure 4.24: Removal of target solutes (duplicate) for PES18-0 CSMM-PEG$_{200}$ membrane

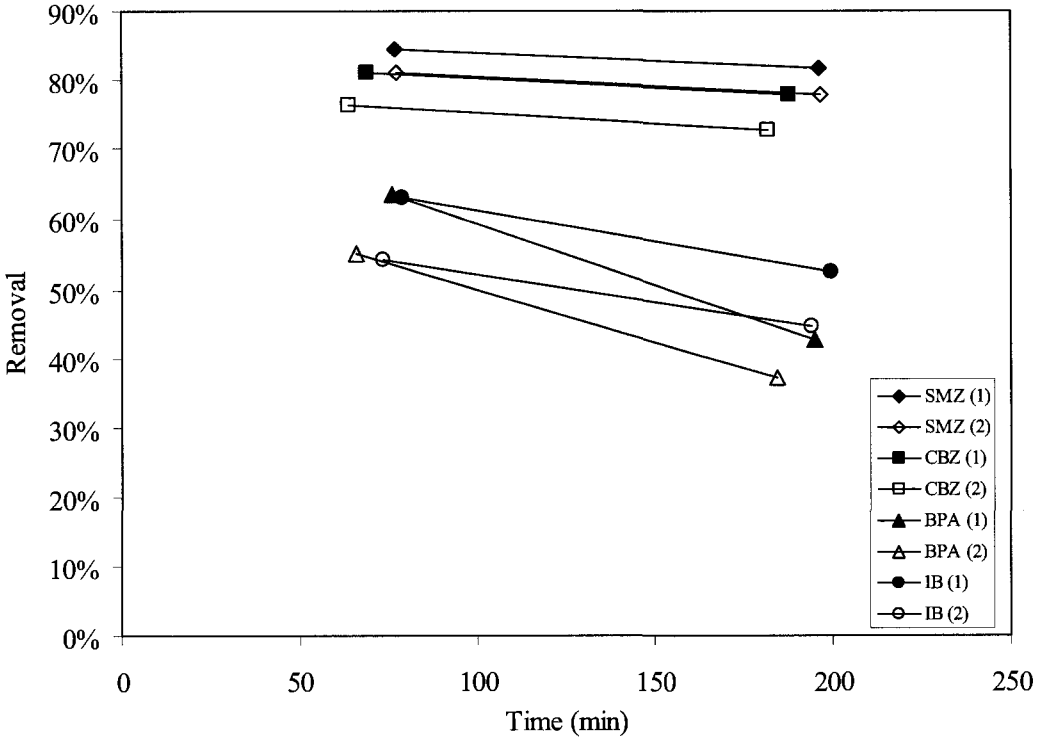


Figure 4.25: Removal of target solutes (duplicate) for NF270 (Dow/Filmtec)

From Figure 4.26, it appears that BPA and IB are removed better than SMZ and CBZ. Initial removal ranges from -25.3 to 16.3%, -0.9 to 28.9%, 18.5 to 73% and 16.9 to 53.4% for SMZ, CBZ, BPA and IB, respectively. The negative removals of SMZ (tested first) and CBZ (tested second) are presumed to be caused by a timeline which includes removal right at the start of the test followed by desorption into the filtrate due to competition with stronger adsorbing PhACs (that were adsorbed earlier in the testing sequence and not removed during the rinsing/flushing cycle), this is frequently referred to as the chromatographic effect. In the case of SMZ, the chromatographic effect may have been caused by residual PEG or PEO from the MWCO solute tests. Generally, however, initial removals are around 6%, 9%, 40% and 30% for SMZ, CBZ, BPA and IB, respectively. The better removal of BPA and IB in comparison to SMZ and CBZ can be explained by plotting the initial removal as a function of the compound log K_{OW}. From Figure 4.27 two general trends can be seen: removal reaches a maximum at bisphenol A and removal increase with log K_{OW}. The latter trend was expected for all membranes, however only occurred with the CSMM-PPG membranes (at all three casting conditions). The trend seen with the CSMM-PEG_{200} and CSMM-PEG_{400} additives was unexpected however could be attributed to two different mechanisms. Either there is a maximum removal as a function of log K_{OW} (around the log K_{OW} of BPA) or IB is weakly adsorbed due to competitive adsorption with the more strongly adsorbed BPA.

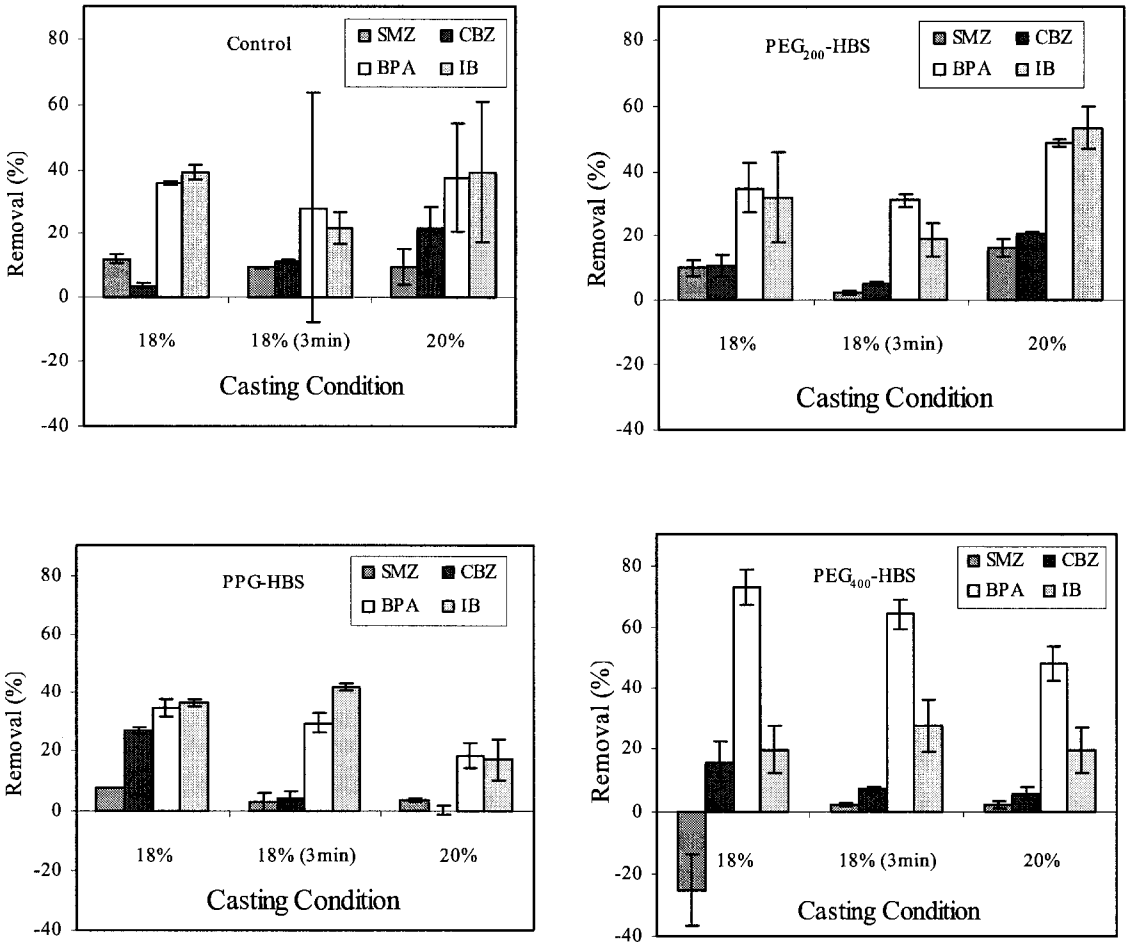


Figure 4.26: Initial removal of PhACs and EDC for modified and unmodified membranes as a function of casting condition

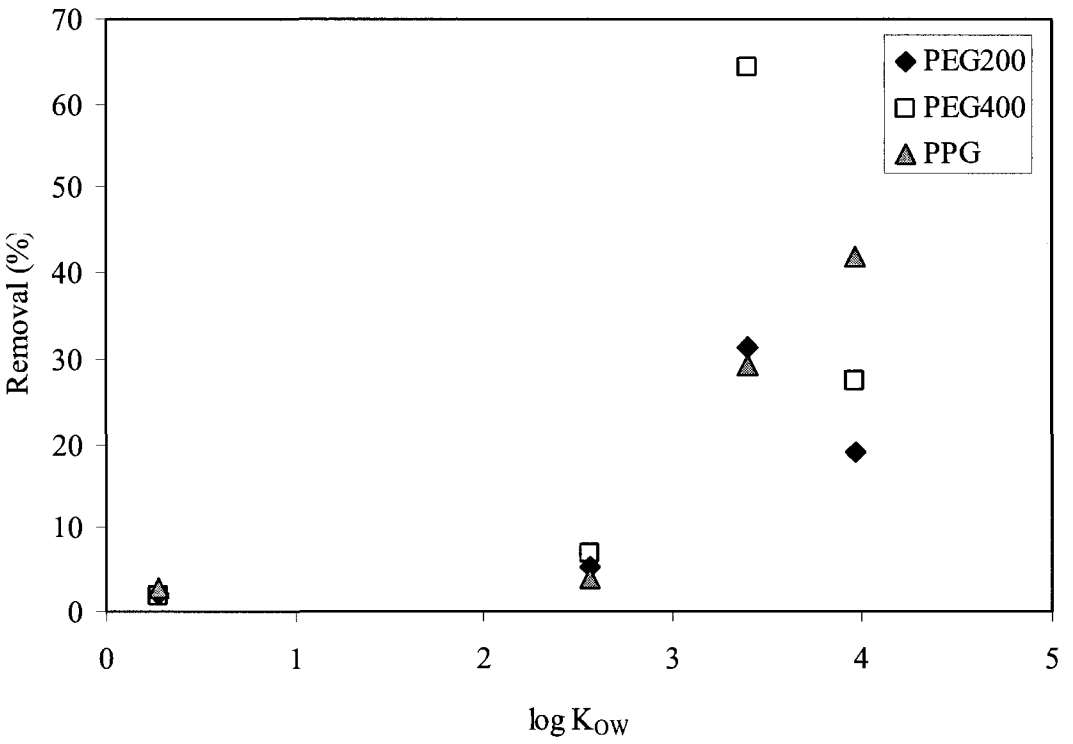


Figure 4.27: Initial removal as a function of log K_{OW} for PES18-3 condition

Figure 4.28 illustrates the initial removal performance of all the membranes for the four target solutes at the three casting conditions. For SMZ, the control exhibits a higher initial removal than the modified membranes. When compared to the modified membranes, the control membranes have worse initial removal at the PES18-0 casting conditions and perform significantly better at the PES18-3 and PES20-0 casting conditions. Initial removal of BPA is comparable for the controls and the modified membranes at PES18-0 and PES18-3 conditions with the exception of the CSMM-PEG_{400} membrane, which performs better. On the other hand, the PES20-0 cast CSMM-PEG_{400} membrane has comparable BPA removals to the control (at PES20-0) membrane in terms of initial removal (whereas the membranes incorporating the other two CSMMs have lower performances at PES20-0). Finally for IB, the initial removal does not follow any specific

trend with respects to the different casting conditions. From these graphs, it may be possible to conclude that overall the CSMM-PPG and CSMM-PEG_{400} additives perform better when compared to the CSMM-PEG_{200}. They do not however significantly out-perform the control membrane.

These figures also illustrate the removal variability between casting conditions for the different CSMM modified membranes. None of the CSMMs or casting conditions yield distinctive trends regarding the removal of the four target compounds. The only significant relationship derived from these tests is that the initial removal of the target compounds is related to log K_{OW}. In order to identify any potential trends, initial removal is compared to membrane characteristics in the following section.

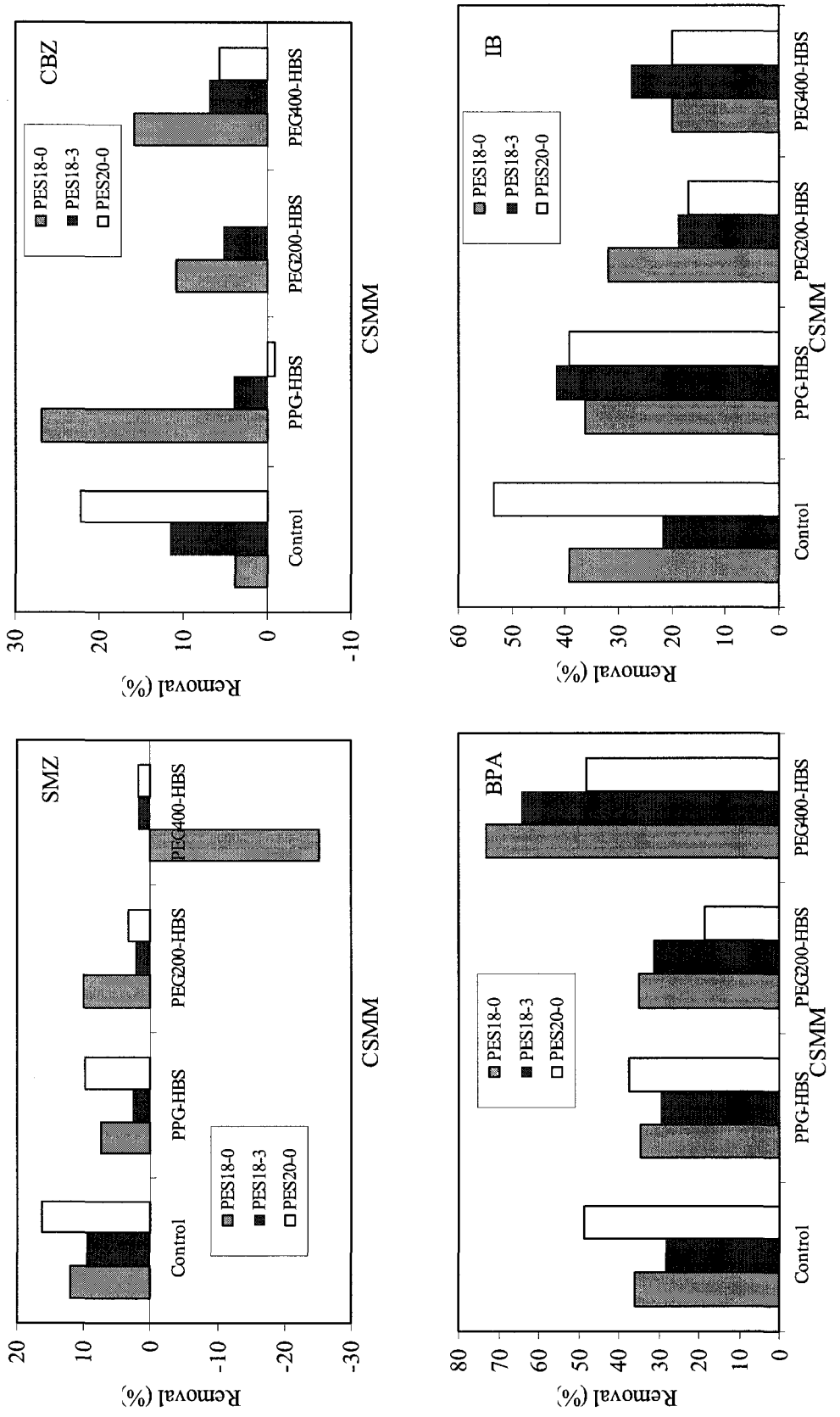


Figure 4.28: Initial removal of three PhACs and one EDC as a function of membrane and casting condition

4.3.2 Membrane characteristics and removal

In an attempt to explain the variation in initial removal for the different membranes, initial removal was compared to flux, MWCO, pore size, surface porosity, surface charge and contact angle. Most comparisons did not yield any correlations (Appendix I). Unfortunately, there appears to be no correlation between initial removal and charge; from this the initial removal mechanism cannot be charge repulsion, and is most likely adsorption onto the membrane.

4.3.3 Removal via adsorption onto the membrane

To quantify the mass of solute adsorbed by the membranes, mass balances were performed on the results of the filtration tests for BPA and IB solutions and compared to the baseline adsorption results. The details of the mass balance calculations are presented in Appendix J. Adsorption of SMZ and CBZ was assumed to be too small to quantify and therefore no mass balance was performed on these membranes. Figures 4.29 and 4.30 illustrate the mass adsorbed of BPA and IB, respectively, in comparison to the mass adsorbed for the baseline tests. It was expected that the mass of solute adsorbed to the membranes be greater than the baseline. This was not the case for IB or BPA, the mass adsorbed surpassed the baseline later than expected (it was expected to initially be greater than the baseline since the membrane provided additional surface area). It is unclear at this point what the source of the discrepancy is, however the difference may lie in the exposed areas of the system. During the baseline adsorption test, there were no membranes in the system and the solution was recycled via the permeate and retentate lines to the feed tank. When the membrane filtration experiments were run, most of the

permeate was collected for analysis, and therefore the permeate did not recycle back to the feed tank via the permeate lines. It is possible that the difference in available sites be due to the larger surface area during the baseline test (from the permeate lines). In order to properly assess the system baseline adsorption, a "surrogate membrane" (onto which a known amount (or no amount) of solute would adsorb) would need to be inserted in the system. When the baseline adsorption tests were initially attempted, aluminum plates were tested for use as membrane replacements, however they were found to oxidize and it was concluded that leaving these plates in the system may cause more harm than good. In retrospect, a satisfactory substitute should have been used.

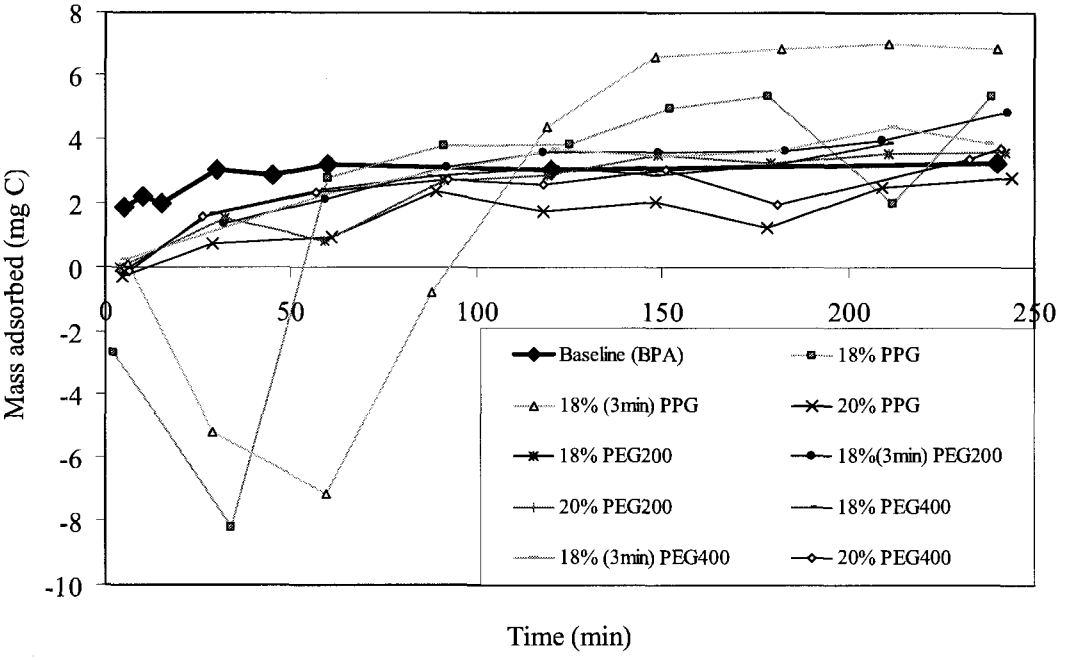


Figure 4.29: Mass of BPA adsorbed for filtration tests in comparison to baseline adsorption

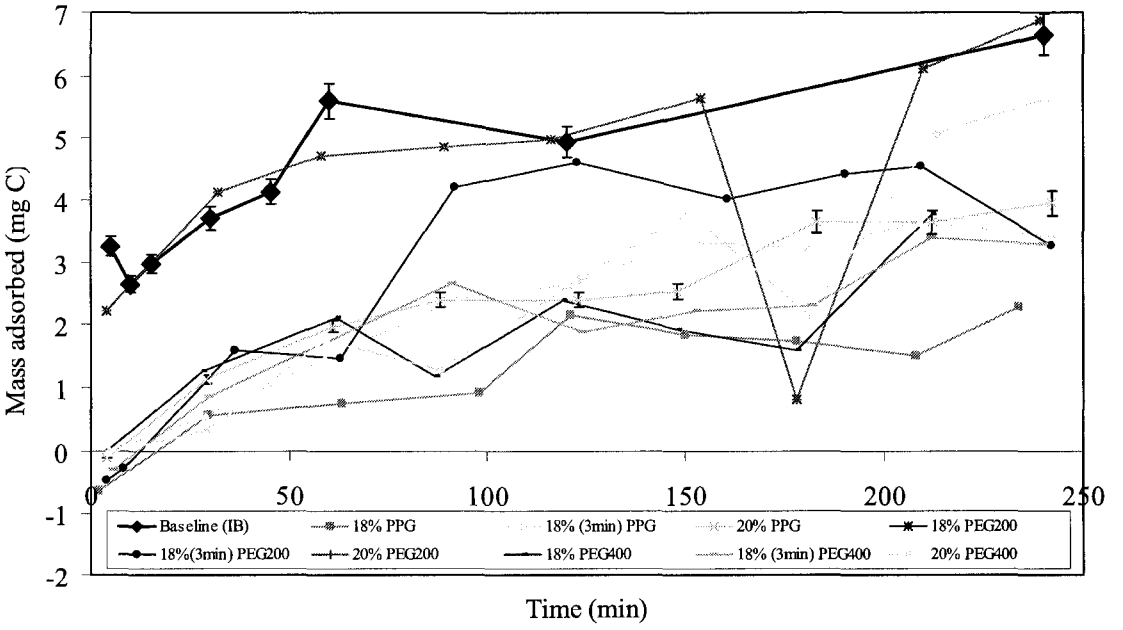


Figure 4.30: Mass of IB adsorbed for filtration tests in comparison to baseline adsorption

Due to the unexpected trends seen in Figures 4.29 and 4.30, the mechanism associated with the high initial removal cannot be conclusively attributed to adsorption. Based on the removal curves, however, adsorption is likely the removal mechanism. It is recommended that further system characterization be conducted in order to confirm these hypotheses. Additionally, membrane batch adsorption tests could be conducted to assess the level of adsorption to the membranes.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

From the results of this thesis, the following general conclusions can be made:

1. The incorporation of the novel CSMMs with the experimental PES ultrafiltration membranes produced membranes that were tight and less charged than the control membranes, however they were not very successful in removing the PhACs and EDCs from ultrapure water. A tighter and more strongly charged membrane material is likely more promising and may be achieved at increased PES concentrations.

2. The initial partial removal of the PhACs and EDC by the experimental membranes was a function of increasing solute hydrophobicity. This is a significant indication that the initial removal mechanism is adsorption. Initial removal could not be linked to any other membrane properties evaluated.

3. The different experimental additives did not have clear impacts on membrane characteristics and performance that were consistent for all the membrane preparation conditions.

4. CSMMs tested generally produced less hydrophilic membranes at the PES18-3 and PES20-0 casting conditions when compared to the unmodified PES membranes. There is no significant impact of CSMMs on hydrophilicity at the PES18-0 condition. When CSMMs are incorporated in the membranes, it appears as though the CSMMs make the surface more hydrophobic, either due to increased roughness or due to the HBS end-cap. Characterizing surface roughness may confirm that the HBS end-cap is not the reason for decreased hydrophilicity.

5. Membrane charge decreased with respect to the control membranes at PES18-0 and PES18-3 however increased considerably at PES20-0. It appears the CSMMs developed for this study do not offer the significant variation in charge expected when compared to the base polymer used, PES. Additionally, the diverging effect of casting conditions on charge raises questions about i) the charge measurement procedure and ii) the effect of PES concentration on the strength of surface modification. The CSMMs used in this thesis were end-capped with HBS, performance may also be improved by developing new CSMMs with more highly charged end-groups.

6. Pre-gelation time appears to improve NSF for modified membranes. The pre-gelation time produced more porous membranes, without compromising pore size. The effect of pre-gelation time at increased polymer concentrations may yield the desired membrane properties: high flux (from high surface porosity) and high rejection (from tighter pores and increased CSMM effect).

7. Based on advancing contact angle results, CSMM migration is more pronounced with increased PES concentration (i.e., 20% PES versus 18% PES). The PES20-0 casting condition appears most promising as it generally produces tighter membranes and CSMM effects appear most prominently.

8. CSMM-PEG_{400} is the most promising CSMM based on flux and MWCO, especially at PES20-0. From removal results, both CSMM-PEG_{400} and CSMM-PPG achieve higher removals than CSMM-PEG_{200}, however the removals are not significantly greater than the control membranes. The strength or effect of the CSMMs on membrane surface characteristics (i.e., charge and contact angle) may not be sufficient to achieve charge repulsion; however the effect of the CSMMs on membrane morphology may lead to the desired properties for the removal of PhACs and EDCs.

5.1.1 Minor conclusions

Additional conclusions made over the course of this study are:

1. Temperature increases in the cell-in-parallel system were too significant to ignore and were adjusted using a shell and tube heat exchanger and a cold water recirculation bath.

2. Three minute migration, when compared to one and a half and five minutes appeared to yield the most promising flux and MWCO for the target application based on the results of CSMM-NDS and control PES membranes.

3. It is hypothesized that at 18% PES concentration, the CSMMs are at equilibrium in the casting solution, whereas at the 20% PES concentration, the need for the CSMMs to reach the lower surface free energy is greater because of the higher polymer concentration, and thus a more marked effect from the CSMMs is seen at this condition.

5.2 Recommendations

Over the course of this study, the following items were noticed and are recommended for future work and consideration:

1. From the literature review and results of this study, it can be concluded that due to the wide range of properties of PhACs and EDCs, it is impossible to select one key process to remove them all. Two solutions could be presented to remove these target solutes: i) developing and refining modifications to these membranes to improve removals, as seen in recommendations 2, 3 and 4 below ii) combining advanced technologies, such as ozonation or an AOP followed by membrane filtration. The purpose of combining oxidation with membranes would be to degrade the compounds and to remove oxidation by-products which are currently unknown and may pose more risks than the target compounds.

2. Investigate increased PES concentrations (i.e., 20+% PES) with pre-gelation time to see if: i) the effect of CSMMs becomes more pronounced, ii) a tighter membrane can be produced to achieve consistent removals for the target application and iii) pre-gelation time will increase surface porosity and thus ensure high production rates.

3. In order to attribute trends and correlations more conclusively, more casting conditions should be examined. It is also recommended that a design of experiment be conducted with to narrow down the effects of pre-gelation times, specifically focusing at increased PES concentrations in order to achieve desired removals as well as due to the more pronounced CSMM effect).

4. Investigate the development of CSMMs with higher charge.

5. Carry out additional system baseline characterization tests or batch adsorption tests in order to certify the initial removals observed were caused by adsorption onto the membrane.

6. In the future, saturate the filtration system with solutes of high hydrophobicity prior to testing. This could be accomplished by removing the membranes from the cells prior to testing a given solute (i.e., BPA or IB), saturating the system with the solute by running a solution in recycle mode and once saturation is reached inserting the membranes back into the cells and filtering at the desired concentration. Additionally, a better cleaning method should be investigated, in order to prevent the competitive adsorption shown by negative removals. This could involve longer flushing and/or soaking of the membranes in ultrapure water to allow the solutes to desorb.

7. Investigate the effect of pore size and transmembrane pressure on the measurement of zeta potential. Also refine the streaming potential apparatus to

minimize variability, specifically by investigating the use of new electrodes and installing in-line conductivity meter.

8. Measure surface roughness to see if this is the cause of increased contact angle with the presence of CSMMs. Measuring the contact angle of the permeate-side of the membrane, though likely variable due to the increased surface roughness, may also yield information as to whether the CSMMs have modified the surface or simply the bulk of the membrane.

9. Further characterize the CSMMs to confirm the hypotheses presented, specifically by measuring charge and molecular weight.

10. If a suitable membrane is developed, assess the feasibility of implementation within a drinking water application by testing various source waters spiked with PhACs and EDCs. The interactions between the membrane, target solutes and water matrix, specifically NOM, should be characterized in order to ensure proper implementation.

11. The following modifications to the testing protocol should be considered: i) testing six membrane coupons to increase accuracy, ii) implementing an automated flow control system to reduce pressure and flow variability in the system and iii) improving the operation of the cleaning/rinse cycle method which is labour intensive and inefficient (i.e., replacing the use of 20 L buckets as feed tanks with a unit that could provide the flow desired for the duration of the cleaning period without compromising water quality or draining the distilled water reserves of the building).

12. It would be interesting to calculate the charge density of the membrane and the individual pores to assess what could be repelled as well as what order of magnitude charge the membrane should be designed to have such that it could repel these target solutes in order to better tailor the membranes.

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APPENDIX A

Procedure used in the synthesis of CSMMs (source: Rana, 2008)

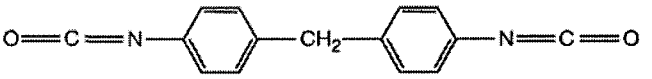
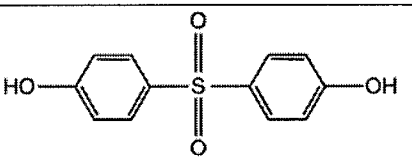
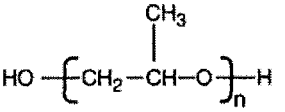
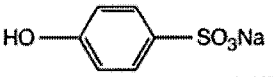
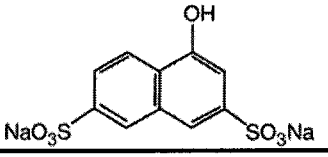
The reagents used in this work are listed in the Table A.1. The CSMMs, end-capped with charged groups were synthesized using a two-step solution polymerization method. The synthesis steps for the preparation of hydrophilic SMM (LSMM), which are very similar to those used for the preparation of CSMMs, were published by our research group (Rana et al., 2006). The initial step involved the reaction of methylene bis-p-phenyl diisocyanate (MDI) with a di-ol in a solvent, for example, N,N-dimethylacetamide (DMAc). This mixture formed a urethane prepolymer solution. The prepolymer is a segment-blocked urethane oligomer having both ends capped with isocyanate. The reaction was then terminated by the addition of a reagent, with one side having a charged group and the other a hydroxy group, resulting in a solution of CSMM. The schematic presentation of the CSMM synthesis procedure is presented in Figure A.1.

In the first reaction, the segment-blocked polyurethane both ends capped with charged groups is synthesized. To eliminate the effects of moisture, all the glass apparatus was dried at 120°C, and the prepolymerization reaction and end capping steps were performed in a controlled atmosphere of nitrogen inside the reaction vessel. 0.1 moles (42.5 gm) of degassed poly(propylene glycol), PPG, in 500 mL of degassed DMAc was added drop wise to 0.15 moles (37.5 gm) of MDI in 250 mL of degassed DMAc in 2 L Pyrex round bottom flask with a stirrer. The temperature was controlled at 48-50°C. PPG and MDI were allowed to react for 3 hrs.

The second step polymerization reaction involves the following procedure: 0.1 moles (13.22 gm) of hydroxybenzene sulfonate sodium salt, HBS, dissolved in 250 mL of degassed DMAc were added drop wise. The solution was stirred for 24 hrs at 48-50°C, resulting in a solution of CSMM, MDI-PPG-HBS. The chemical reaction is presented in Figure A.1. The reaction is the same for each CSMM, with the specific additives added instead of PPG or HBS. The CSMM solution was added drop wise into a 4L beaker filled with distilled water under vigorous stirring to precipitate the CSMM. The CSMM was filter with a Büchner funnel and washed with water in order to leach out residual solvent, and dried in an air circulation oven at 120°C for 3 days. The synthesized CSMMs in this project are shown in the Figure A.2.

The glass transition temperature (T_g) was examined by differential scanning calorimeter (DSC) equipped with universal analysis 2000 program (DSC Q1000, TA Instruments, New Castle, DE, USA). Values for the four CSMMs are found in Table 3.1. Indium was used for the calibration of the temperature. About 10 mg of polymer was crimped into an aluminum pan. The polymers were annealed at about T_g +50°C for 10 min and then quenched to -50°C, and scanned at a heating rate of 10°C/min. The T_g was recorded at the midpoint of the corresponding heat capacity transition.

Table A.1: Reagents used for the synthesis of CSMMs

ID	Chemical Name	Chemical Structure
MDI	Methylene diisocyanate	
Soft segment, HO-R-OH		
DEG	Diethylene glycol	$HO\text{-}(CH_2)_2\text{-}O\text{-}(CH_2)_2\text{-}OH$
DPS	Diphenylol sulfone	
PEG	Poly(ethylene glycol)	$HO\text{-}(CH_2\text{-}CH_2\text{-}O)_n\text{-}H$ *Typical M_n 400 Dalton*
PPG	Poly(propylene glycol)	 *Typical M_n 425 Dalton*
Ends capping, HO-R'		
HBS	Hydroxybenzene sulfonate, sodium salt	
NDS	Naphthol disulfonate, disodium salt	

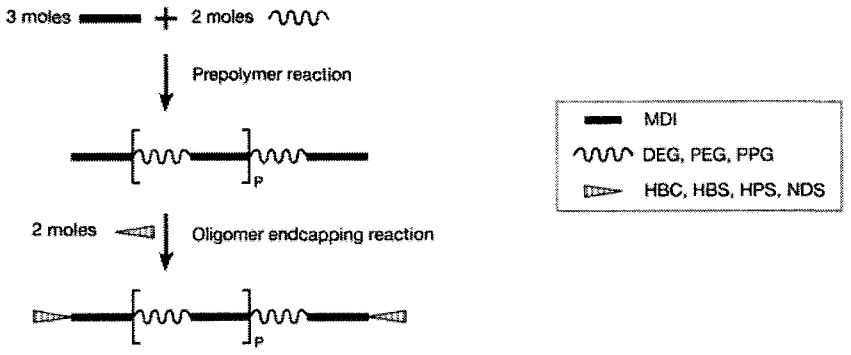


Figure A.1: Schematic presentation of the CSMM synthesis reaction

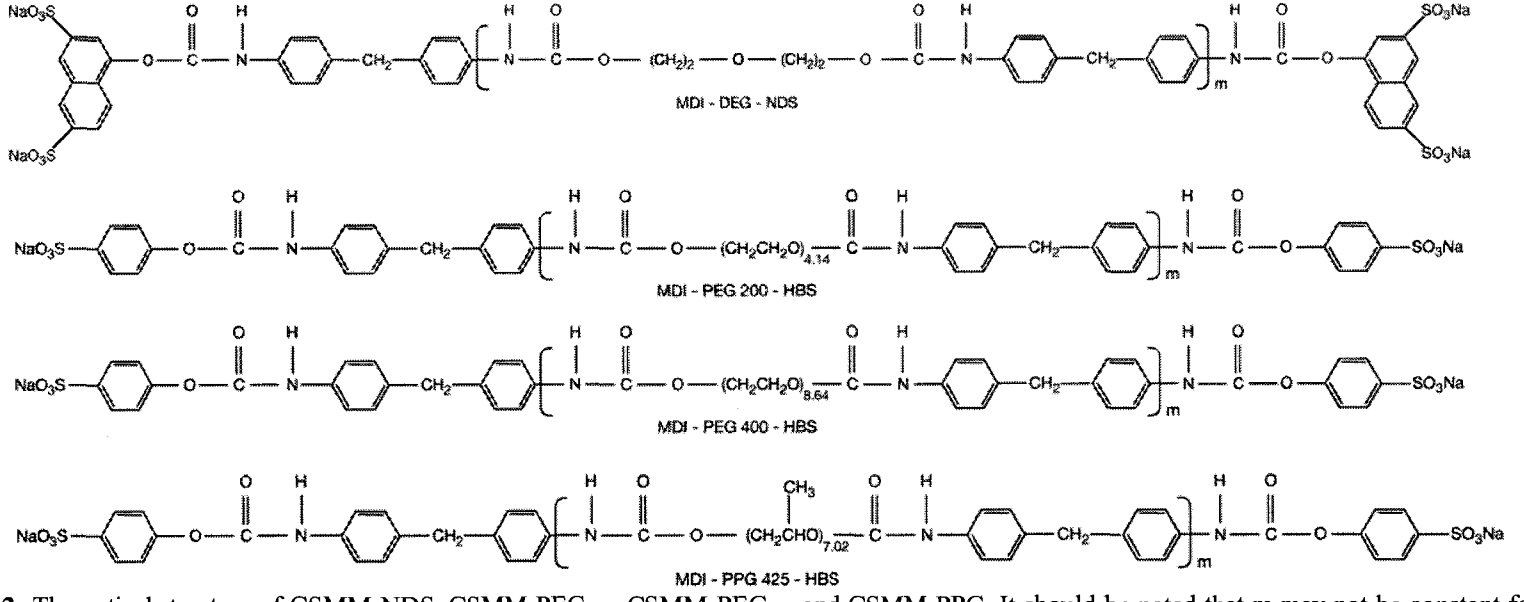


Figure A.2: Theoretical structure of CSMM-NDS, CSMM-PEG_{200}, CSMM-PEG_{400} and CSMM-PPG. It should be noted that m may not be constant for each of the SMMs

APPENDIX B

Considerations for converting a serial membrane filtration test system to parallel

In order to convert the original bench scale membrane filtration system from serial to parallel configuration, various configurations were evaluated for feasibility and cost. A simple preliminary design was proposed; having one header feed six cells. Each cell would be preceded by a metering valve and pressure gauge and followed by a metering valve and rotameter, returning to a common header before going through the cooler and into the feed tank. Upon consultation with technicians, students, and obtaining material cost estimates, variations to this plan were proposed and evaluated. Primary layout variations included:

- Replacing the metering valves with a back pressure regulator,
- Having two headers feeding three cells each and using a common rotameter to measure retentate flow for each header, and
- Having one common rotameter for the measurement of all six retentates.

Additionally, reducing the tubing size from ¼ inch to 3/8 inch was also evaluated for i) the whole system and ii) the retentate side. Each design and modification was evaluated for implementation feasibility, desired system operating conditions and cost. Based on the desired operating conditions, the design options were narrowed down by the following criteria:

- the use of two headers (each feeding three cells) instead of one (feeding all six) to ensure minimal head loss,

- tubing on the feed-side of the cells should be 3/8'' in order to minimize head loss and maintain high flows, and
- the use of one or two common rotameters on the retentate side would likely be feasible (as opposed to one per cell), but the tubing layout should be tested prior to implementation

From these specifications, and the design variations presented above, three designs (A: using one common rotameter, B: using two common rotameters and C: using six rotameters) were costed for different scenarios, maintaining all tubing at 3/8'' and changing the retentate-side tubing to ¼'', using quick connects or three-way valves to link the retentate. The design replacing the metering valves with back pressure regulators was not included since each regulator was approximately three times more expensive than metering valves. The use of quick connects was tested and found to be impractical for quick flow measurements and implementation with fixed stainless steel lines. Finally the use of a common rotameter (to all six cells as opposed to two rotameters common to three cells) was found adequate and also did not restrict flow (Westgate, 2008). The results of designs the analysis were implemented successfully.

APPENDIX C

MWCO: Mathematical development and sample calculation

The following is from the development by Michaels (1980). It should be noted that this is a hydrated pore size model. The pore size distribution of a given ultrafiltration membrane can be characterized by log-normal distribution:

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

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 of the pore diameter. The μ_p is determined from the 50% probability of solute diameter (f=50%) and the σ_p can be calculated as follows:

$$\sigma_p = \frac{solute\ diameter\ at\ f = 84.13\%}{solute\ diameter\ at\ f = 50\%} \qquad \text{C.2}$$

It is assumed the solute diameter is equivalent to the pore diameter and that their geometric standard deviations are the same.

The particle size of the probe solutes, PEG and PEO, is estimated using the respective Stokes radius (a) expressions, which are function of the molecular weight (MW) of the probe solutes. Stokes radius is used since it approximates the radius based on the assumption that the particle behaves as a hypothetical sphere which diffuses similarly to the particle (probe solute) in question.

$$a_{PEG} = 16.74x10^{-10} MW^{0.557} \qquad \text{C.3}$$

$$a_{PEO} = 10.44x10^{-10} MW^{0.587} \qquad \text{C.4}$$

The above expressions are based on empirical expressions of intrinsic viscosities and the Stokes-Einstein diffusivity expressions, as derived by Singh et al. (1998).

The Hagen-Poiseuille equation, modified for a porous membranes and assuming laminar flow is the basis for the expressions for the pore density (N) and surface porosity (S_p), (Mosqueda-Jimenez, 2005).

$$N = \frac{128\eta\delta J}{\pi\Delta P\sum_{d_{\min}}^{d_{\max}} f_i d_i^4} \qquad \text{C.5}$$

Where η is the solvent viscosity (N-s/m^2), δ is the pore length (the thickness of the membrane based on the assumption of no pore tortuosity) (m), ΔP is the transmembrane pressure (Pa) and J is the membrane flux (m^3/m^2/s). From this, the surface porosity can be determined:

$$S_p = \left(\frac{N\pi}{4}\sum_{d_{\min}}^{d_{\max}} f_i d_i^2\right) * 100\% \qquad \text{C.6}$$

Using the removal performance of the test membranes for various sizes of probe solutes (Tables C.1 and C.2), the MWCO could be estimated. Likewise, the surface porosity could be quantified by using the flux and transmembrane pressure at the corresponding operating conditions. Finally, the pore size distribution can be determined from the log-normal probability as a function of the solute removals.

Table C.1: Probe solute removal (%) as a function of casting condition for control and CSMM-NDS modified membranes

	Solute MW	**PES18-0**			**PES18-3**			**PES20-0**		
	(kDa)	**a**	*b*	**c**	**a**	**b**	*c*	**a**	**b**	*c*
Control	**0.342**	6.91	*4.42*	9.50	-	-	-	25.95	10.92	*-34.65*
	0.4	11.32	*7.40*	15.04	24.34	23.17	*55.87*	27.19	17.50	*-57.69*
	0.6	18.56	*13.62*	17.89	-	-	-	41.56	23.94	*13.11*
	1	23.46	*12.14*	22.31	31.11	21.27	*34.73*	60.30	39.74	*20.07*
	8	19.72	*22.41*	19.12	71.05	53.39	*81.97*	64.52	51.71	*18.23*
	14	30.95	*34.26*	34.70	86.88	69.06	*89.52*	83.58	85.39	*79.20*
	35	50.61	*63.11*	43.15	91.77	88.80	*85.88*	89.96	94.95	*98.49*
	100	98.03	*96.21*	98.62	95.05	99.21	*97.81*	91.90	98.10	*94.48*
		a	*b*	*c*	**a**	*b*	**c**	*a*	*b*	*c*
CSMM-NDS	**0.4**	-	-	-	17.44	*15.94*	19.19	-	-	-
	1	39.06	*-144.28*	*165.51*	16.60	*15.19*	18.42	-	-	-
	4	41.38	-	-	-	-	-	-	-	-
	6	99.22	*100.00*	*100.00*	-	-	-	-	-	-
	8	97.05	*12.22*	-	73.90	*66.98*	46.90	-	-	-
	14	97.31	*20.00*	-	86.51	*88.51*	78.99	-	-	-
	35	98.10	-	-	93.24	*94.86*	91.63	-	-	-
	100	98.40	-	-	96.69	*91.36*	93.30	-	-	-

Note: columns in *italics* are replicates that were eliminated, columns with a **bold** header are coupons that were retained

Table C.2: Probe solute removal (%) as a function of casting condition for CSMM-PEG_{200}, -PEG_{400} and -PPG modified membranes

	MW	PES18-0			PES18-3			PES20-0		
	(kDa)	**a**	*b*	**c**	**a**	**b**	*c*	**a**	**b**	*c*
		a	**b**	*c*	*a*	**b**	**c**	*a*	**b**	**c**
CSMM-PPG	**0.4**	18.95	19.94	*12.68*	-	-	-	-	-	-
	1	36.78	39.44	*44.39*	*30.94*	16.81	20.01	*9.20*	39.36	50.60
	8	52.27	63.95	*80.32*	*29.21*	25.85	31.67	*47.83*	34.17	54.85
	14	76.39	74.62	*87.67*	*41.61*	35.41	55.11	*56.89*	64.74	75.81
	35	83.58	82.20	*93.13*	*56.08*	41.89	63.79	*58.51*	77.93	84.31
	100	96.26	96.62	*98.39*	*98.17*	96.99	96.50	*67.44*	98.72	98.99
		a	**b**	**c**	*a*	**b**	**c**	**a**	*b*	**c**
CSMM-PEG_{200}	**1**	*8.07*	16.82	15.45	*20.13*	20.13	20.26	6.72	*4.06*	5.02
	8	*52.63*	75.87	39.22	*23.06*	39.20	32.03	50.56	*87.86*	61.52
	14	*78.44*	88.67	73.37	*66.94*	78.81	55.07	82.25	*81.80*	75.06
	35	*92.83*	94.24	85.79	*82.76*	85.97	71.05	88.87	*82.57*	84.93
	100	*93.16*	97.08	97.30	*95.30*	98.50	98.16	90.73	*44.25*	81.80
		a	**b**	*c*	**a**	**b**	*c*	*a*	**b**	**c**
CSMM-PEG_{400}	**1**	15.95	25.50	*22.24*	15.9	12.3	*48.5*	*35.21*	39.34	19.46
	4	63.33	70.93	*23.79*	-	-	-	-	-	-
	6	82.07	96.16	*88.27*	-	-	-	-	-	-
	8	75.27	80.52	*55.51*	46.4	46.7	*86.4*	*76.36*	90.39	49.41
	14	57.44	83.33	*93.44*	68.5	73.1	*91.2*	*89.12*	95.03	74.68
	35	42.37	86.99	*98.14*	77.0	80.4	*93.0*	*94.14*	98.01	85.42
	100	94.97	97.08	*98.94*	96.7	97.4	*98.4*	*89.97*	98.97	98.02

Note: columns in *italics* are replicates that were eliminated; columns with a **bold** header are coupons that were retained

To determine the MWCO, the probability of removal (function of the removal data) at a given pore size (using the size of the probe solute) is plotted against the logarithm of the Stokes radius. From this data, a linear regression is conducted. Figures C.1 to C.5 illustrates the linear regressions of the duplicates and triplicates. The MWCO is determined based on the probability of 90% removal from the linear regression. The geometric standard deviation is determined from the 84.13% probability of the same regression as well as the 50% removal, which gives the mean pore size. From the regression, the pore size distribution can also be plotted, as shown in Figures 4.19 and 4.20. MWCO, geometric standard deviation, mean pore size, surface porosity and pore size distribution were determined for each coupon and the average of those values are reported in this thesis.

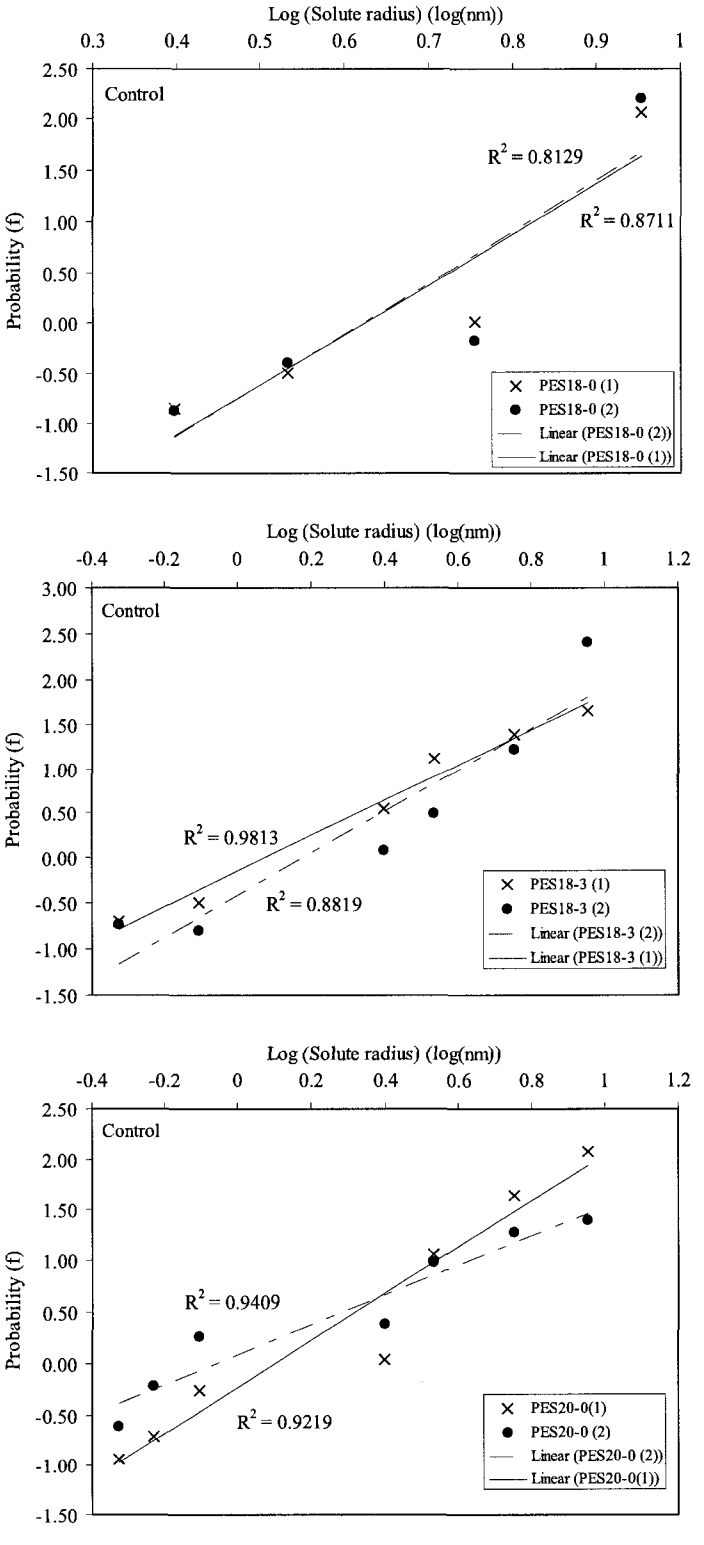


Figure C.1: Probability of removal as a function of stokes radius for control membranes

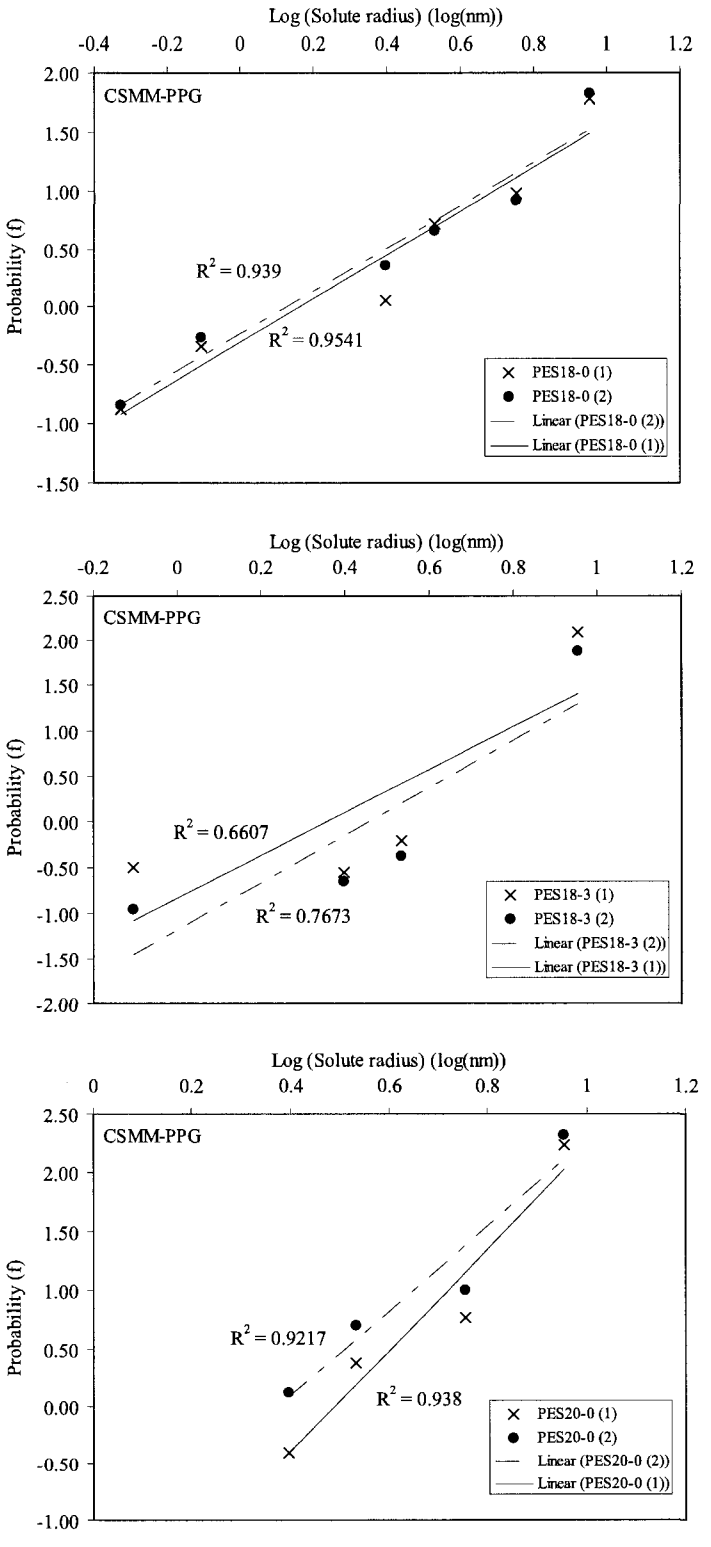


Figure C.2: Probability of removal as a function of stokes radius for CSMM-PPG membranes

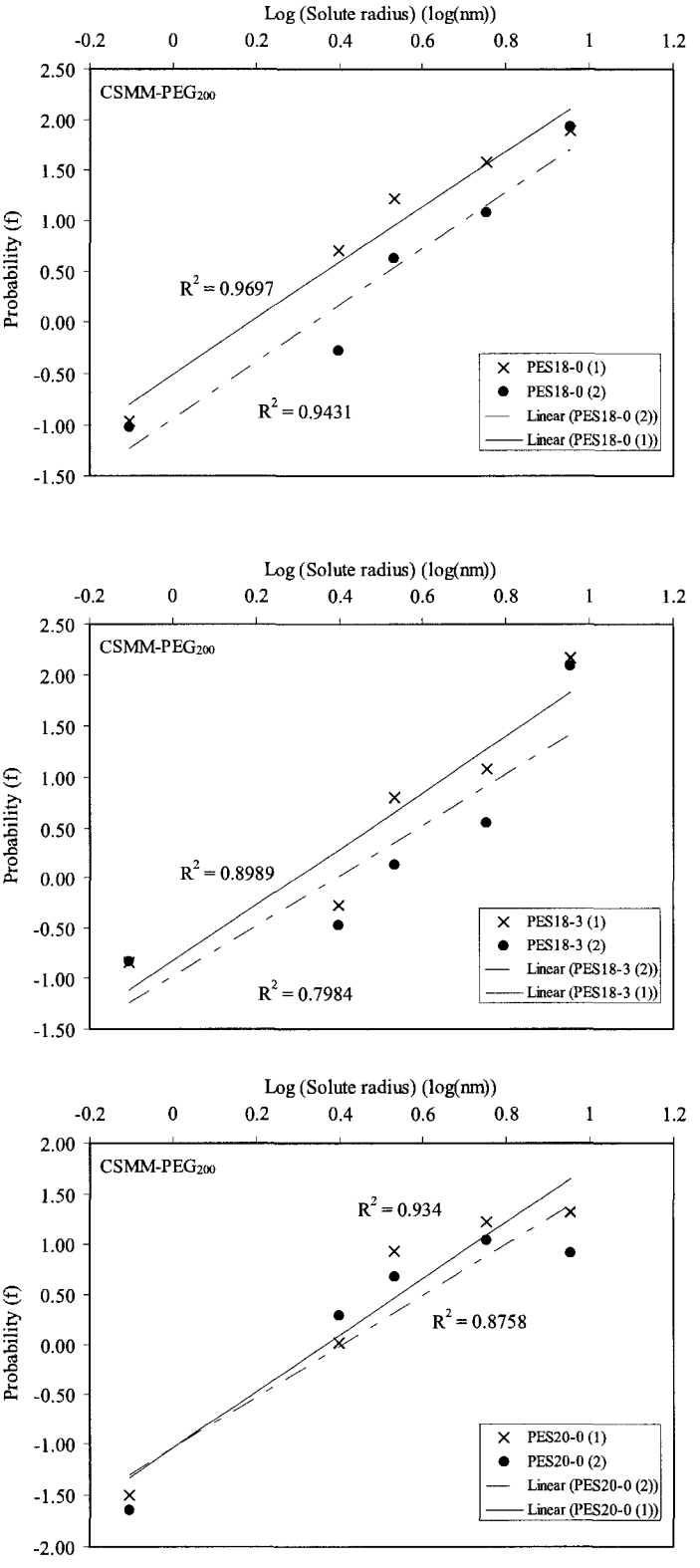


Figure C.3: Probability of removal as a function of stokes radius for CSMM-PEG$_{200}$ membranes

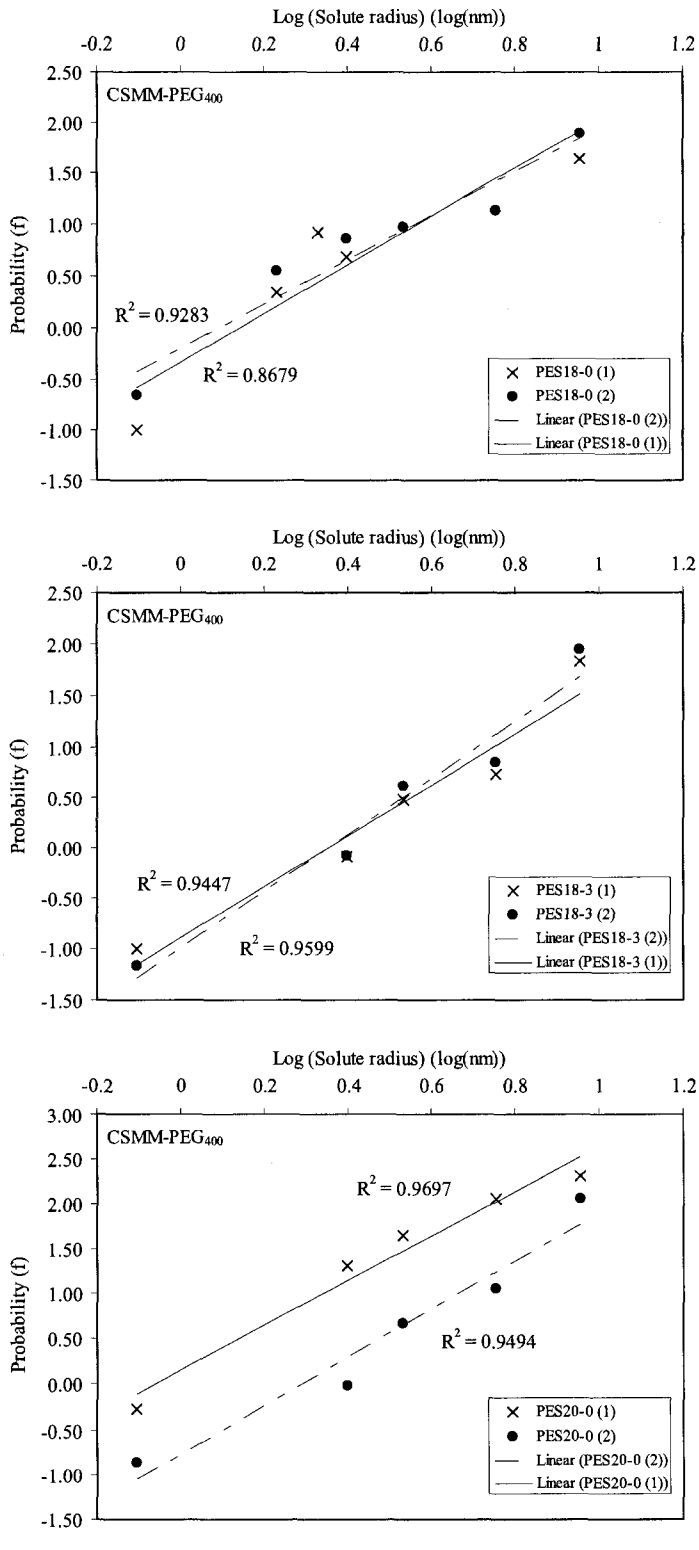


Figure C.4: Probability of removal as a function of stokes radius for CSMM-PEG$_{400}$ membranes

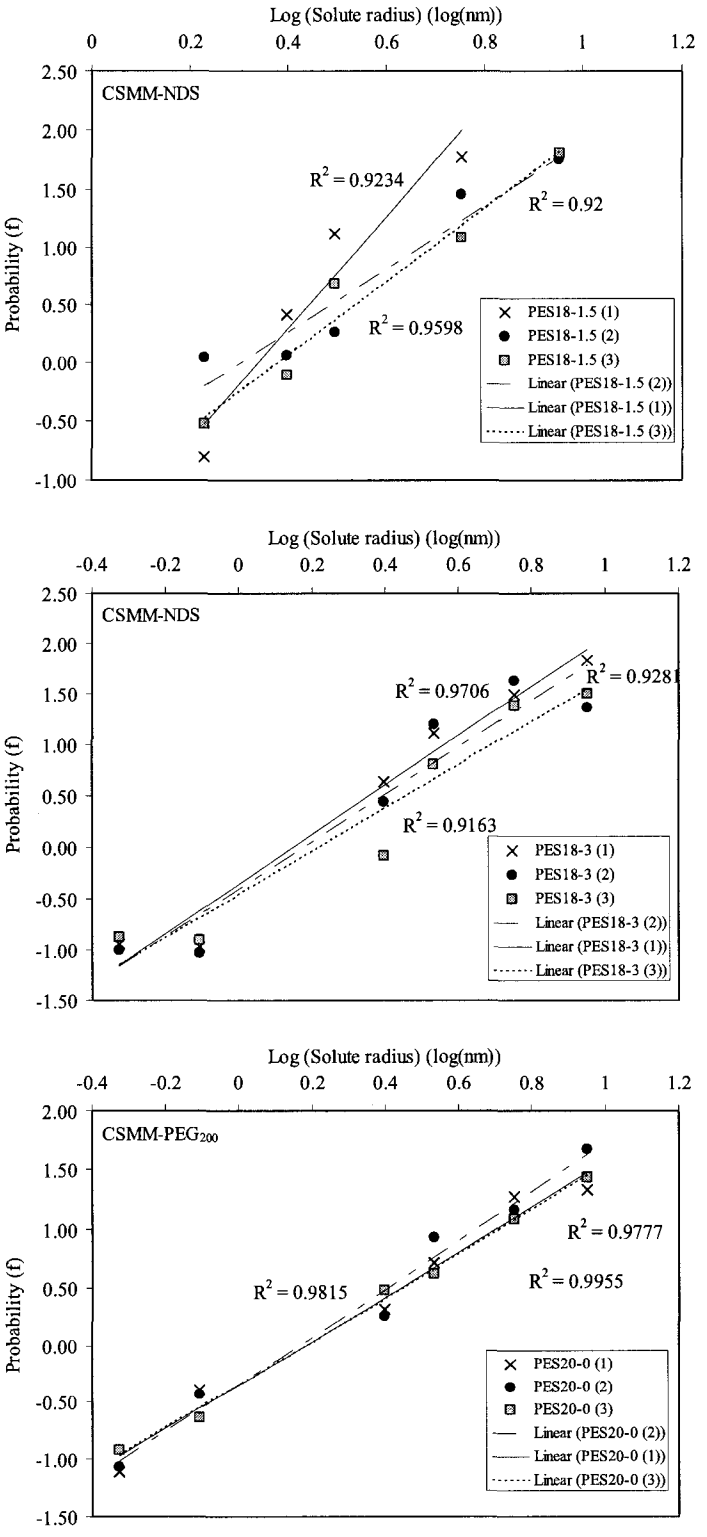


Figure C.5: Probability of removal as a function of stokes radius for CSMM-NDS membranes

APPENDIX D

System baseline adsorption of carbamazepine and sulfamethazine

The baseline adsorption tests carried out for sulfamethazine and carbamazepine show that there are no losses onto the test apparatus. The system concentration of both solutes over the course of the baseline test is shown in Figure D.1. The low values recorded for CBZ appear to indicate adsorption, however those samples were analyzed later and when compared to the standards, indicate that there is no adsorption.

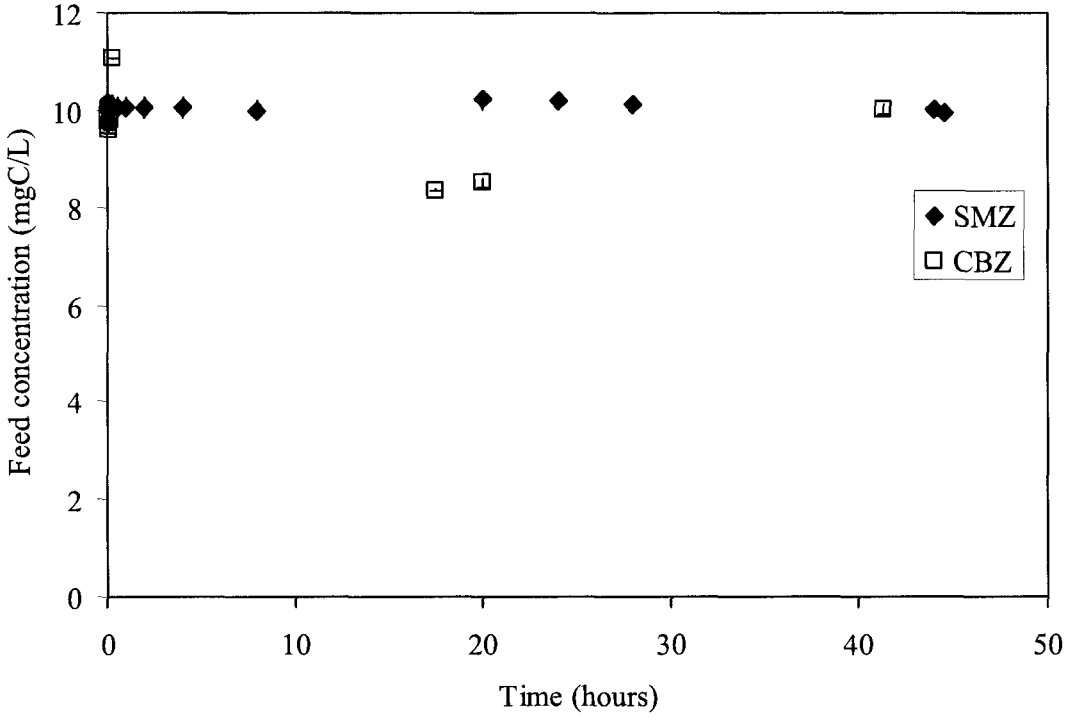


Figure D.1: Feed concentration of SMZ and CBZ to determine baseline losses

APPENDIX E

Preliminary effect of pre-gelation time on charge and hydrophilicity

The effect of pre-gelation time on charge and hydrophilicity were first assessed using CSMM-NDS modified membranes. Pre-gelation times of 1.5, 3 and 5 minutes were used. Figure E.1 and E.2 illustrate the variation in hydrophilicity and charge of the modified membranes at these times when compared to the controls (no CSMM).

From Figure E.1, it is interesting to note that the variation between 1.5, 3 and 5 minutes is inversed for the two membranes. For the control membrane, pre-gelation time was not expected to change the hydrophilicity since there were no additives. The variation in contact angle at this condition could therefore be explained by a less porous surface which would therefore be less rough; decreasing the contact angle (a rougher surface generally yields a higher contact angle). It should be noted, however, that the decrease in contact angle for the control membranes is within the standard deviation. The effect of pre-gelation time on the modified membranes was expected to yield more hydrophilic membranes (Rana, 2008). In this case, migration of CSMM-NDS appears to have increased hydrophobicity by approximately 20%, regardless of time (the contact angles at all three pre-gelation times are within their standard deviations of the measurements). From Figure E.1, it could be concluded that the impact of CSMM is observed within 1.5 minutes and that longer pre-gelation times may simply alter the membrane morphology as opposed to its surface characteristic (longer pre-gelation time has no greater effect on contact angle). It is interesting to see that the large change with respect to the control seen with contact angle is also seen with surface charge.

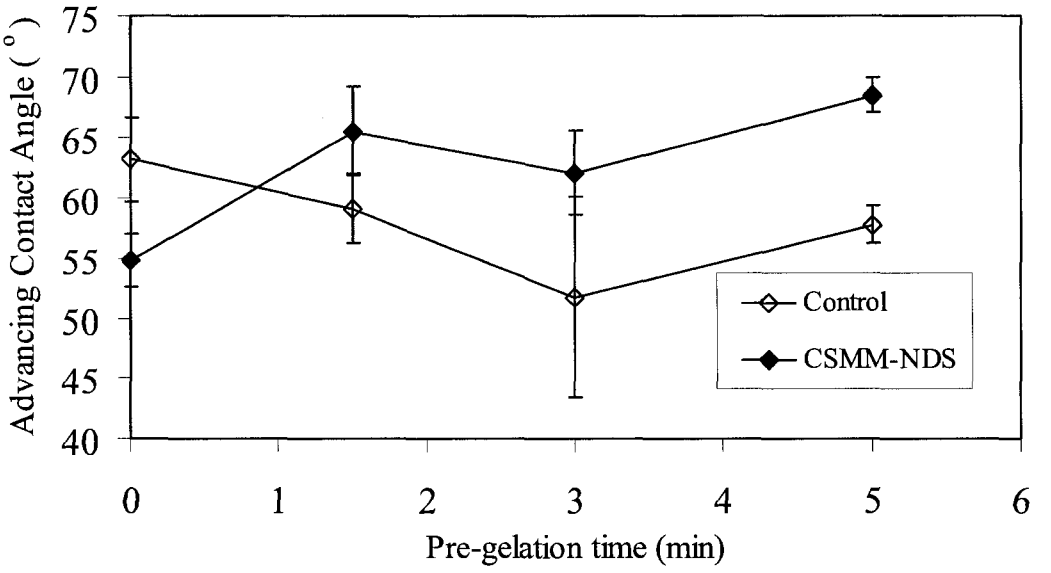


Figure E.1: Effect of pre-gelation time on hydrophilicity for modified (CSMM-NDS) and unmodified (control) membranes made with 18% PES (error bars represent one standard deviation)

Figure E.2 illustrates the effect of pre-gelation time on charge for the same membranes discussed above. It is interesting to note that the trend is the mirror image of that seen in Figure E.1. Although it initially appears that the charge becomes increasingly negative with pre-gelation time for the CSMM-NDS modified membranes, it should be noted that the membrane charge at 1.5, 3 and 5 minutes are within the standard deviations. It is also unclear how much effect the pre-gelation time has on the membrane charge, since several of the values are within the standard deviations.

From the mirror imaging of Figure E.2 and E.1, it can be concluded that an increase in membrane charge (i.e., becoming more negative) translates to a more hydrophobic membrane. This makes sense since if a membrane becomes more negatively charged, it would repel the water molecules which have a negative dipole. Figure E.3 demonstrates

the correlation between charge and contact angle for the modified and unmodified membranes, showing the decrease in charge increases hydrophilicity.

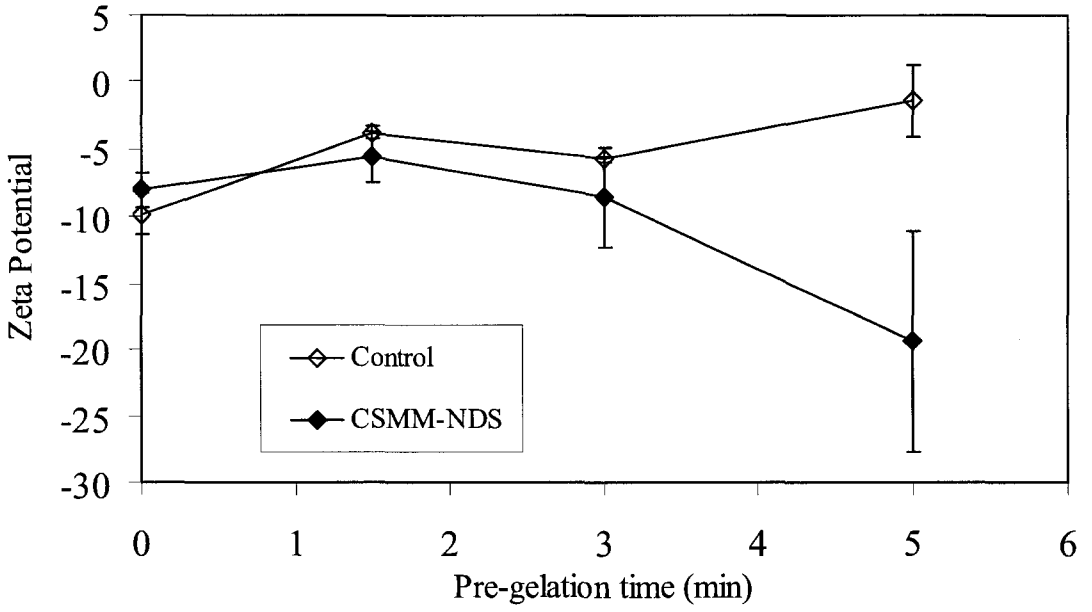


Figure E.2: Effect of pre-gelation time on charge for modified (CSMM-NDS) and unmodified (control) membranes made with 18%PES (error bars represent one standard deviation)

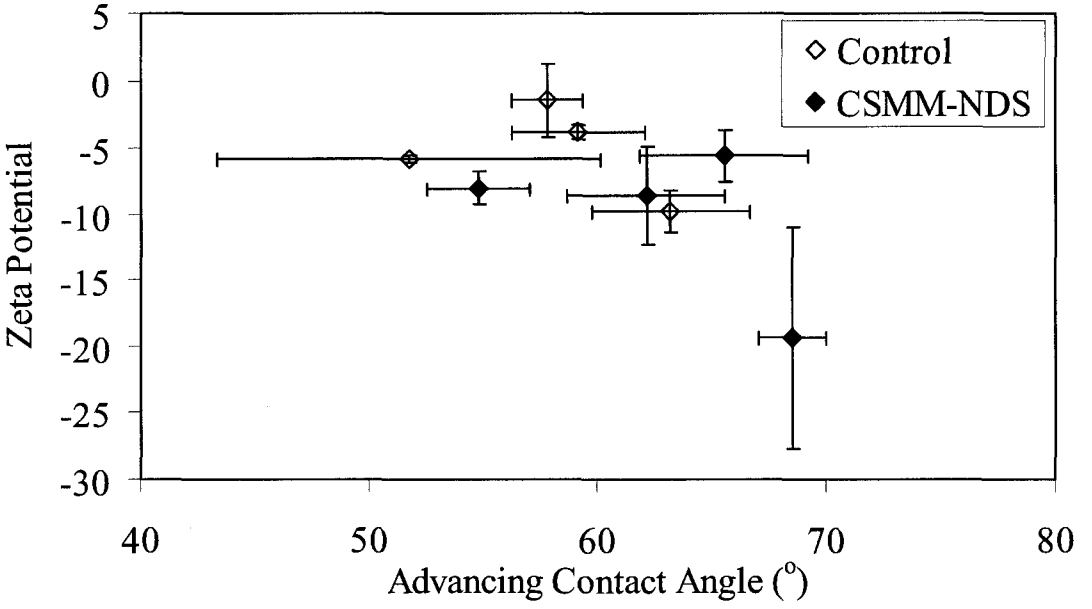


Figure E.3: Correlation between membrane hydrophilicity and charge

APPENDIX F

Correlation of NSF versus surface porosity

As discussed above, the flux is a direct function of surface porosity. By examining the surface porosity and fluxes of the membranes developed, as shown in Figure F.1, the linear correlation is very evident. It is interesting to note two things: firstly, the PES20-0 condition led to a linear correlation – there is no scatter in the data and the range which it covers spans the range of the other two conditions; secondly, at both the PES18-0 and PES18-3 conditions, the data appears to "clump" together. The points deviating from these clusters are the controls (no CSMM). The deviation from the control membranes may be due to the fact that the CSMM-modified membranes contain more polymer.

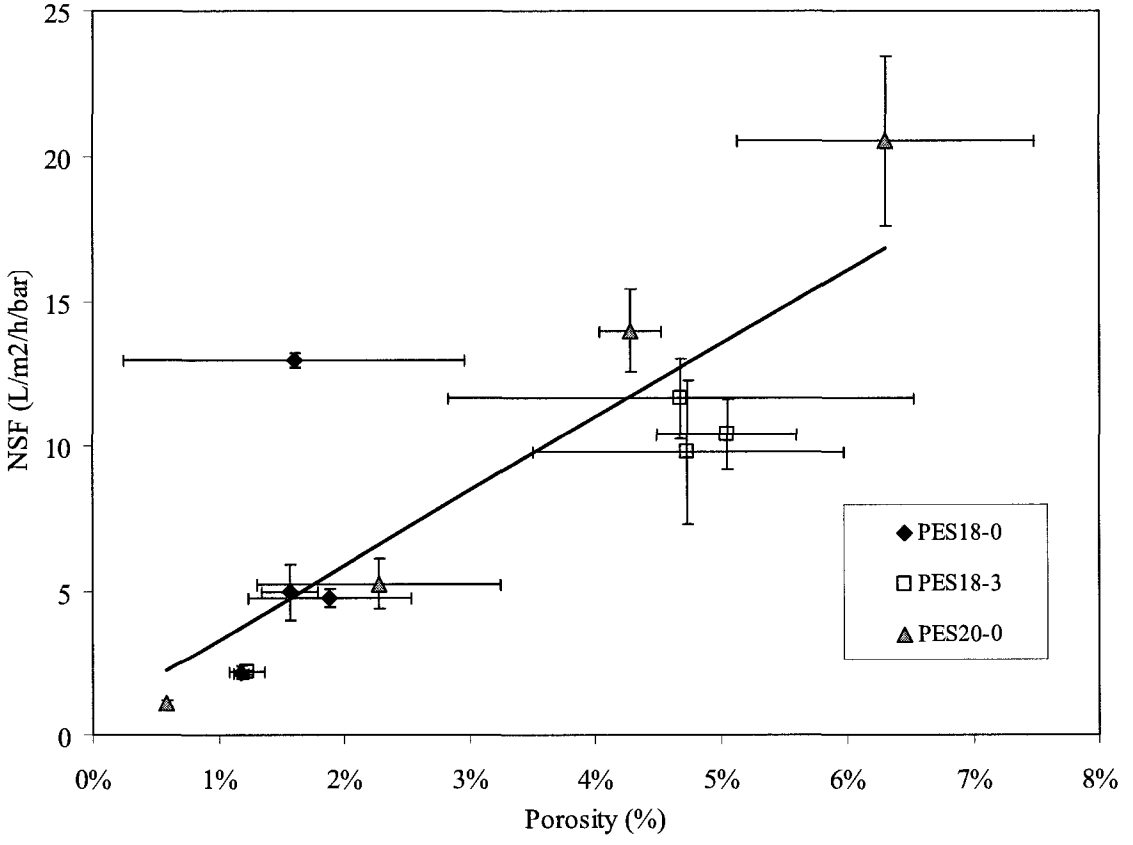


Figure F.1: Flux versus surface porosity for modified and unmodified membranes

APPENDIX G

Effect of hydrophilicity and charge on flux

The effect of hydrophilicity and charge on normalized standard flux was discussed in Section 4.2.3.3. Figures G.1 and G.2 below include the standard deviation.

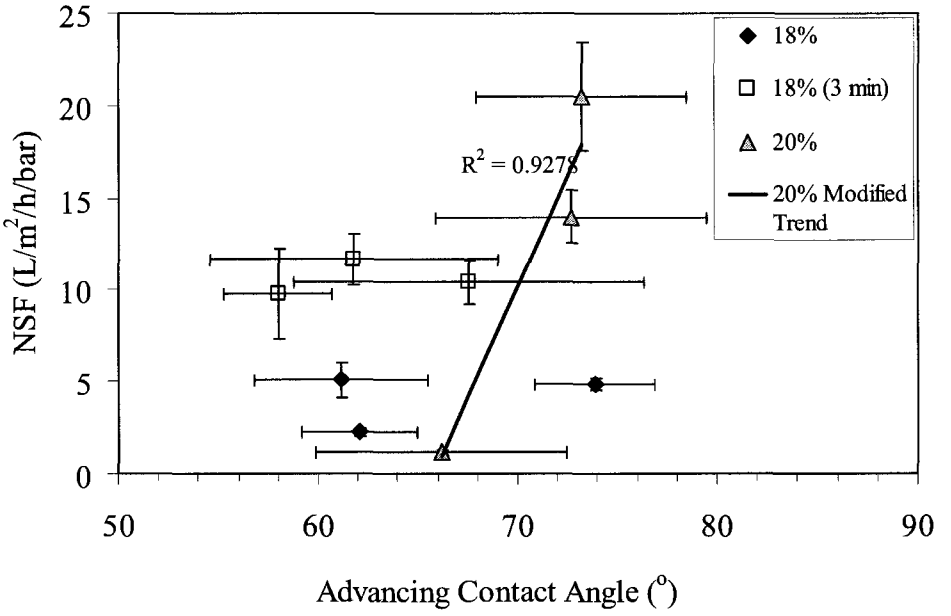


Figure G.1: Comparison of advancing contact angle and normalized standard flux for CSMM modified membranes

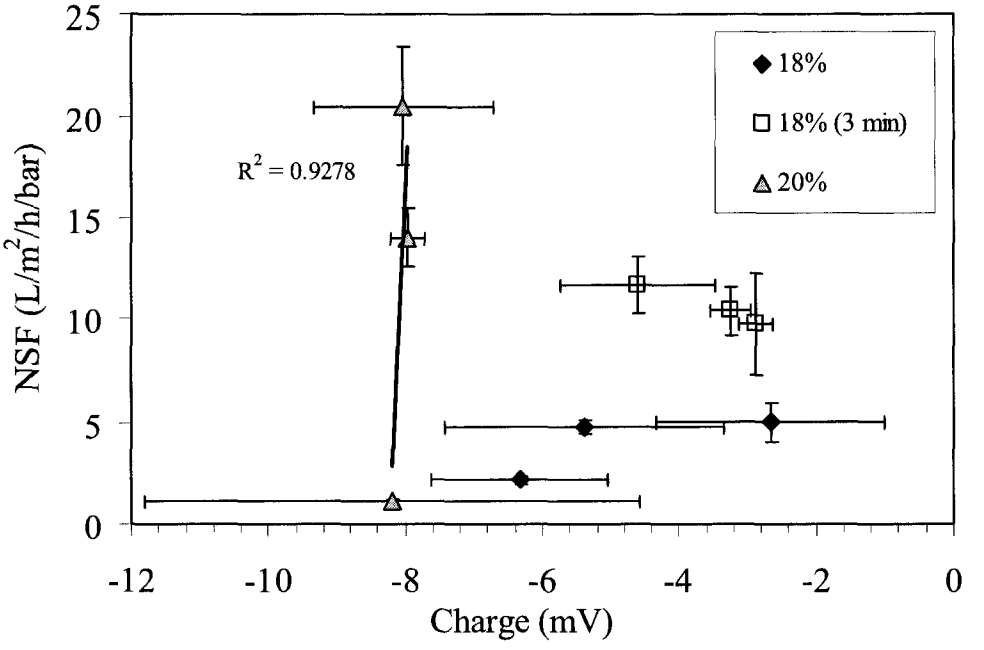


Figure G.2: Comparison of charge and normalized standard flux for CSMM modified membranes

APPENDIX H

Removal of PhACs and EDC by novel membranes as a function of time

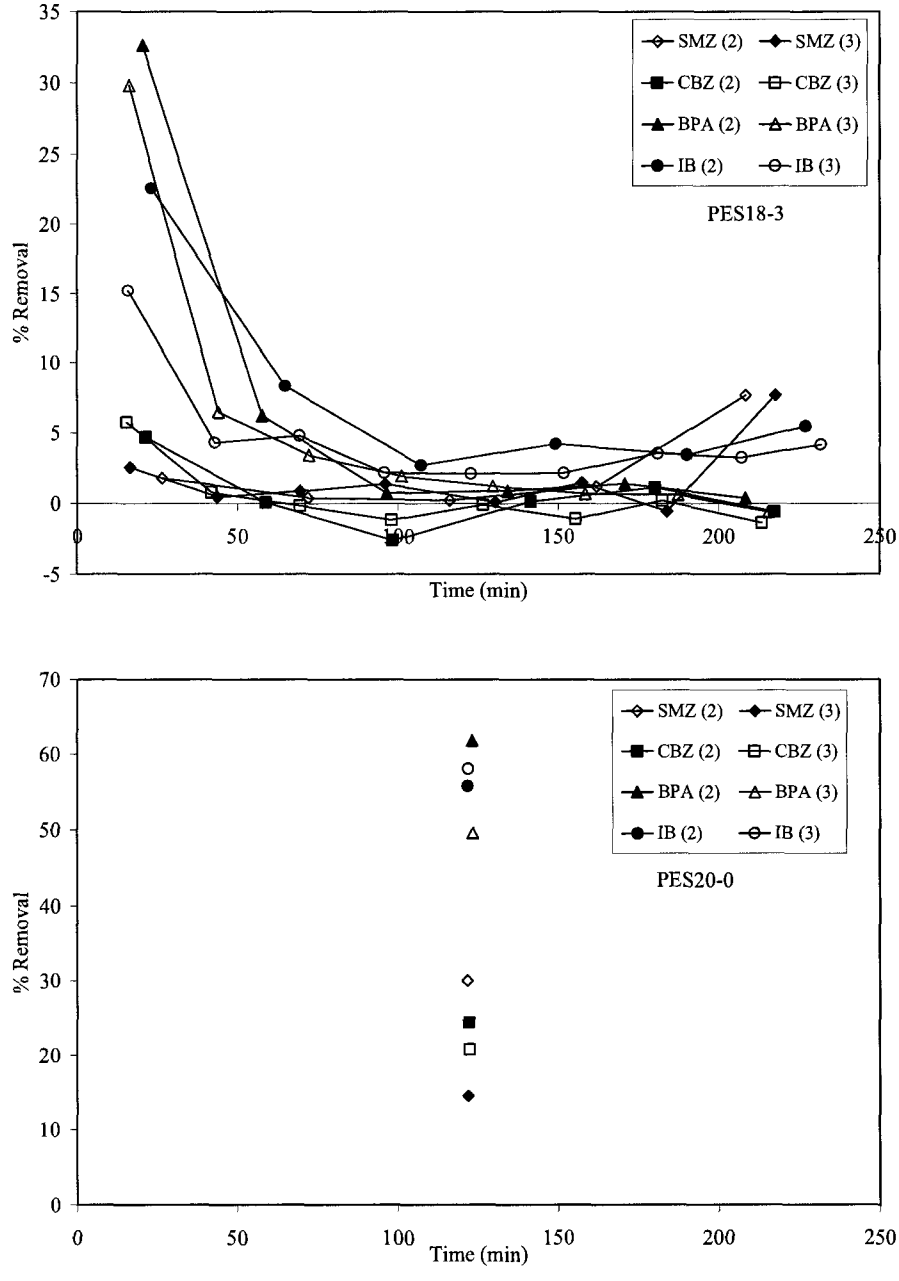


Figure H.1: Removal of PhACs and EDC by CSMM-PEG_{200} modified membranes

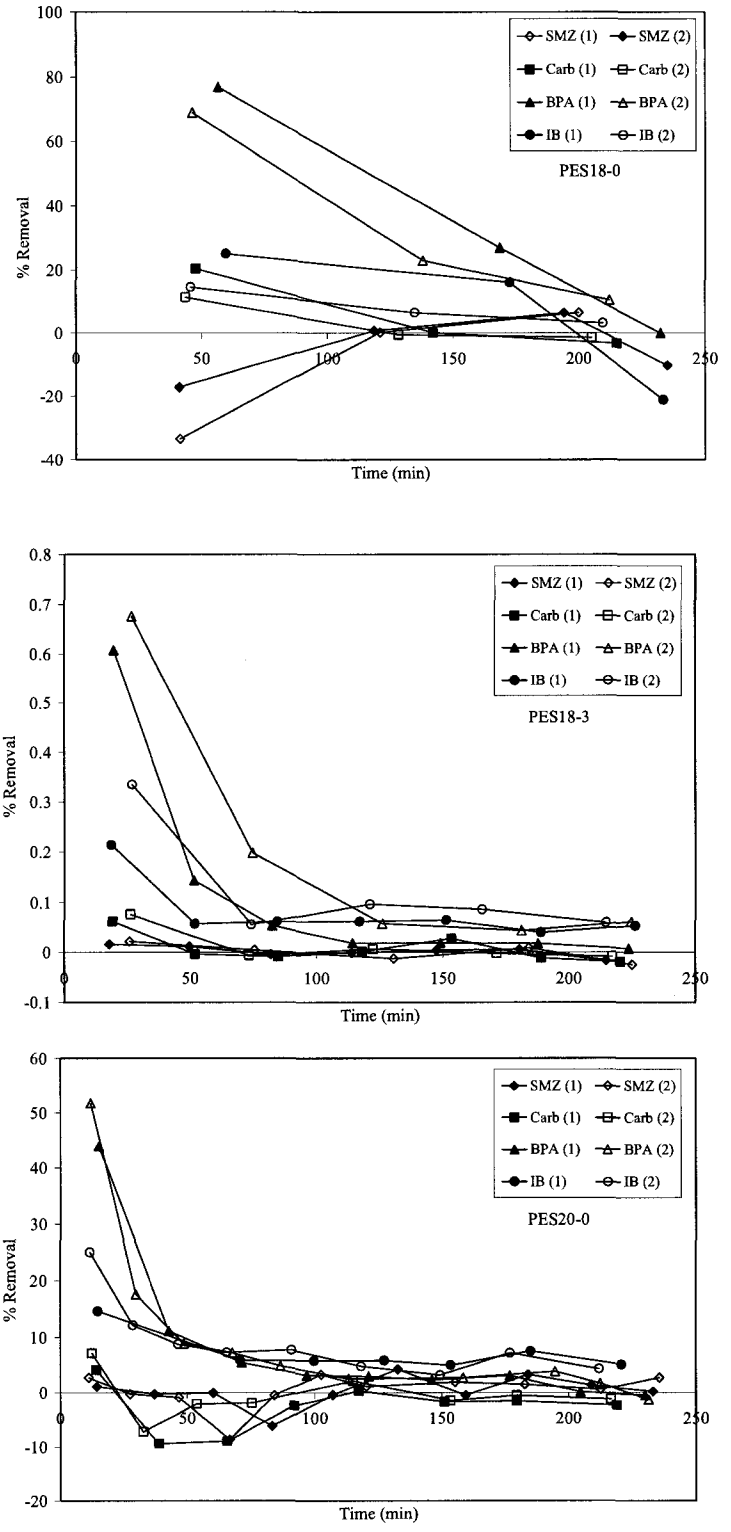


Figure H.2: Removal of PhACs and EDC by CSMM-PEG$_{400}$ modified membranes

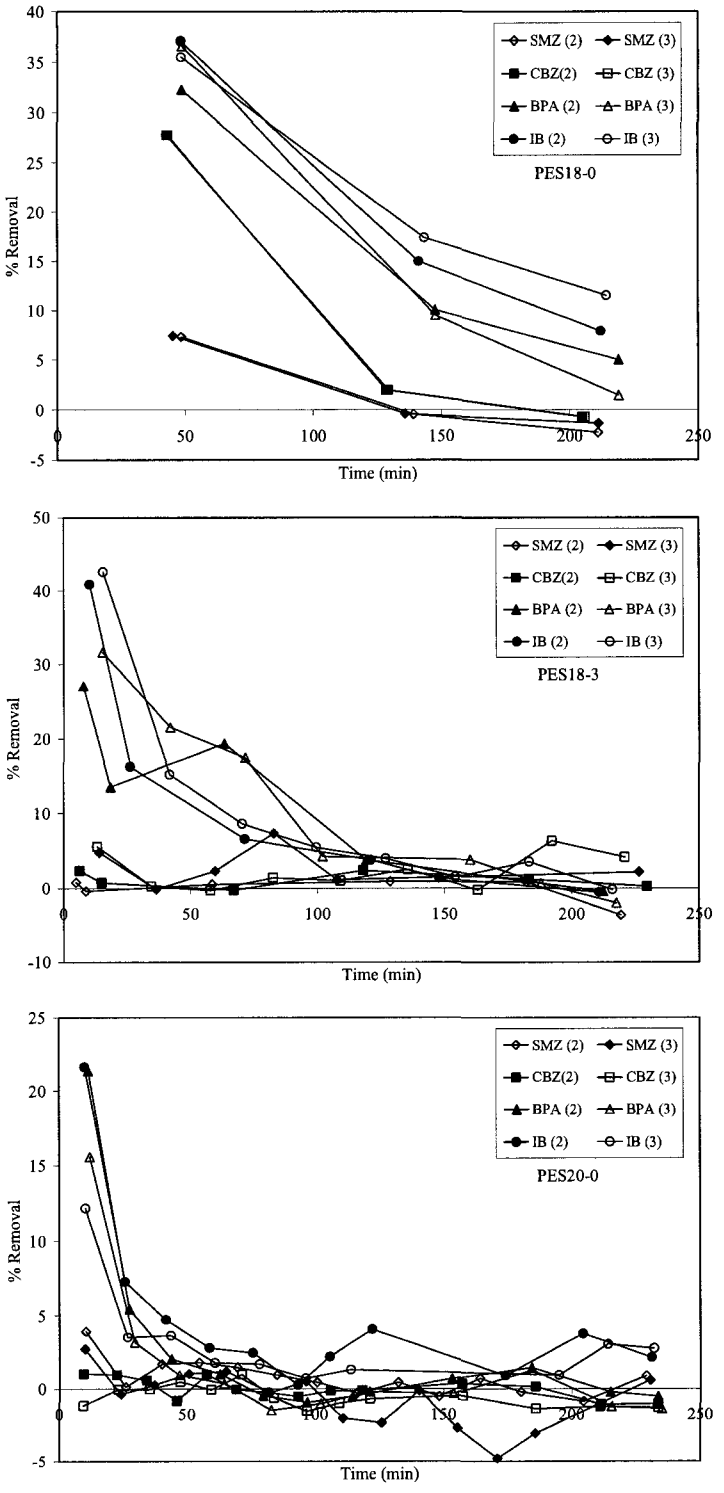


Figure H.3: Removal of PhACs and EDC by CSMM-PPG modified membranes

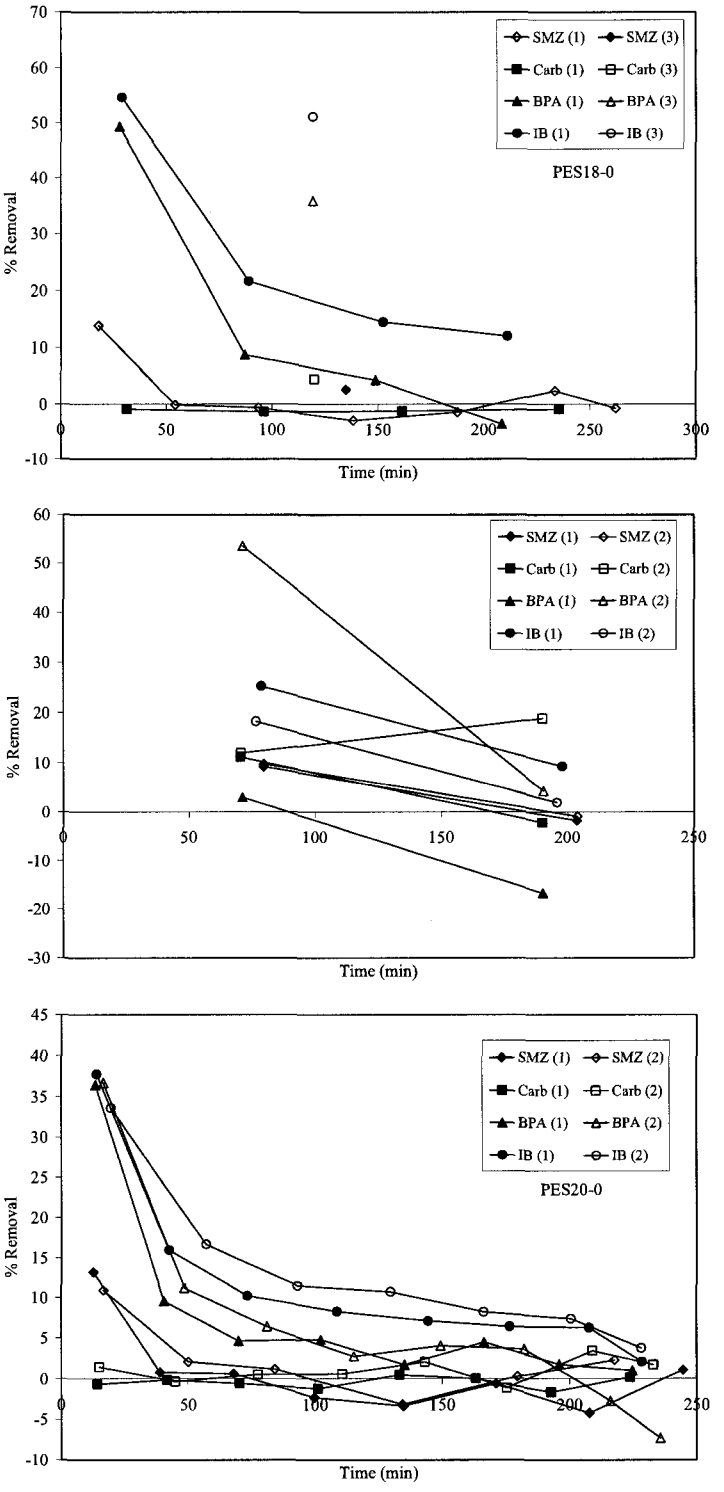


Figure H.4: Removal of PhACs and EDC by control membranes

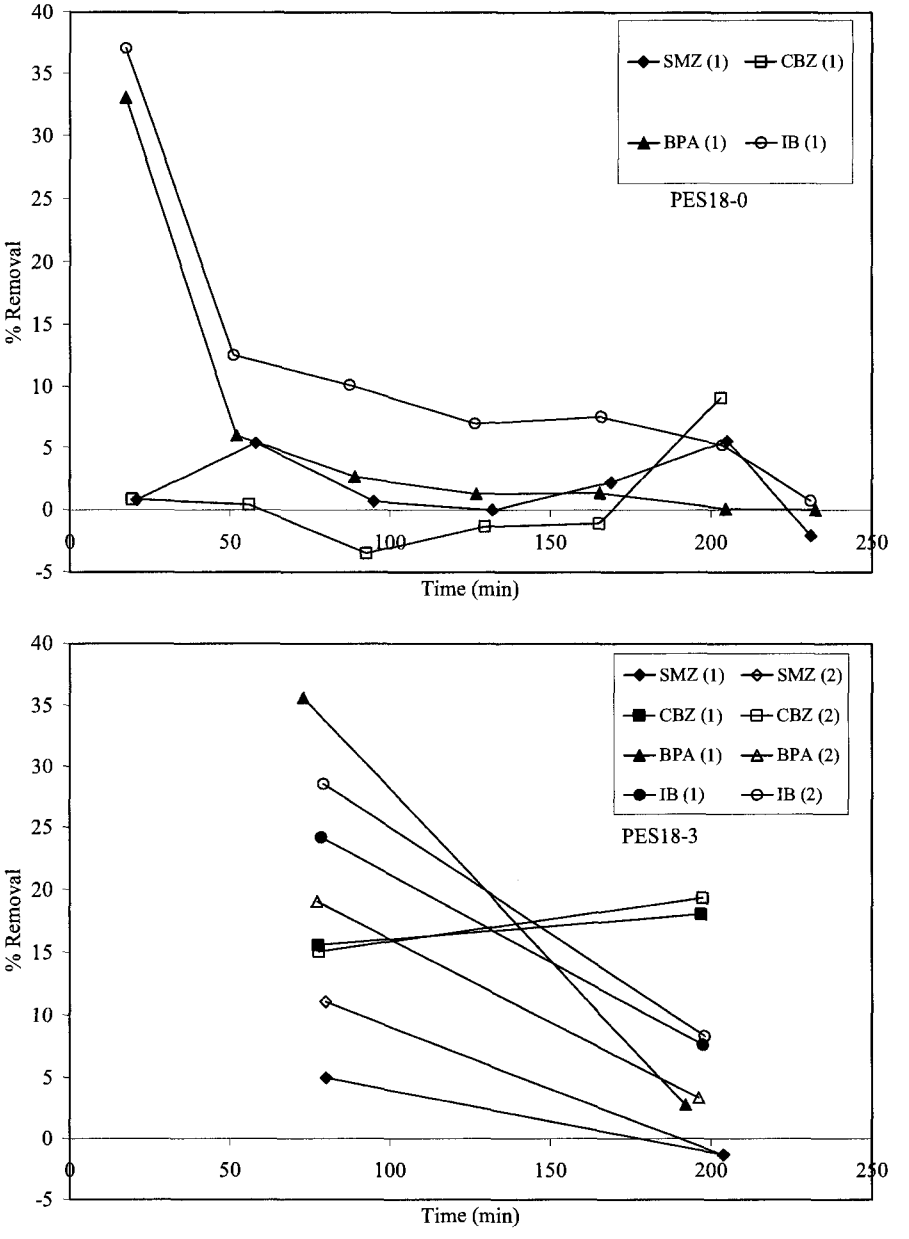


Figure H.5: Removal of PhACs and EDC by CSMM-NDS modified membranes

APPENDIX I

Correlation between membrane properties and initial removal

In order to attach the initial removal of target solutes to membrane characteristics, initial removal was plotted against the various characteristics evaluated. This was done both as a function of additive (Figures I.1 to I.6) and as a function of casting conditions (not shown). Neither set of figures yielded many trends, and when some were found they could not be linked to other trends or explained clearly. It should also be noted that this type of analysis is greatly hampered by limited number of points (i.e., three) for every subset and the fact that there were no clear trends that applied over the entire data set.

The most interesting trends were seen with initial removal and contact angle or charge. Figure I.1 illustrates initial removal as a function of charge. In this set of figures, only two trends were found: a linear decrease in removal with decrease in charge for the removal of SMZ and BPA using the CSMM-PPG blended membrane. It is interesting that this trend be seen only with BPA and SMZ and not CBZ and IB, but may be attributed to the relative charges of these solutes at the time of filtration. Charge repulsion may therefore aid in the removal, or have some part in this initial removal. From Figure I.2, a second set of linear trends are found with CBZ and IB. The decrease in initial removal of CBZ with increasing hydrophilicity is interesting – one would expect a more hydrophobic membrane to allow more sorption. In this case, maybe the more hydrophilic solute (CBZ has a log K_{OW} around 2.56) attaches itself easier onto the higher hydrophilic membranes. This trend may also be a function of the surface morphology (i.e., roughness, leading to

contact angle variation). As for the correlation between IB, this trend may be falsely found due to the closeness of the two data points at the higher hydrophobicity.

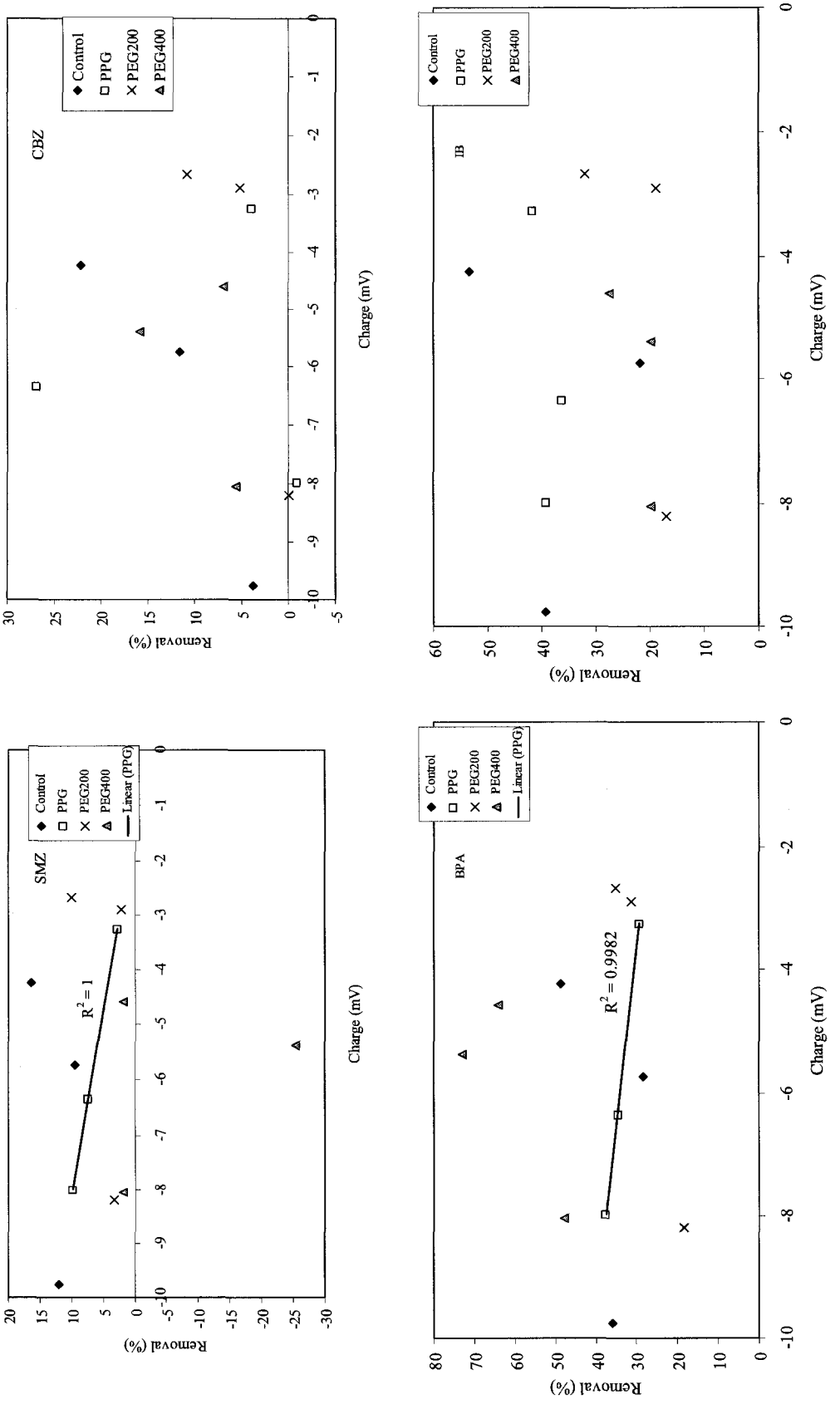


Figure I.1: Removal of PhACs and EDC by modified and unmodified membranes as a function of membrane charge

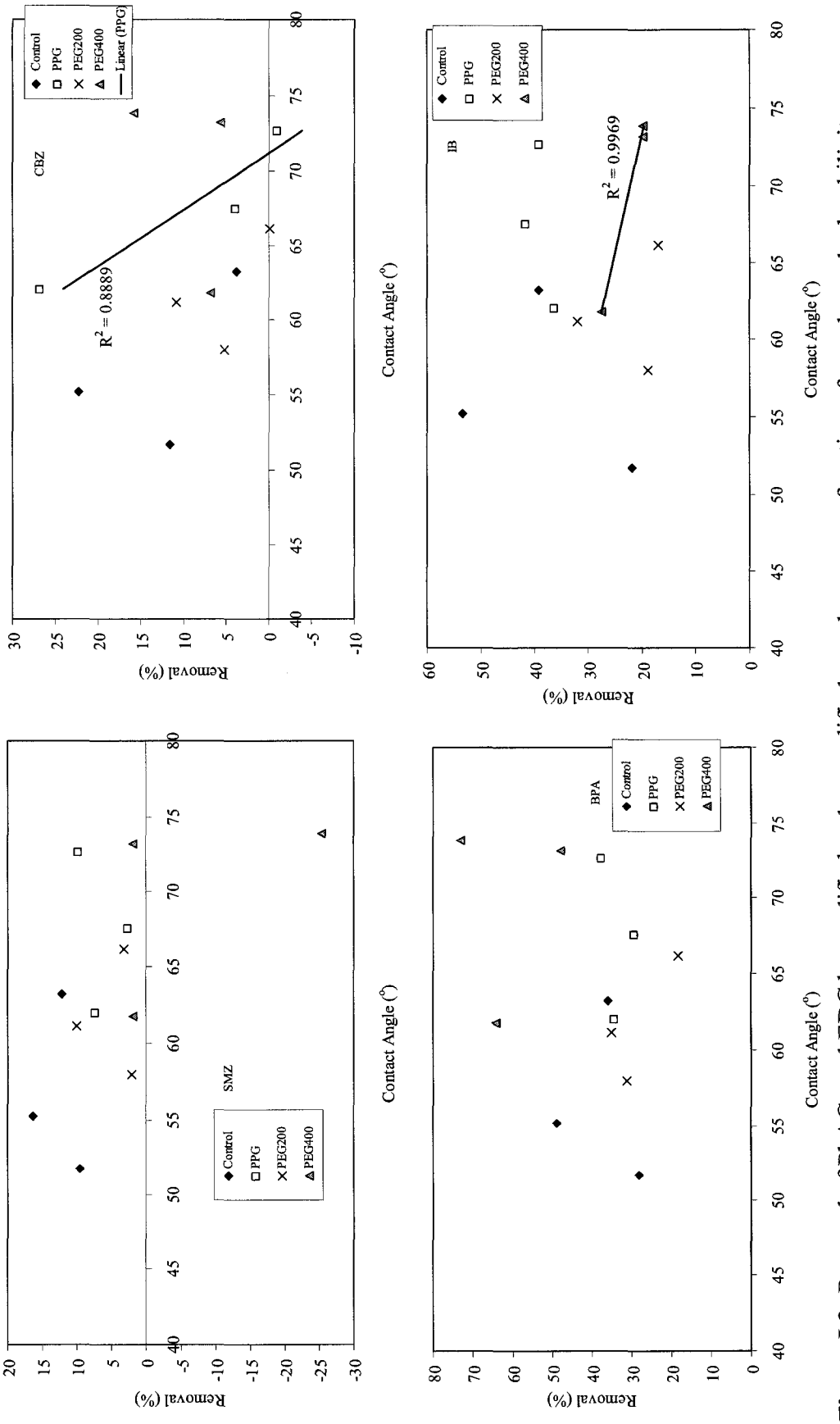


Figure I.2: Removal of PhACs and EDC by modified and unmodified membranes as a function of membrane hydrophilicity

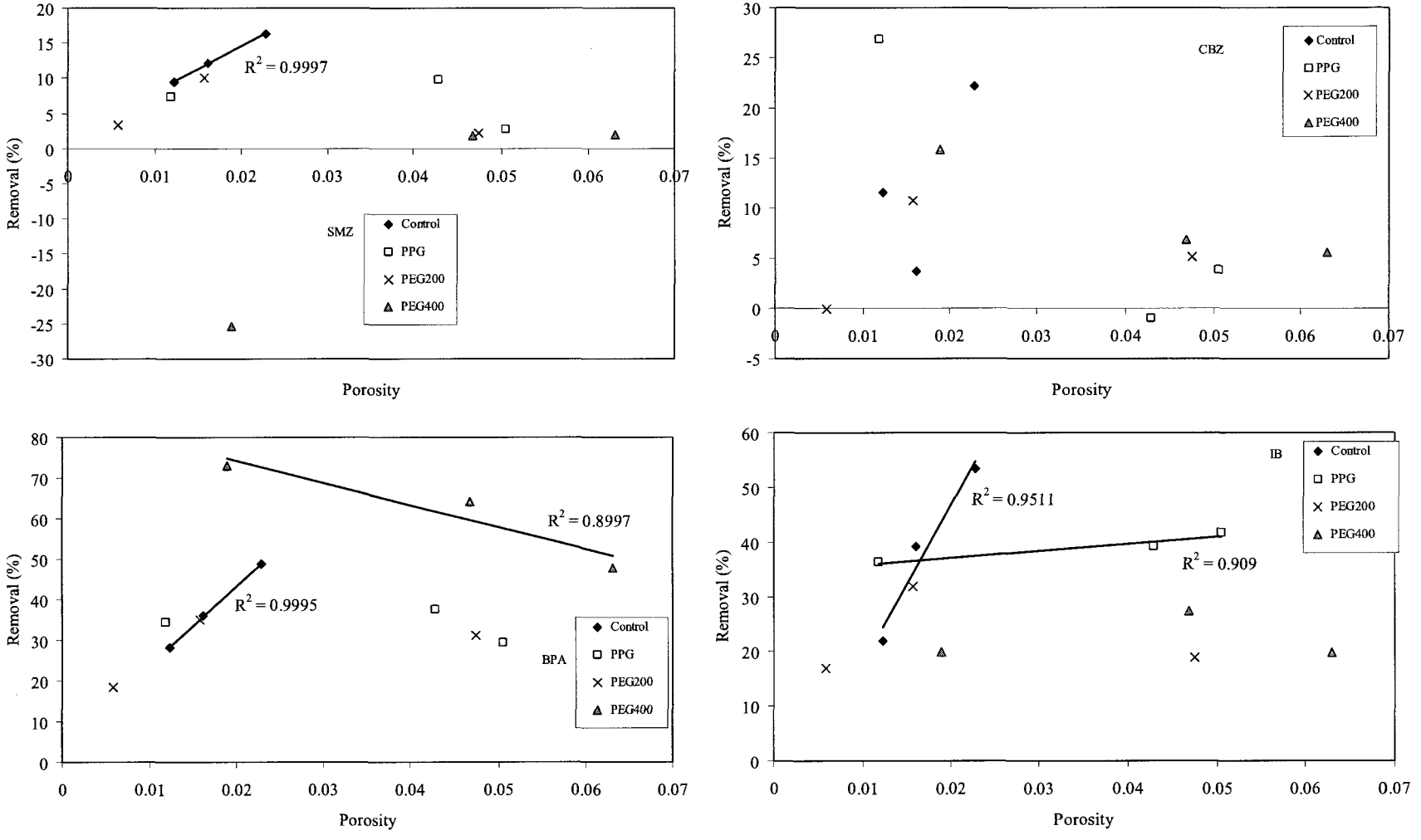


Figure I.3: Removal of PhACs and EDC by modified and unmodified membranes as a function of membrane surface porosity

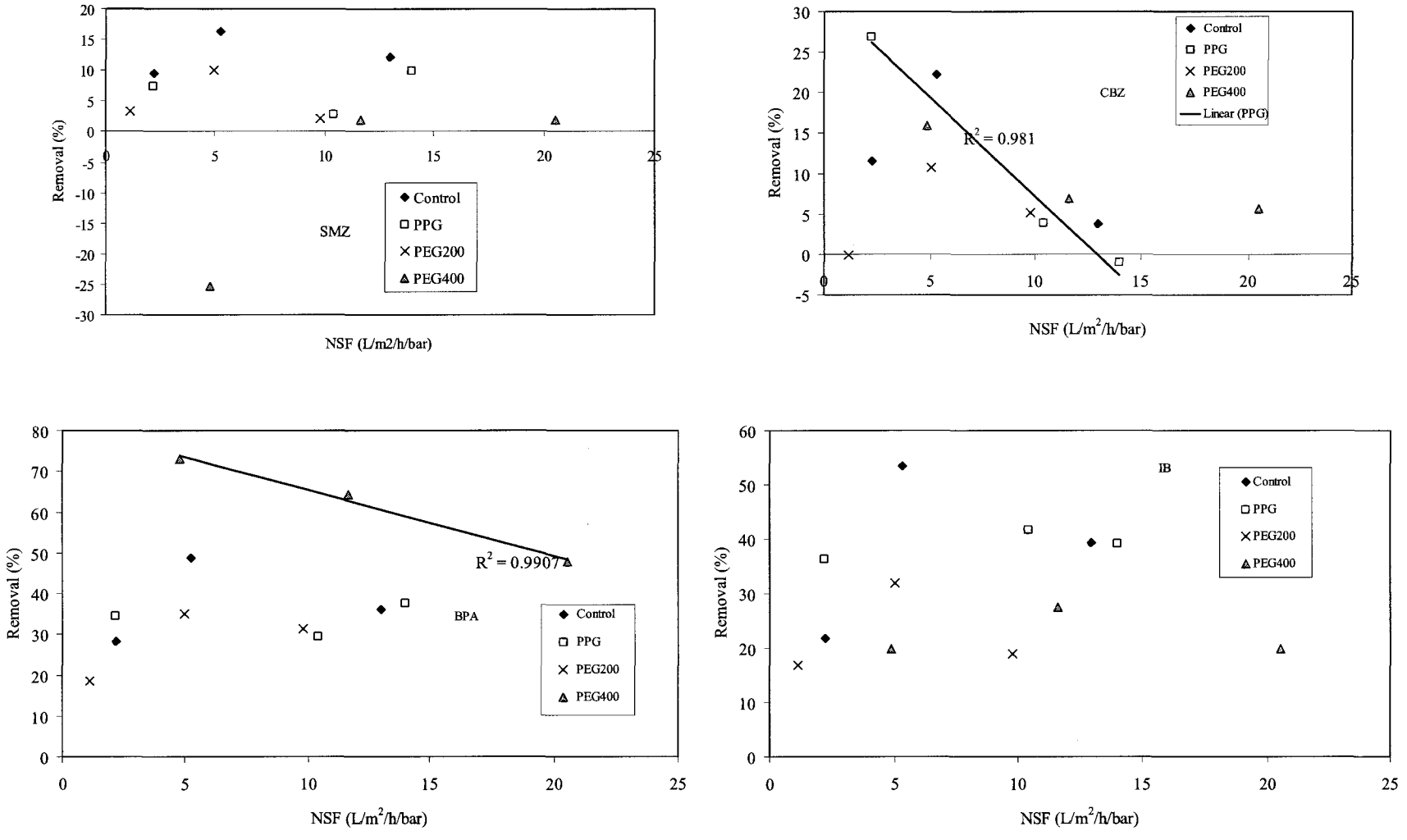


Figure I.4: Removal of PhACs and EDC by modified and unmodified membranes as a function of membrane flux

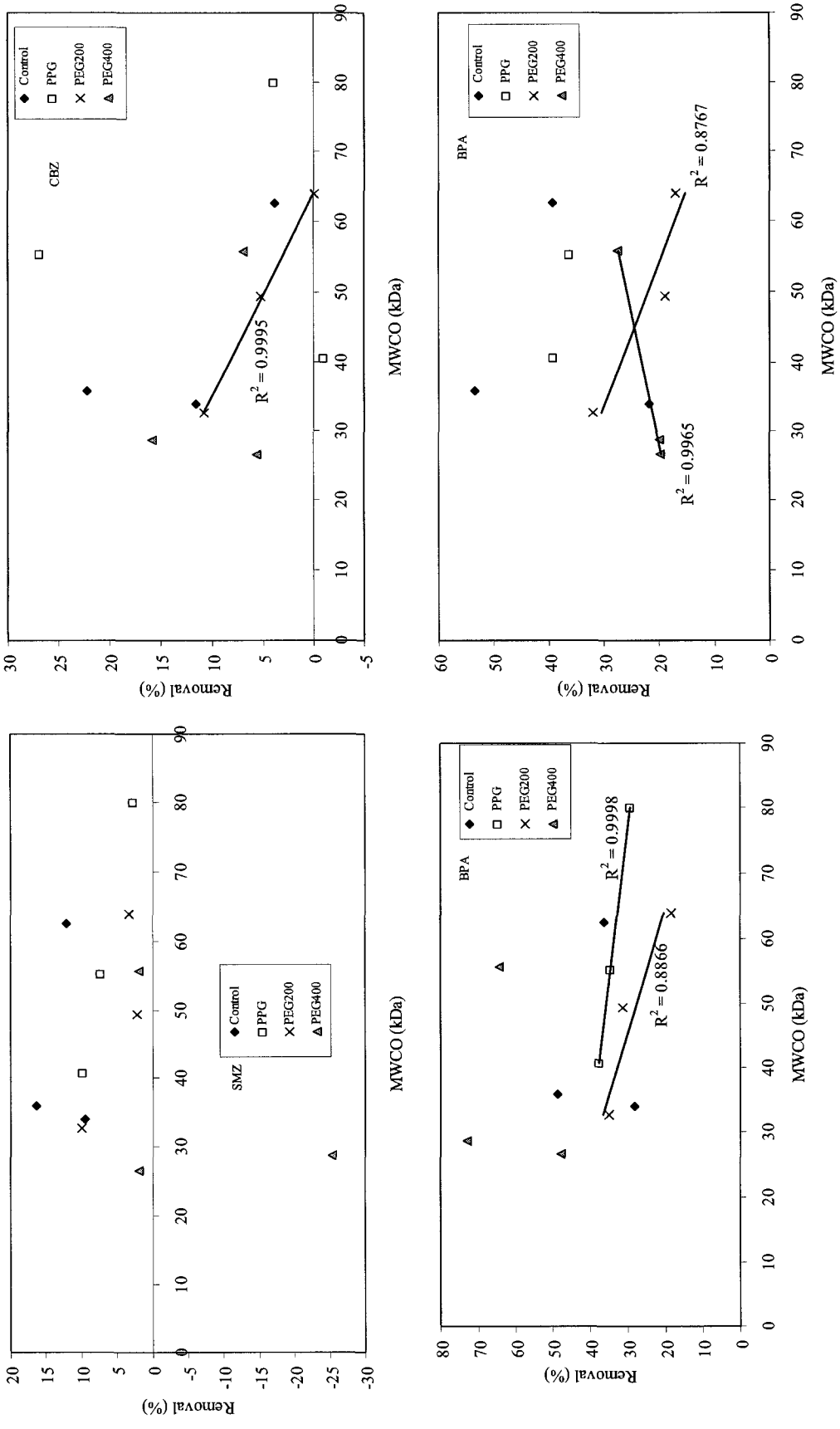


Figure I.5: Removal of PhACs and EDC by modified and unmodified membranes as a function of molecular weight cut off

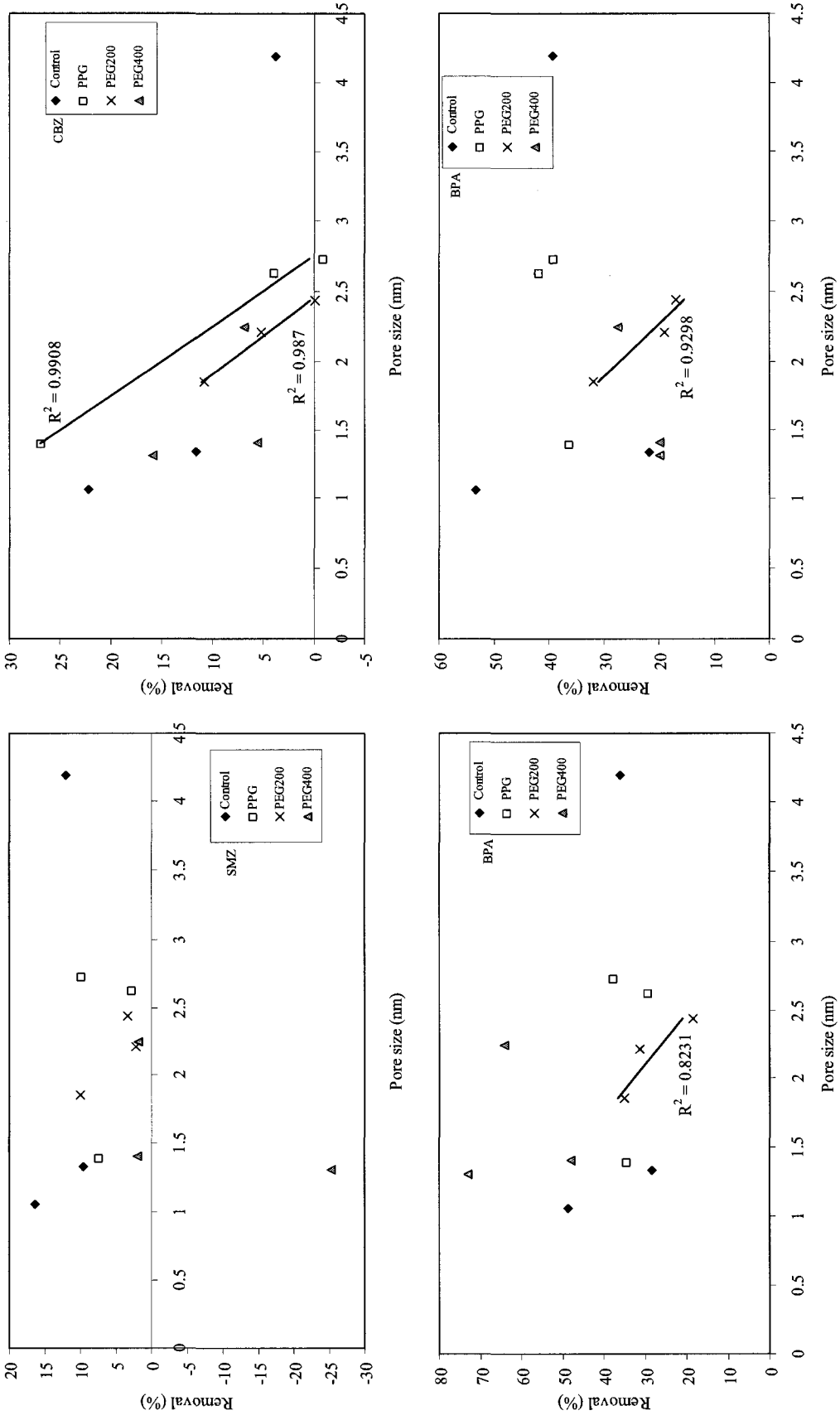


Figure I.6: Removal of PhACs and EDC by modified and unmodified membranes as a function of nominal pore size

APPENDIX J

Mass balance of solute adsorption during filtration tests

To determine the mass of target solute adsorbed to the membrane, the change in mass of solute in the system must be determined. The system is run in recycle mode, and therefore the quantity of mass in the system should only vary as a function of the samples removed (mass and volume removed). The initial mass in the system can be determined using the stock solution, where:

$$M_{initial} = C_{stock} * [4\text{L} - V_{stock\ sample}] \qquad \text{J.1}$$

Where $M_{initial}$ is the initial mass in the system (mgC), C_{stock} is the concentration of the stock sample, as measured by the low temperature TOC analyzer; $V_{stock\ sample}$ is the volume of stock sample used to determine the concentration; and 4L is the total volume of stock solution.

The stock solution is diluted using 4 L of MQ water (so the volume became 8L), however there is water remaining in the system which must be accounted for. Assuming there is no adsorption in the system within the first five minutes of filtration, and that the concentration has stabilized, the initial volume of solution is approximated by the following expression:

$$V_{initial} = \frac{(M_{initial} - C_{diluted\ stock} \bullet V_{diluted\ stock\ sample})}{0.5 \bullet (C_{set\ up} + C_{feed1})} \qquad \text{J.2}$$

Where $V_{initial}$ is the initial volume of solution in the system (L), $M_{initial}$ is the initial mass of target solute in the system, $C_{diluted}$ stock is the concentration of the feed solution after dilution from 4L to 8L, $V_{diluted\ stock\ sample}$ is the volume of the latter sample, $C_{set\ up}$ is the concentration in the system once the system is started (within the first two minutes) and C_{feed1} is the concentration in the system after 5 minutes (±1min) of filtration.

With the initial conditions of the system defined, the mass adsorbed in the system (on the membranes and the apparatus) will be the difference between the theoretical mass in the

system (the initial mass in the system minus all the samples withdrawn) and the actual concentration (measured via the feed samples analyzed in the low temperature TOC analyzer). Therefore the theoretical mass remaining in the system at time t is determined via:

$$M_{remaining,t} = M_{initial} - \sum_{i}^{t} C_{sample,t} \bullet V_{sample,t} \qquad \text{J.3}$$

Where $M_{remaining,\ t}$ is the mass of target solute remaining in the system at time t, $M_{initial}$ is the initial mass of solute in the system, $C_{sample,t}$ is the concentration of any given sample at time t and $V_{sample,\ t}$ is the volume of corresponding sample taken at time t.

The mass adsorbed as a function of time can be determined via the following equation:

$$M_{adsorbed,\ t} = M_{remaining,t} - C_{feed\ sample,t} \bullet V_{feed\ sample,t} \qquad \text{J.4}$$

The mass adsorbed can then be plotted versus time, and compared to the system baseline adsorption test in order to determine the adsorption onto the membranes (the difference between the two). As discussed in Section 4.3.3, the solute adsorption curves were lower than the baseline, which was unexpected and therefore it was not possible to quantify the adsorption onto the coupons. It is suggested that batch adsorption tests be conducted in order to properly evaluate saturation levels and how much of the removal quantified in these tests was due to adsorption.