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

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in the

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EVALUATION OF NOVEL POLYETHERSULFONE MEMBRANES INCORPORATING CHARGED SURFACE MODIFYING MACROMOLECULES FOR THE REMOVAL OF PHARMACEUTICALS AND ENDOCRINE DISRUPTING COMPOUNDS FROM DRINKING WATER

By

Amy Westgate

Master of Applied Science Thesis

Submitted to the School of Graduate Studies and Research

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To my parents, for their love and support

To Anne-Marie, I could not have done this without you

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ABSTRACT

Recently, there has been an increased concern of the potential effects of pharmaceuticals, personal care products (PPCPs) and endocrine disrupting compounds (EDCs) in drinking water. Their presence in surface waters has resulted in the skewing of sex ratios in aquatic biota and the effect on humans, as yet, remains unknown. Investigation into the effective removal of these compounds by water treatment plants (WTPs) has shown that conventional treatment processes are not very effective in removing these trace compounds. Studies have shown PPCPs and EDCs have been successfully removed by commercial nanofiltration (NF) and reverse osmosis (RO) membranes, but have low flux and high cost. North American WTPs, using membrane separation processes, are typically equipped with microfiltration (MF) or loose ultrafiltration (UF) membranes which, thus far, have proven ineffective for the removal of these target compounds.

This thesis focuses on the development of a tight charged UF membrane that effectively removes PPCPs and EDCs from drinking water while still maintaining a high flux and is cost effective. Novel membranes were developed by incorporating charged surface modifying macromolecules (CSMMs) in the manufacturing of polyether sulfone (PES) based membranes. The charged additives were expected to enhance the removal of PPCPs and EDCs by charge repulsion. Controls and three different CSMM (DEG-HBS, DEG-HBC and PPG-HBC) blended membranes were prepared at three different casting conditions and subsequently evaluated for various properties: flux, molecular weight cut-off (MWCO), porosity, charge and contact angle. Experimental membranes were further evaluated for the removal of four representative target compounds, sulfamethazine

(SMZ), carbamazepine (Carb), bisphenol A (BPA) and ibuprofen (IB). Removal by a commercial nanofiltration membrane, NF270 (DOW/FilmTec) was compared to the experimental membranes.

Removal results from the experimental membranes indicate membranes were unable to sustain effective removal of the target compounds. Typically, removal was initially high but decreased over the run. Membrane characteristics showed membranes had significantly larger pores than the target compounds indicating size exclusion was not the removal mechanism. Charge results indicated CSMM blended membranes were generally unchanged from the control membrane indicating, in addition to the un-sustained removal, that charge repulsion was not the removal mechanism. From the shape of the removal curves, it is assumed the removal mechanism is the result of membrane adsorption.

The CSMMs were found to have modified the membranes, though not sufficiently, to be considered significantly different than the controls in many respects. Membrane characteristics varied as a result of each CSMM incorporated and depending on each casting condition. Contact angle results for both PES-DEG-HBS and PES-PPG-HBC membranes at all three casting conditions increased in comparison to the controls, presumably because of changes in surface roughness. PES-DEG-HBC, on the other hand, decreased in contact angle at 18%, and increased in contact angle at 20% in comparison to the respective controls. Incorporation of migration time, particularly in the case of DEG-HBC, increased membrane flux without affecting MWCO. Increased PES

concentration (from 18 to 20%) saw an increased target compound removal. With the success of the DEG-HBC CSMM, incorporation of migration time at higher PES concentrations appears promising for achieving the desired characteristics. It is recommended that further optimization using CSMM DEG-HBC at increased PES concentrations with migration time be investigated for this application.

RESUME

Récemment, l'inquiétude des effets potentiels causés par les produits pharmaceutiques, produits d'entretien personnels (PPCPs) et les composés perturbateurs du system endocrinien (EDCs) dans l'eau potable augmente. Leur présence dans l'eau de surface cause un biais des ratios de sexe de la vie aquatique mais l'effet sur l'humain est présentement inconnu. Les enquêtes dans l'efficacité de l'enlèvement de ces composés par les usines de traitement d'eaux (WTPs) a démontré que les procèdes conventionnels n'éliminent pas efficacement ces composés. Des études démontrent que les PPCPs et EDCs peuvent être enlevés avec succès par des membranes commerciales de nanofiltration (NF) et d'osmose inverse (RO) mais elles ont des taux de perméation bas et un prix d'opération élevé. Les WTPs nord-americaines utilisent typiquement soit la microfiltration (MF) ou l'ultrafiltration (UF) lâche comme procédé de séparation par membrane, qui, jusqu'à présent est inefficace pour l'enlèvement des composées cibles.

Cette thèse centre sur le développement d'une membrane d'ultrafiltration serrée et chargée qui est efficace à l'enlèvement des PPCPs et EDCs de l'eau potable tout en etant capable de soutenir un taux de perméation haut économiquement. Les membranes a base de polyether sulfone (PES) développées pour cette thèse ont été modifiées par l'incorporation de molécules chargés qui modifient la surface (CSMMs), donc il est attendu que les additifs chargés vont augmenter la réjection des PPCPs et EDCs par la répulsion chargée. Des contrôles et trois différents CSMMs (DEG-HBS, DEG-HBC et PPG-HBC) ont été incorporés dans des membranes à trois conditions de moules différentes et ensuite évaluées pour: perméabilité, coupure de masse molaire (MWCO),

porosité, charge et angle de contact. Les membranes expérimentales ont ensuite été évaluées pour la réjection de quatre composés cibles représentatifs, sulfaméthazine (SMZ), carbamazepine (Carb), bisphénol A (BPA) et ibuprofen (IB). Une membrane nanofiltration commerciale, NF270 (DOW/Filmtec), a aussi été testée pour la réjection des mêmes composées cibles et comparée aux membranes expérimentales.

Les résultats de réjection par les membranes expérimentales ont indiquées que les membranes n'ont pas été capables de soutenir un réjection efficace des composés cibles. La réjection était initialement haute mais a diminué au cours du test de filtration. Les caractéristiques des membranes expérimentales démontrent que la taille des pores des membranes était significativement plus grande que les composées qui indique que l'élimination par taille n'est pas le mécanisme de réjection. La charge des membranes indique que les membranes avec CSMM n'ont généralement pas été changées en comparaison aux membranes contrôles, qui indique que la répulsion par charge n'est pas le mécanisme de réjection. D'après la forme des courbes de réjection, l'assomption est que la réjection est le résultat d'adsorption par la membrane.

Les CSMMs ont modifiés les membranes, mais pas assez pour être distinctement différents des contrôles dans plusieurs respects. Les caractéristiques de la membrane ont variés en fonction de chaque CSMM incorporé et la condition de moule. Les résultats de l'angle de contact des membranes PES-DEG-HBS et PES-PPG-HBC, aux trois conditions moules, démontrent une augmentation en hydrophobicité, qui est présumé d'être le résultat de l'hétérogénéité de la surface. Contrairement, PES-DEG-HBC était

plus hydrophilique à 18%, et plus hydrophobique à 20%, en comparaison aux contrôles respectifs. L'incorporation d'un temps de migration, particulièrement dans le cas du DEG-HBC, à augmenté le changement continuel sans affecter le MWCO. L'augmentation de la concentration du PES (de 18% à 20%) a produit une augmentation en réjection des composées cibles. Avec le succès du CSMM DEG-HBC, l'incorporation du temps de migration à des plus haute concentrations de PES apparait comme la direction probable pour obtenir les caractéristiques désirées. Comme recommandation envers cette application, plus d'optimisation devrai être fait en utilisant le CSMM DEG-HBC a des concentrations de PES plus élevées avec de différents temps de migration.

NOMENCLATURE

Ag	Silver
AgCl	Silver chloride
APEO	Alkylpolyethoxylates
BPA	Bisphenol A
CA	Cellulose acetate
Carb	Carbamazepine
CSMM	Charged surface modifying macromolecule
Da	Dalton
DEG	Di-ethylene glycol
EDC	Endocrine disrupting compound
GAC	Granular activated carbon
HBC	Hydroxyl benzene carbonate
HBS	Hydroxyl benzene sulfonate
HCl	Hydrochloric acid
IB	Ibuprofen
KCl	Potassium chloride
log K_{OC}	Organic-carbon partition coefficient
log K_{OW}	Octanol-water partition coefficient
LOQ	Level of quantification
MF	Microfiltration
MQ	Milli-Q water
MW	Molecular weight

MWCO	Molecular weight cut-off
NaOH	Sodium hydroxide
NF	Nanofiltration
NMP	1-methyl-2-pyrrolidone
NOM	Natural organic matter
NSF	Normalized standard flux
PA	Polyamide
PAC	Powder activated carbon
PCP	Personal care product
PEO	Polyethylene oxide
PES	Polyether sulfone
PES18	18 wt% PES
PES18-3	18 wt% PES with 3 min migration
PES20	20 wt% PES
PPCP	Pharmaceutical and personal care product
PPG	Poly-propylene glycol
PSf	Polysulfone
PWP	Pure water permeabilitiy
RO	Reverse osmosis
SMM	Surface modifying macromolecules
SMZ	Sulfamethazine
Tg	Glass transition temperature
TOC	Total organic carbon

UF	Ultrafiltration
UV	Ultra-violet
WTP	Water treatment plant
WWTP	Wastewater treatment plant

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CHAPTER 1

INTRODUCTION

In the recent past, the threat of emerging contaminants has increasingly become a greater cause for concern. Notably, the presence of pharmaceuticals, personal care products (PPCPs) and endocrine disrupting compounds (EDCs) in source water has caused concern due to their observed effects on aquatic life (notable skewing of sex ratios) and their unknown effects on humans. These contaminants enter surface waters primarily via wastewater effluents but could also be the result of agricultural activities. Some may adsorb to sediment while others degrade; however, since they are constantly being introduced into the environment, they are considered pseudo-persistent.

Due to the complex and unique nature of wastewaters, and the fact that effluent discharges are not the only source of contamination, water treatment plants (WTPs), with a somewhat simpler water matrix, appear to be most promising as a starting point for the removal of PPCPs and EDCs.

Research has shown that membrane processes are one of the few technologies capable of removing these types of compounds. The use of commercial membranes has been extensively investigated for the removal of these compounds. Due to the low molecular weight of PPCPs and EDCs, successful removal has only been achieved by tighter membranes (i.e., nanofiltration and reverse osmosis membranes) but it is accomplished at lower flux. North American drinking WTPs, if they do employ membranes as a treatment step, use micro- or ultrafiltration membranes which have high fluxes but poor

removal of PPCPs and EDCs. Currently, there is no one membrane capable of removing PPCPs and EDCs while still maintaining a high flux.

One method to modify a membrane is via the incorporation of an additive, In fact all commercial membranes contain one or more undisclosed additive to improve membrane characteristics. Recent studies by Mosqueda-Jimenez et al. (2004 a, b, c, 2006) and Nguyen et al. (2007) have investigated the use of a group of additives, denominated Surface Modifying Macromolecules (SMMs) since during the casting process they migrate to the surface of PES based membranes. The addition of this type of additive and manufacturing of membranes via the phase inversion technique (Matsuura, 1994) has proven successful.

The objective of this thesis is to develop tight ultrafiltration membranes incorporating charged SMMs (CSMMs) and evaluate them for the removal of a select number of PPCPs and EDCs. Small pore-sized membranes are desired so the small molecular sized PPCPs and EDCs cannot pass through the membrane (i.e., size exclusion). The charge resulting from the incorporation of these additives may assist in the removal of these target compounds.

CHAPTER 2

LITERATURE REVIEW

The following literature review will discuss emerging contaminants, the associated environmental issues, and their removal by conventional and advanced drinking water treatment processes including membrane separation processes. The review will also discuss membrane process types, their capabilities, membrane manufacturing and the incorporation of surface modifying additives in membrane preparation.

2.1 Emerging contaminants

There are numerous contaminants affecting our environment today. Awareness of emerging contaminants such as PPCPs and EDCs has resulted in concern of the effects to the aquatic environment and ultimately to humans. A PPCP can be defined as a compound that is used for medicinal purposes (such as a prescription drugs) or found in products for personal maintenance (such as shampoos, cosmetics, sunscreens or detergents). An EDC is a compound that directly affects the endocrine system of an organism. EDCs may be PPCPs but they are also found within many other groups of compounds. EDCs may result in the skewing of sex ratios of a population (Sanderson et al., 2004). All of these compounds are typically of low molecular weight (200-500 g/mol) and size and are found in low concentrations in surface water, in the μg/L to ηg/L range. Examples of common PPCPs and EDCs are shown in Table 2.1.

Table 2.1: Examples of Common PPCPs and EDCs

Group	Examples of Compounds	
Analgesics and Non-Steroidal Anti-Inflammatory Drugs	Codeine Ibuprofen Acetylsalicylic acid	Diclofenac Naproxen Ketoprofen
Antibiotics	Erythromycin	Sulfamethazine
Veterinary Antibiotics	Carbadox	Tylosin
Antidepressants	Diazepam	Fluoxetine
Anti-Epileptics	Carbamazepine	Primidone
Blood Lipid Regulators	Gemfibrozil	Clofibric acid
Endocrine Disrupting Compounds	Bisphenol A Octylphenol	Nonylphenol Perfluorooctanoic acid (PFOA)
Natural and Synthetic Hormones	17α-estradiol 17β-estradiol 17α-ethynyl estradiol	Estrone Progesterone Testosterone
UV Filters	Octocrylene Benzophenone	Ethylhexyl methoxycinnamate 4-Methylbenzylidene camphor

2.2 Environmental impact of PPCPs and EDCs

Input of PPCPs and EDCs into the environment results from a wide variety of human activities. Most commonly, they enter via municipal or industrial wastewaters (Ternes et al., 2002), agricultural run-off (Jones et al., 2004; Hirsch et al., 1999; Metcalfe et al., 2003b), landfill leachate (Heberer, 2002a; Metcalfe et al., 2003a). Improvements in analytical techniques and lower detection limits have led to the detection of these compounds. As a result, studies carried out by Kolpin et al. (2002), Heberer (2002b), Ternes et al. (2002) and Ferrari et al. (2003) have attempted to determine the environmental concentration and contamination of these compounds. Concentrations in surface water and wastewater typically are in the μg/L to ηg/L range. While this can be considered a low range, there are many problems associated with PPCPs and EDCs, resulting in effects on aquatic biota (Sanderson et al., 2004).

2.2.1. Occurrence in drinking water sources

Sewage effluent is attributed as the primary source of environmental contamination of PPCPs and EDCs (Roberts and Thomas, 2006; Lindqvist et al., 2005; Petrovic et al., 2003b; Heberer, 2002a; Andreozzi et al., 2003; Metcalfe et al. 2003b). When PPCPs or EDCs are consumed, the active ingredients are not fully metabolized; they have been found to remain between 30-90% in their active or conjugated forms when excreted. (Kummerer, 2004; Andreozzi et al., 2003; Metcalfe et al., 2003b; Heberer, 2002a). Studies by Liebig et al (2006), Zuccato et al. (2006) and Anderson et al. (2004) have found that WTP influent concentrations of certain drugs may be calculated based on population size and the approximate removal efficiencies of each treatment step within the wastewater treatment plant (WWTP).

The threat of PPCPs to the aquatic environment was not an issue when wastewater treatment processes were first designed. However, with the advances in analytical techniques, it is now possible to detect and characterize the performance of water and wastewater plants for the removal of these target compounds. Properties of target compounds are quite variable and consequently removal varies, however, in general, removal has been found to be quite low. Despite the increased knowledge about the occurrence and concentration of PPCPs and EDCs in wastewaters, currently there are no wastewater effluent standards which would require advanced treatment in an effort to remove these contaminants. Another concern with these compounds is their potential for re-activation during the treatment process (Roberts and Thomas, 2006). Lindqvist et al. (2005) found that although concentrations downstream from urban WWTPs decreased,

the PPCPs and EDCs remained in the same proportion, meaning the waste stream had only been diluted by the receiving water. Similarly, antibiotics and/or pesticides as a result of agricultural activities have, to a lesser extent, contributed to contamination (Hirsch et al., 1999; Metcalfe et al., 2003b). It has been shown by Zuccato et al. (2006) and Metcalfe et al. (2003b) that wastewater contamination may be characterized by the presence of caffeine and nicotine; however, there are many other anthropogenic compounds present in surface water.

Groundwater is generally considered a less contaminated source water (Hohenblum et al., 2004), and consequently, there have been fewer investigations into its contamination. However, in that same study, Hohenblum et al. (2004) found instances of contamination by nonylphenol and bisphenol A. Similarly, a study by Heberer (2002a) found polar compounds such as clofibric acid, carbamazepine, primidone and sulphonamide antibiotics leached from surface water into groundwater during bank filtration.

2.2.2 Fate

Roberts and Thomas (2006) found some compounds entering the WWTP are active or can become reactivated during treatment as concentrations of some compounds rose between influent and effluent readings or between unit operations. Once in the environment, some compounds do degrade while others remain active and are adsorbed to sediment or are adsorbed by aquatic species. It is important to note that the persistence of PPCPs and EDCs in the environment is difficult to quantify because they are constantly being introduced. They can therefore be considered pseudo-persistent.

There are four main mechanisms which can impact compound concentrations when these solutes are introduced into the aquatic environment. Solutes may adsorb to sediment, natural organic matter (NOM), colloids or aquatic species in the receiving water; degrade biologically, with the help of light (photolysis) or via hydrolysis, or may remain unchanged and simply be diluted. Lai et al., (2000) stated sorption to NOM and sediment could be predicted based on the octanol-water partition coefficient, log K_{OW} or organic carbon partition coefficient, log K_{OC}. Higher partition coefficient indicates higher sorption potential. For some compounds, such as ibuprofen, biological degradation may be the main removal mechanism (Tixier et al., 2003). The same study concluded naproxen and ketoprofen were likely removed by both biodegradation and photodegradation. Hydrolysis, on the other hand, is an unlikely mechanism as pharmaceuticals are designed to resist degradation.

2.2.3 Effects

Concern of the effects of PPCPs and EDCs is increasing. Richardson (2003) reported that low environmental concentrations have repeatedly been shown to cause noticeable effects to wildlife. Most commonly known is the skewing of sex ratios (androgenic and estrogenic effects) in a population, attributed to the presence of these compounds, primarily EDCs, in the environment. For example, the active ingredient of the birth control pill (17β-ethynyl estradiol) at a concentration of 0.1 ηg/L has been proven to result in the feminization of male fish (Purdom et al., 1994). The effect on humans, however, remains unknown (Andreozzi et al., 2003) but EDCs have been attributed,

without proof, with decreased sperm counts, breast and reproductive tract cancers and early breast development (Snyder et al., 2005; Liu et al., 2005).

Mixture effects from PPCPs and EDCs are greater cause for concern. The presence of multiple active compounds in the environment, even at low concentrations has been found to have significant effect on aquatic species. A study by Wilson et al. (2003) using a combination of triclosan, ciprofloxacin and Tergitol© 10, containing the surfactant nonylphenol ethoxylate, found significant effects on algal communities. Another report found a mixture containing ibuprofen, Prozac© and ciprofloxacin at concentrations 10 to 200 times lower than human doses was harmful to plankton, aquatic plants and fish (Jones et al., 2004). Calamari et al. (2003), using a cocktail of atenolol, bezafibrate, carbamazepine, cyclophophamide, ciprofloxacin, furosemide, hydrochlorothiazide, ibuprofen, lincomycin, ofloxacin, rantidine, salbutamol and sulphamethoxazole at environmental concentrations observed at 30% decrease of *in vitro* cell growth of both the liver cells of zebrafish and human embryonic cells (HEK293). The effects on aquatic life have only recently begun to be studied and there have yet to be reports on the direct effects to humans (Jones et al., 2004). There is, however, concern for the potential accidental drug interaction in the portion of the population most susceptible, namely people with compromised immune systems, children and the elderly.

2.2.4 Seasonal variation

The type and concentration of PPCPs and EDCs detected can vary based on the season as reported by both Loraine and Pettigrove (2006) and Lindqvist et al. (2005). A study by

Buser et al. (1998) noticed winter concentrations of diclofenac, an analgesic, exiting a Swiss lake increased in comparison to the summer. This may be the result of higher consumption (Herberer, 2002a) or a decrease in removal efficiency by WWTP caused by the lower temperature and consequently slower degradation (Vieno et al., 2006; Lindqvist et al., 2005). Seasonal effects are also evident in WTPs (Jasim et al., 2003, 2004; Vieno et al., 2006).

2.2.5 Occurrence and removal during water treatment

Conventional water treatment plants treating surface waters generally consist of coagulation/sedimentation/filtration followed by a media filter before disinfection and distribution. Most North American water treatment plants do not include advanced treatments such as activated carbon, ozonation or membrane treatment (Section 2.3).

Studies have shown PPCPs and EDCs are detected at the inlet of the WTPs and in finished drinking water. In fact, several studies have been conducted to characterize removal by current water treatment methods and investigate performance by advanced treatment processes. Characterization of finished drinking water has also detected the presence of PPCPs and EDCs including: bisphenol A, clofibric acid, carbamazepine, diazepam, diclofenac, estrone, gemfibrozil, ibuprofen, ketoprofen, sulfamethoxazole, triclosan and tylosin. Table 2.2 contains some of the more frequently detected compounds in drinking water.

Table 2.2: Detection of PPCPs and EDCs in finished drinking water

Compound	Concentration (ng/L)					Detection Frequency	Location	References
	LOQ	Max	Median	Mean	General			
17α-estradiol	0.1	0.3	0.3	0.3		1 of 10	Germany	Kuch and Ballschmiter (2001)
17α-ethynylestradiol		2.4						Heberer (2002a)
	0.05	0.5	0.35	0.35		4 of 10	Germany	Kuch and Ballschmiter (2001)
17β-estradiol	0.1	2.1	0.3	0.7		5 of 10	Germany	Kuch and Ballschmiter (2001)
Acetaminophen (paracetamol)					detected	1 of 2	Louisiana, USA	Boyd et al. (2003)
					detected		Canada	Boyd et al. (2003)
Bezafibrate		27					Germany	Jones et al. (2004)
Bisphenol A					detected	2 of 2	Louisiana, USA	Boyd et al. (2003)
					detected		Canada	Boyd et al. (2003)
	0.02	2	1.1	1.1		10 of 10	Germany	Kuch and Ballschmiter (2001)
	1000	420					USA	Stackelberg et al. (2004)
Caffeine	14	119					USA	Stackelberg et al. (2004)
Carbamazepine	11	258					USA	Stackelberg et al. (2004)
Clofibric Acid					detected		UK	Jones et al. (2004)
		170	19	40.08	14 WTPs	12 of 14	Germany	Heberer (2002b)
		270					Germany	Heberer (2002a)
		70					Germany	Jones et al. (2004)
		165					Germany	Jones et al. (2004)
		270					Germany	Jones et al. (2004)
		170					Germany	Jones et al. (2004)
	1.5	5.3			3.2-5.3		Lodi, Italy	Zuccato et al. (2000)
DEET (*N,N*-diethyl-meta toluamide)	500	66					USA	Stackelberg et al. (2004)
Diazepam		10					UK	Jones et al. (2004)
	0.02				0.2		Varese, Italy	Zuccato et al. (2000)
	0.02	23.5			19.5-23.5		Lodi, Italy	Zuccato et al. (2000)
Diclofenac		6					Germany	Jones et al. (2004)
Estrone					detected		Ontario, Canada	Boyd et al. (2003)
	0.05	0.6	0.4	0.4		4 of 10	Germany	Kuch and Ballschmiter (2001)
	0.1			0.16		5 of 5	Germany	Verstraten et al. (2003)

Compound	Concentration (ng/L)					Detection Frequency	Location	References
	LOQ	Max	Median	Mean	General			
Estrone (con't)					detected	2 of 2	Louisiana, USA	Boyd et al. (2003)
Gemfibrozil		70					Canada	Jones et al. (2004)
Ibuprofen					detected		Germany	Heberer (2002a)
		1350		930		2 of 15	USA	Loraine and Pettigrove (2006)
		3					Germany	Jones et al. (2004)
Nonylphenol	0.05	16	6.6	8		10 of 10	Germany	Kuch and Ballschmiter (2001)
Octylphenol	0.04	4.9	1.8	2		10 of 10	Germany	Kuch and Ballschmiter (2001)
Phenazone					detected		Germany	Heberer (2002a)
		250		150		2 of 2	Germany	Zuhlke et al. (2004)
		400					Germany	Reddersen et al. (2002)
Propyphenazone		80				1 of 2	Germany	Zuhlke et al. (2004)
				120		6	Germany	Reddersen et al. (2002)
Triclosan				734		1 of 15	USA	Loraine and Pettigrove (2006)
Tylosin		1.7			0.6-1.7		Lodi, Italy	Zuccato et al. (2000)

LOQ – Level of Quantifiaction

2.2.5.1 Chemical treatment

Water treatment processes, like wastewater treatment processes were not designed for removal of these compounds. Several studies investigated chemical dosage at the beginning of the water treatment process for the removal of PPCPs and EDCs. A study by Adams et al. (2002) using aluminum sulfate and ferric sulfate for coagulation indicated "no significant removal" of any of the tested compounds (carbadox, sulfachloropyridazine, sulfadimethozine, sulfamerazine, sulfathiazole, trimethoprim). Westerhoff et al. (2005) used the same coagulants as Adams et al. (2002) and achieved no significant removal (<25%) in Ohio River water. Similar conclusions were reached by Petrovic et al. (2003a) when removing clofibric acid, diclofenac, carbamazepine, bezafibrate and Vieno et al. (2005) for elimination of ibuprofen and ketoprofen. All studies indicate chemical treatment is insufficient for the removal of PPCPs and EDCs from drinking water and additional treatment is required.

2.2.5.2 Activated carbon

There are two main forms of activated carbon employed in water treatment, powder activated carbon (PAC) and granular activated carbon (GAC). PAC is less desirable to use as an adsorbent since it cannot be regenerated and the PAC contaminant loading is in equilibrium with the outlet concentration of the contaminated water. It is typically used for seasonal taste and odour concerns or if there is a problem with the source water, such as a spill. GAC, on the other hand, theoretically achieves 100% removal for at least a certain period of time, accommodates a greater contaminant loadings and can be regenerated; therefore, it is generally a more economical option. Most North American WTPs incorporate activated

carbon, as a taste and odour polishing step using PAC (Crittenden et al., 2005). Many European WTPs incorporate GAC to compensate for the more contaminated raw river water.

Adsorption using PAC was investigated by Westerhoff et al. (2005), Boyd et al. (2003) and Adams et al. (2002). Adams et al. (2002) achieved a significant removal of PPCPs, with removal varying between 51 and 97% with a 10 mg PAC/L dose and 81 to 98% with a 20 mg PAC/L dose. With a higher dose (>20 mg PAC/L), higher removal (>90%) was achieved for all compounds. However, the effectiveness of PAC is dependent on the target compound. In a study by Boyd et al. (2003), PAC, at a low dosage of 2 mg/L was found to be ineffective in the removal of naproxen in Mississippi River water. While the removal was not complete, it was significant. PAC cannot achieve complete removal of pharmaceuticals in part due to the nature of PAC contact processes whose upper performance limit is in equilibrium with the effluent, which leads to much less than 100% removal.

Petrovic et al. (2003b) found GAC removed 73% of alkylpolyethoxylates (APEOs) at an average feed concentration of approximately 1.5 mg/L. Clofibric acid was not removed in the same study. Stackelberg et al. (2004) also found that carbamazepine, among others, persisted in WTP despite filtration and GAC treatment. Vieno et al. (2005) concluded the use of GAC for the removal of ibuprofen and ketoprofen was incomplete at only 33% and 23%, respectively. While removal by GAC has not proven to be as successful as PAC, the use of PAC is intermittent and quite costly. WTPs that do use activated carbon regularly are usually equipped with a GAC column.

2.2.5.3 Oxidation

Oxidation is the degradation of a target compound particularly with the use of chlorine or ozone. A study by Westerhoff et al. (2005) found chlorine reactivity with pharmaceuticals (trimethoprim, sulfamethoxazole, dilantin, triclosan and erythromycin) was high and the removals greater than 90% for a residual chlorine dose of 0.5 to 1 mg/L after 24 hours contact time (depending on the source water). Such a long contact time within a clearwell is uncommon; however it may be achievable within the distribution system, especially in large urban centers.

Ozone had comparable removal capabilities. Diclofenac and carbamazepine were reduced by more than 90%, bezafibrate by 50% (Ternes et al., 2002). Adams et al. (2002) obtained pharmaceutical (carbadox, sulfachloropyridazine, sulfadimethoxine, sulfamerazine, sulfathiazole and trimethoprim) removal greater than 95% within 1.3 minutes. Westerhoff et al. (2005) oxidized more than 80% of 62 PPCPs and EDCs; however atrazine and ibuprofen were not removed. These results are also backed by the findings of Boyd et al. (2003), who concluded that both chlorination and ozonation were effective for the removal of PPCPs (clofibric acid, naproxen, ibuprofen, acetaminophen, caffeine, fluoxetine, chlorophene and triclosan) and EDCs (bisphenol A, estrone and 17β-estradiol). The downfall of oxidation may lie in the formation of EDC by-products, of which the effects are unknown (Westerhoff et al., 2005).

2.3 Membranes

A membrane is a semi-porous material which allows for the selective separation of compounds in a fluid solution. The process yields a less concentrated stream, the one that has passed through the membrane, called the permeate and a more concentrated stream, the retentate.

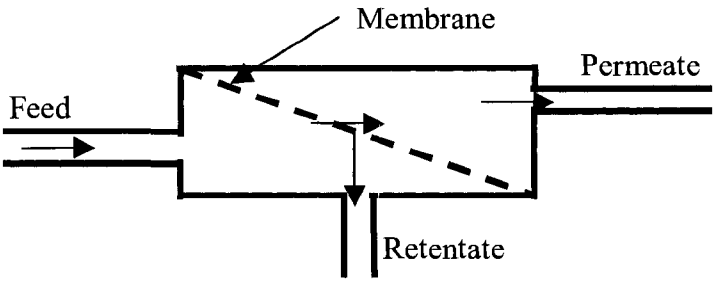


Figure 2.1: Schematic diagram of membrane separation

Membranes have a wide variety of fluid separation applications, including the dairy industry, for the production of electronics (ultrapure water), gas separation, water treatment, wastewater treatment, the treatment of landfill leachate, etc. The principal removal mechanisms are steric (size) exclusion or charge repulsion. Steric exclusion is separation based on the relative size of the pore to the target compound. Charge repulsion, on the other hand, is the exclusion of a compound based on the relative charge of the membrane and the compound. Another, less significant removal mechanism is adsorption to the membrane itself. This mechanism may initially dominate filtration but adsorption sites are quickly exhausted and steric or electrostatic repulsion quickly governs.

2.3.1 Membrane classification and materials

Classification of membranes is based on their pore size, which is not distinct. In order of decreasing pore size, the membrane categories are: microfiltration (MF), ultrafiltration (UF),

nanofiltration (NF) and reverse osmosis (RO). To increase market competition, pore sizes can be modified. UF and NF membranes have been sub-divided into loose and tight; loose UF membranes compete with MF membranes while tight UF membranes compete with loose NF membranes. The selection of one membrane over the other is dependent on the flux and separation desired.

Materials for these membranes are quite diverse but can be divided into two general categories, inorganic (metals, glasses, ceramics) and organic (polymers) (Mallevialle et al., 1996). These membranes may be made of a wide variety of materials, primarily polyamide (PA), cellulose acetate (CA) or polysulfone (PSf). The preparation of the membrane materials is accomplished via a variety of methods, either sintering, stretching, track etching, a coating technique or phase inversion (Mallevialle et al., 1996); some of these methods are only suitable for the preparation of certain types of membranes. Most promising for further advances in membrane technology is the phase inversion technique since this method has great potential for membrane tailoring using the same base polymer (Mallevialle et al., 1996). Membranes produced using this method are asymmetrical meaning they have a selective layer (which can be tailored with the addition of additives) and a porous supporting material (Nunes and Peinemann, 2001). The first application of this preparation method was the production of an asymmetric RO membrane made of cellulose acetate in the 1960s (Mallevialle et al., 1996, Taylor and Jacobs, 1996). Since then, one of the most important developments has been the production of thin film composite membranes accomplished by interfacial polymerization, a two-step process. This method led to the development of NF and improved RO membranes and ultimately to the further development of UF membranes.

The primary objective of conventional water treatment is the removal of turbidity caused by particulates, bacteria and protozoan cysts. The North American membrane market for surface water treatment is dominated by loose UF and MF membranes due to their greater flux and ability to reduce bacteria and protozoan cysts. Currently, there are no treatment standards for viruses, so the implementation of tighter (and more expensive) membranes such as a UF membrane is not required. UF and MF membranes only achieve a limited removal of natural organic matter (NOM) – a key precursor of the toxic chlorine disinfection by-products. Due to the high cost and energy requirements, few North American plants use NF membranes for NOM removal; however they are used for water softening (Nunes and Peinemann, 2001).

2.3.2 PPCP and EDC removal via membranes

PPCPs and EDCs are very diverse in properties and uses but are all of low MW, typically 200-300 Da. Membranes investigated for the removal of these target solutes have focused on tight commercial membranes. These membranes are made of polyamide, cellulose acetate and to a lesser extent polysulfone. Polyamide membranes are best suited for the removal of hormone mimicking compounds (Xu et al., 2005) and their removal is dominated by size exclusion (Yoon et al., 2007; Kimura et al., 2004). Cellulose acetate has effectively removed pesticides and other micropollutants (Yoon et al., 2004) with electrostatic repulsion as the main removal mechanism. Table 2.3 contains properties of commercial membranes tested for the removal of PPCPs and EDCs. The removals of specific target compounds achieved by these membranes can be found in Appendix A. As not all of the compounds are charged,

the dominant removal mechanism for membranes is size exclusion. Therefore, only a tight NF or RO membranes would be able to effectively remove these compounds.

2.3.2.1 Comparison of tight NF and RO membranes

There is market competition between tight NF and RO membranes. Tight NF membranes are classified as having a MWCO of 200 Da or less (Drewes et al., 2005; Xu et al., 2005). One of the key differences between the two membranes is the pressure/energy requirements. In these cases, the membrane surface charge is more important for rejection than MWCO (Drewes et al., 2005). Drewes et al. (2005) compared the use of tight NF and RO membranes for the rejection of hydrophilic ionic (including ibuprofen, diclofenac, ketoprofen, naproxen and gemfibrozil), hydrophilic non-ionic (such as primidone and caffeine) and hydrophobic non-ionic (including 17β-estradiol, estriol and testosterone) compounds. A looser NF membrane (NF-200) proved to have good rejection (89%) of ionic pharmaceuticals. Three of the tested membranes (one tight NF (NF-90), one ultra low pressure RO (ULPRO) and one RO (TFC-HR)), all having rejections of ionic compounds greater than 95%, show that tight NF and RO membranes are comparable for this application. Xu et al. (2005) compared tight NF and RO membranes as well using hydrophilic ionic compounds (ibuprofen, diclofenac, ketoprofen, naproxen, gemfibrozil and mercoprop) and a non-ionic compound, primidone. A tight NF (NF-90), ULPRO (XLE) and RO membrane (TFC-HR) were able to reject the ionic compounds 97.1, 93.5 and 95.8%, respectively. In the presence of NOM, the rejection increased to 97.7, 99.3 and 97.2%, respectively. The disadvantage of these membranes, however, is the lack of market acceptance (for drinking water treatment) due to the low flux

Table 2.3: Properties of commercial membranes used in PPCP and EDC removal studies

Type	Membrane	Manufacturer	MWCO (Da)	Material	Contact Angle	Reference
Tight UF	GM	Desal/Osmonics	8000±1000	Sulfonated Polyethersulfone (PES) coated with Ultrathin Polyamide Thin Film Composite (TFC)	46±2.1[1,2], 58 [3]	1, 2, 3,15
	PW	Desal	10000	Polyethersulfone	66	3
	PES 5K	Milipore	5000	Polyethersulfone	-	3
	PES 10K	Milipore	10000	Polyethersulfone	-	3
NF	ESNA	Hydranautics	600±200	Aromatic Polyamide TFC	57±1.8	1, 2,15
	NE 1812-70	Saehan Industries Inc.		Polysulfone support with Polyamide Active Layer		8
	NE 4040-90	Saehan Industries Inc.		Polysulfone support with Polyamide Active Layer		8
	NF-270	FilmTec, Minneapolis, MN		Semi-Aromatic Piperazine based Polyamide Layer on top of a Microporous Polysulfone Support (Polyamide TFC)		4, 5, 11
	NF-200	Dow/Filmtec	300	Polyamide TFC	30.3	6, 7
	NF-90	FilmTec, Minneapolis, MN	200	Semi-Aromatic Piperazine based Polyamide Layer on top of a Microporous Polysulfone Support (Polyamide TFC)	63.2	4, 5, 6, 7, 11
	RF	Saehan Industries Inc.	200~500	Polyamide TFC	43	3
	TFC-S	Koch Membrane Systems	200	Polyamide on polysulphone support	30-45	6, 10, 12, 13

Type	Membrane	Manufacturer	MWCO (Da)	Material	Contact Angle	Reference
NF	TFC-SR2	Koch Membrane Systems	400	Polyamide on polysulphone support	55.3[7], 10-20[15]	6, 7, 10, 12, 13, 14
NF/RO	TFC-ULP	Koch Membrane Systems		Polyamide on polysulphone support	30-45	10, 12, 13
	TFC-SR1	Koch Membrane Systems		Polyamide on polysulphone support	10-20	10, 12, 13
ULPRO	XLE	Dow/Filmtec	100[7,8], <200[13]	Polyamide TFC	66.3	6, 7, 9
RO	ACM-4	Trisep Corporation		Polyamide-urea composite	30-45	10, 12, 13
	CTA	Koch Membrane Systems	100	Cellulose Triacetate		6
	D2731	Barnstead		Cellulose Acetate – low pressure		15
	Re 4040-BLN	Dow/Filmtec		Polysulfone support with Polyamide Active Layer		8
	SC-3100	Toray	200-300	Cellulose Acetate		9
	TFC-HR	Koch Membrane Systems	100	Polyamide-TFC	35	6, 7,16
	TS-80	Trisep Corporation		Polyamide-urea composite	30-45	10, 12, 13
	X-20	Trisep Corporation		Polyamide-urea composite	30-45	10, 12, 13
	XN-40	Trisep Corporation		Polyamide-urea composite	30-45	10, 12, 13

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](Drewes et al., 2005), [7](Xu et al., 2005), [8](Shah et al.,2005), [9](Kimura et al., 2004), [10](Nghiem et al., 2004a), [11](Nghiem et al., 2004b), [12](Nghiem et al., 2002a), [13](Nghiem et al., 2002b), [14](Nghiem et al., 2002c), [15](Yoon et al., 2007), [16](Snyder et al., 2007)

and high energy requirement. To improve market acceptance, a loose NF or tight UF membrane is desirable for this application.

2.3.2.1 Comparison of tight NF and RO membranes

There is market competition between tight NF and RO membranes. Tight NF membranes are classified as having a MWCO of 200 Da or less (Drewes et al., 2005; Xu et al., 2005). One of the key differences between the two membranes is the pressure/energy requirements. In these cases, the membrane surface charge is more important for rejection than MWCO (Drewes et al., 2005). Drewes et al. (2005) compared the use of tight NF and RO membranes for the rejection of hydrophilic ionic (including ibuprofen, diclofenac, ketoprofen, naproxen and gemfibrozil), hydrophilic non-ionic (such as primidone and caffeine) and hydrophobic non-ionic (including 17β-estradiol, estriol and testosterone) compounds. A looser NF membrane (NF-200) proved to have good rejection (89%) of ionic pharmaceuticals. Three of the tested membranes (one tight NF (NF-90), one ultra low pressure RO (ULPRO) and one RO (TFC-HR)), all having rejections of ionic compounds greater than 95%, show that tight NF and RO membranes are comparable for this application. Xu et al. (2005) compared tight NF and RO membranes as well using hydrophilic ionic compounds (ibuprofen, diclofenac, ketoprofen, naproxen, gemfibrozil and mercoprop) and a non-ionic compound, primidone. A tight NF (NF-90), ULPRO (XLE) and RO membrane (TFC-HR) were able to reject the ionic compounds 97.1, 93.5 and 95.8%, respectively. In the presence of NOM, the rejection increased to 97.7, 99.3 and 97.2%, respectively. The disadvantage of these membranes, however, is the lack of market acceptance (for drinking water

treatment) due to the low flux and high energy requirement. To improve market acceptance, a loose NF or tight UF membrane is desirable for this application.

2.3.2.2 Comparison of tight UF and NF membranes

Commercial UF and NF membranes have similar removal capabilities In a study by Yoon et al. (2004), greater than 95% 17β-estradiol and fluoranthene removal was achieved in the absence of NOM using a tight UF sulfonated polyethersulfone membrane (GM, MWCO 8000±1000 Da). The same removal was achieved using an NF aromatic polyamide membrane (ESNA, MWCO 600±200 Da). Similarly, Yoon et al. (2006) used the same membranes with two different target compound mixtures, one group (Group 1, Table A2 in Appendix A) containing predominantly pharmaceuticals and the other (Group 2, Table A2 in Appendix A) containing predominantly PCPs. The GM membrane achieved less than 40% removal for Group 1 except for a few compounds [triclosan (87%), oxymenzone (77%), progesterone (56%)]. With the second group of target compounds, a higher retention was achieved with the exception of a few compounds (α- and β-BHC, fluoranthene, hydrocodone, metolachlor, and musk ketone). The ESNA membrane proved to have a higher retention (44-99%) with the exception of naproxen, which was not retained. As with the GM membrane the retention of Group 2 compounds by ESNA was higher than Group 1. These results indicate no difference in the retention of target compounds as a result of the membrane type but rather as a result of the material used. Additionally, Yoon et al. (2007) using the same Group 1 compounds and membranes (ESNA and GM) found that NF membranes had greater retention than UF membranes indicating retention is affected by the pore size of the

membrane. In order for the membrane type to play a key role in retention, an increase in retention with decreasing pore size should have been observed. As the membranes were made of different materials, the interaction between the membrane and the target compound was more likely influential in retention.

Currently, no one membrane (type/classification) has been proven effective for the removal of PPCPs and EDCs. Using more than one type of membrane will increase the energy and capital cost of installing membrane technology. Consequently, it is desirable to have one membrane capable of removing all PPCPs and EDCs. Therefore, a membrane tailored for high removal while still maintaining a high flux; a tight UF membrane having a modified surface to repel the compounds based on charge would be ideal.

2.4 Surface Modifying Macromolecules (SMMs)

Numerous different membranes are currently available on the market. Most commercial membranes have been modified and tailored for specific applications. Optimization of the membrane properties, in conjunction with feed fluid, is key for good performance. Surface modification is common practice for many membranes either by surface coating or etching, plasma or flame treatment chemical reaction or surface grafting to name a few (Qian et al. 2006). These methods require at least one additional step during the manufacturing process.

The alternative is the use of a SMM which is a long chained molecule with charged end groups synthesized in a multi-step process (Rana et al., 2005). These polymeric additives were tailor made to be compatible with polyether sulfone (PES), a common polymer used in the preparation of membranes; if the additive and the polymer phase separate defective membranes will be produced. SMMs may either be synthesized to be hydrophobic or hydrophilic depending on the target application. They are incorporated into membranes manufactured by the phase inversion technique, which is a single step process. The SMM is uniformly mixed in solution when the film is first cast. Given sufficient time, the majority of the SMM will have migrated to the surface, thus modifying the membrane as illustrated in Figure 2.2.

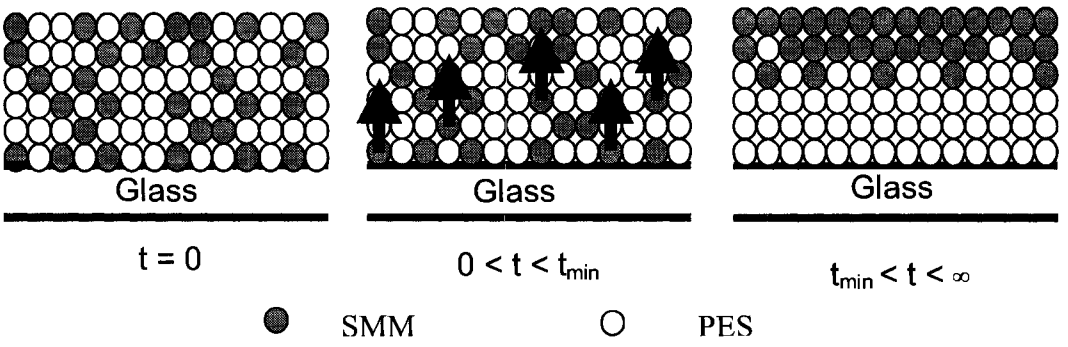


Figure 2.2: SMM migration within the membrane film

Using the phase inversion technique, the SMMs are allowed to migrate to the surface of the membrane during the casting process. It is unknown when migration of the SMM actually occurs; either during membrane film casting prior to gelation (interface: air/solution) where migration of hydrophobic SMMs is more likely or during the gelation bath (interface: water/solution) which will promote migration of hydrophilic SMMs. In

the gelation bath, the solvent migrates outwards into the bath and the membrane solidifies, independently detaching from the glass plate. Modifications can be made not only to the composition of the solution, the environmental conditions (bath T^{o}, etc.) but also to the SMM migration time, i.e., the time between the spreading of the casting solution into a film and immersion of glass plate/film in the gelation bath. By providing a charge (i.e., via the addition of SMMs) at the membrane surface, separation may be possible not only based on the pore size but also by charge repulsion of the target compound at the surface.

Membrane manufacturing using SMMs have recently been extensively investigated for membrane distillation, desalination, pervaporation and food and industrial chemical applications (Khayet and Matsuura, 2003; Mahmud et al, 2001; Rana et al, 2006). Additionally, the selection of base polymer is vital to proper membrane casting. It is important the SMM be compatible with the base polymer to avoid de-mixing of the polymeric solution (Suk et al., 2002). Many studies have investigated the use of SMMs with polyether sulfone (PES), a derivative of polysulfone, as the base polymer (Mosqueda-Jimenez et al., 2004a, b, c, 2006; Mahmud et al., 2001; Ho et al., 2000; Hamza et al., 1997).

One method commonly used to characterize membranes is contact angle. A membrane is determined to be hydrophobic if its contact angle (using water) is greater than 90^{o}; if its angle is less than 90^{o}, it is hydrophilic. Depending on the target application, SMMs can specifically be tailored to be hydrophobic or hydrophilic and compatible with the base

polymer. This particular combination has been found to decrease the possibility of fouling on the membrane surface (Rana et al., 2005) and has been proven to decrease fouling in the case of an oil/water emulsion (Hamza et al., 1997).

Numerous studies have specifically investigated the use of PES as a base polymer. Pham et al. (1999) stated hydrophobic PES pervaporation membranes increase organic compound selectivity. This was contradicted by Mahmud et al. (2001), in a study on the separation of chloroform in an aqueous solution. It was concluded that despite using the same SMMs as Pham et al. (1999), the resulting membranes were water selective. Ho et al. (2000), using fluorinated SMMs were successful in modifying the membrane surface of a PES based membrane without significant effect to the membrane base. Mosqueda-Jimenez et al. (2004a) found membranes prepared using hydrophobic SMMs with 3 min evaporation time and 18% wt PES resulted in low surface fouling when tested for the removal of NOM for drinking water applications. A similar study by Nguyen et al. (2007) found the incorporation of hydrophilic SMMs increased flux by 32% while decreasing NOM deposition by up to 83%.

With the success of SMM blended membranes in pervaporation, membrane distillation and recently for the removal of NOM from drinking water while still maintaining relatively high fluxes, it is proposed to apply this membrane modification method for the removal of PPCPs and EDCs from drinking water. It is proposed to develop a PES based membrane that has a high flux like that of a commercial UF membrane but has the ability to remove low molecular weight compounds (PPCPs and EDCs). This is to be

accomplished by creating tight ultrafiltration membranes and using several charged SMMs synthesized specifically for this application, which could enhance the charge repulsion capabilities of the experimental membranes.

CHAPTER 3

MATERIALS AND METHODS

The objective of this study was to develop SMM blended membranes cast at three different conditions and investigate their performance for the removal of three pharmaceuticals: sulfamethazine (SMZ), carbamazepine (Carb) and ibuprofen (IB) and one endocrine disrupting compound, bisphenol A (BPA). Experimental membranes were developed by casting membranes blended with three CSMMs (3 % wt) using 18 or 20% PES with 0 min migration time and 18% PES with 3 min migration time in addition to control PES membranes under the same conditions. The balance weight of the solution is 1-methyl-2-pyrrolidone (NMP). These membranes were then characterized for permeability, molecular weight cut-off, pore distribution, pore density and porosity, charge and contact angle. Subsequently single solute tests were conducted over a 4 hr period with a feed concentration of 10 ppm Carbon (ppm C) using the selected target compounds.

3.1 Chemicals

All chemicals were of ACS grade unless otherwise stated. Membrane casting solutions consisted of a solvent (1-methyl-2-pyrrolidone (NMP), Sigma-Aldrich), a base polymer (polyether sulfone (PES), MW~17-19kDa, ICI Advanced Materials, Billingham, Cleveland, England) and a charged surface modifying macromolecule (CSMM), either MDI-DEG-HBS, MDI-DEG-HBC or MDI-PPG-HBC, synthesized by Dr. Dipak Rana, a postdoctoral fellow in the Department of Chemical Engineering at the University of Ottawa. The chemical structures of the CSMMs can be seen in Figure 3.1.

The charged portion of the SMM stems from the end groups hydroxyl benzene carbonate (HBC) and hydroxyl benzene sulfonate (HBS). It is expected, assuming all other conditions are the same, that the sulfonated end-group (SO_3Na) would have a greater charge than the carbonate end group (CO_2Na). The greater the MW of the middle section, the greater the bulkiness of the CSMM, the slower will be its diffusion to the surface. Unfortunately, due to a lack of resources and large expense for external analysis, the molecular weight of the CSMMs could not be measured. The middle section of the CSMM determines the rigidity of the SMM. This can be characterized based on the glass transition temperature (Tg). Glass transition temperatures are in Table 3.1.

Table 3.1: Name and glass transition temperature of CSMMs

ID	Tg (°C)
MDI-DEG-HBS	101.29
MDI-DEG-HBC	131.58
MDI- PPG-HBC	111.28

MDI=methylene bis-p-phenyl diisocyanate, DEG=di(ethylene glycol), PPG=poly(propylene glycol)

From Table 3.1, it can be seen that DEG-HBS has the lowest glass transition temperature indicating it is the most flexible while DEG-HBC has the highest indicating it is the most rigid. In terms of their respective mid-sections, PPG has a higher MW than DEG which can be seen based on its chemical structure in Figure 3.1. Therefore, if the number of repeat mid-section units within the three CSMMs is the same then the mobility of DEG containing CSMMs should be greater than the PPG containing CSMM.

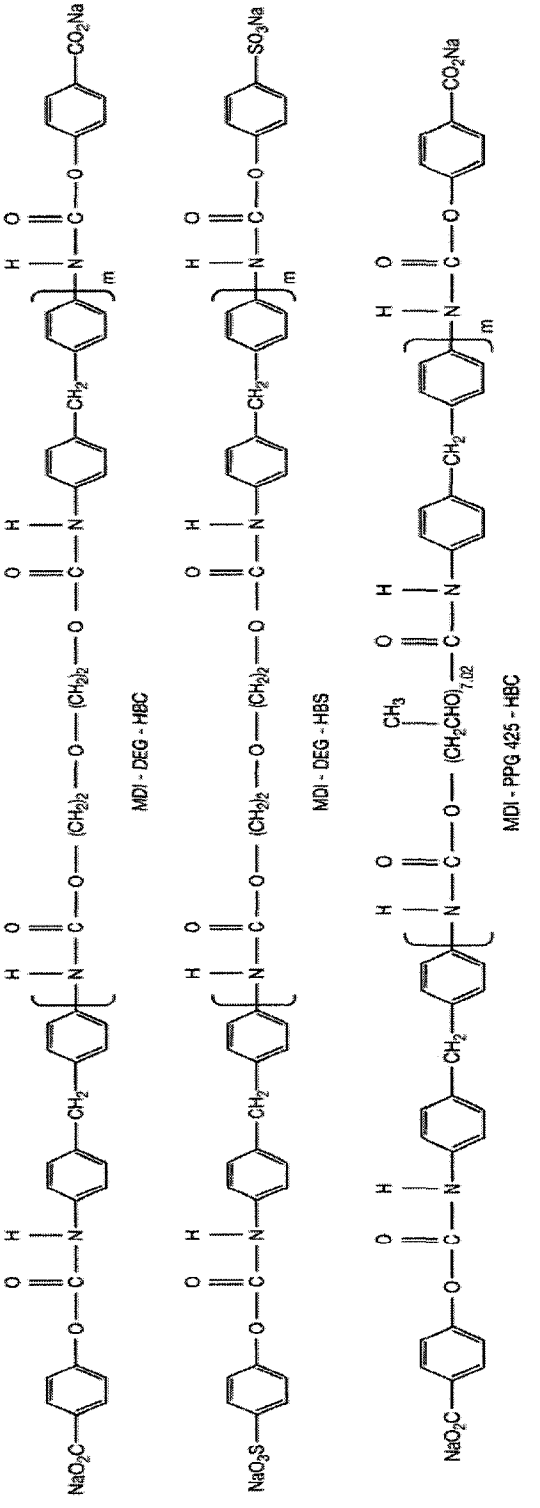
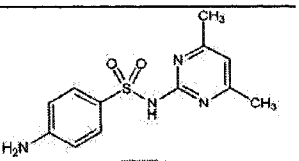
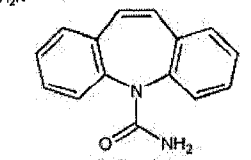
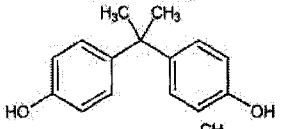
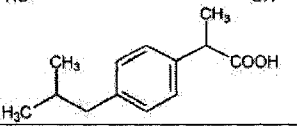


Figure 3.1: Molecular structures of SMMs

Poly-ethylene glycol (PEG) with average molecular weights (MW) of 0.4, 0.6, 1, 1.5, 4, 6, 8, 14, and 35 kDa (Sigma-Aldrich Chemicals, St. Louis MO) and poly-ethylene oxide (PEO) of average molecular weight of 100 kDa were used to prepare single solute stock solutions for the determination of MWCO of each membrane.

The PPCPs and EDC selected for this evaluation were SMZ, 99%, Carb, BPA, 98% and IB, 99+% purchased from Sigma-Aldrich Chemicals, St. Louis MO. They were selected because they have been detected in many source waters, are all of low MW and represent different groups of compounds defined by their wide range of octanol-water partition coefficients (log K_{OW}) scale. This property (log K_{OW}) indicates the affinity of the compound for the organic or water phase. Table 3.2 contains the molecular structure, dissociation constants (pK_a) and log K_{OW} values of the selected compounds.

Table 3.2: Selected PPCP and EDC properties

Compound	MW (g/mol)	pK_a	Log K_{OW}	Molecular Structure
SMZ	278.33	7.4 ± 0.2 2.65 ± 0.2	0.28	
Carb	236.27	<2-2.45; 7	2.56	
BPA	228.29	n/a	3.4	
IB	206.28	4.4-4.9; 5.2	3.97	

Reagents used to determine charge (zeta potential) were hydrochloric acid (HCl, BDH Chemicals, Toronto, ON), sodium hydroxide (NaOH), potassium chloride (KCl, Sigma-Aldrich Chemicals, St. Louis MO). Silver wires (Sigma-Aldrich, St. Louis MO) were used to make the electrodes.

Reagent grade water was prepared using a Milli-Q (MQ) water system by Millipore (Bedford, MA). It was prepared by passing distilled water through a series of ion exchange resins, activated and organic carbon scavenging cartridges and a membrane filter. Resulting water has a resistance of 18 μΩ/cm.

3.2 System set-up

The membrane test system used in this study was assembled by modifying an existing six-cell in series ultrafiltration system used extensively by our research group (Nguyen, 2005 and Mosqueda-Jimenez, 2003). The main changes were replacement of the plastic lines with stainless steel tubing to minimize losses due to adsorption of the target compound and modification of the flow pattern from six cells in series to six cells in parallel. To determine the best modification option within the constraints (materials, operation and financial), an economic feasibility study was conducted (Garand-Sheridan, 2008).

A diagram of the system set-up is shown in Figure 3.2. The feed tank is a 10 L glass carboy with a 5.08 cm (2") diameter neck. The tank feeds a diaphragm pump (Hydracell Model M-03, Wanner Engineering, Inc., Minneapolis, MN) which required priming as a

result of the stainless steel tubing. From the pump, some of the feed solution is fed to the cells and some is recycled back to the feed tank. The amount recycled is used to control the feed pressure and flow and is set with a metering valve. The feed is monitored by a rotameter (GF-5341-2516, Gilmont Instruments, Ottawa, ON) followed by a pressure gauge (Cole-Parmer, Montreal, QC). A header splits the feed in two which then feeds a secondary header feeding three ultrafiltration membrane cells. Between the secondary header and each cell there is a 0.953 cm (3/8") metering valve (SS-6L, Swagelok, Ottawa, ON) which controls the flow to the cells. Following these metering valves are pressure gauges (PGI-63C-PG300-LBG, Swagelok, Ottawa, ON). The cell is an ultra-filtration cell made of stainless steel with 0.953 cm (3/8") inlet and retentate and 0.318 cm (1/8") permeate lines. These UF cross flow cells are described in detail by Mosqueda-Jimenez (2003) and shown in Figures 3.3 and 3.4. Each permeate line is equipped with a 0.318 cm (1/8") 3-way valve (SS-41GXS2, Swagelok, Ottawa, ON) enabling either sample collection or return to the feed tank (Figure 3.3). The retentate lines leaving each of the cells, is reduced from a 0.953 cm (3/8") to 0.635 cm (¼"). A second metering valve 0.635 cm (¼") (SS-4L, Swagelok, Ottawa, ON) is placed at the outlet of each of the cells and is used to control the backpressure of the cells which can be read on the front side pressure gauge. This is followed by a 0.635 cm (¼") 3-way valve (SS-43GXS4, Swagelok, Ottawa, ON). The valve either diverts the retentate flow to a header, designed for minimal losses, which feeds a common rotameter (GF-5341-2516, precision: ±5%, Gilmont, Barnant Industries, Barrington, IL) or to a line shared between two adjacent cells. These three lines join in a common header. This header line is expanded from 0.635 cm (¼") to 0.953 cm (3/8"). Retentate is then cooled by passing

through the tube side of a shell and tube heat exchanger. It is then returned to the feed tank, maintaining the feed at a temperature of 19 ± 1°C. The cooling fluid (water) on the shell side is maintained at 6°C by a circulating bath (VWR Scientific Products, West Chester, PA).

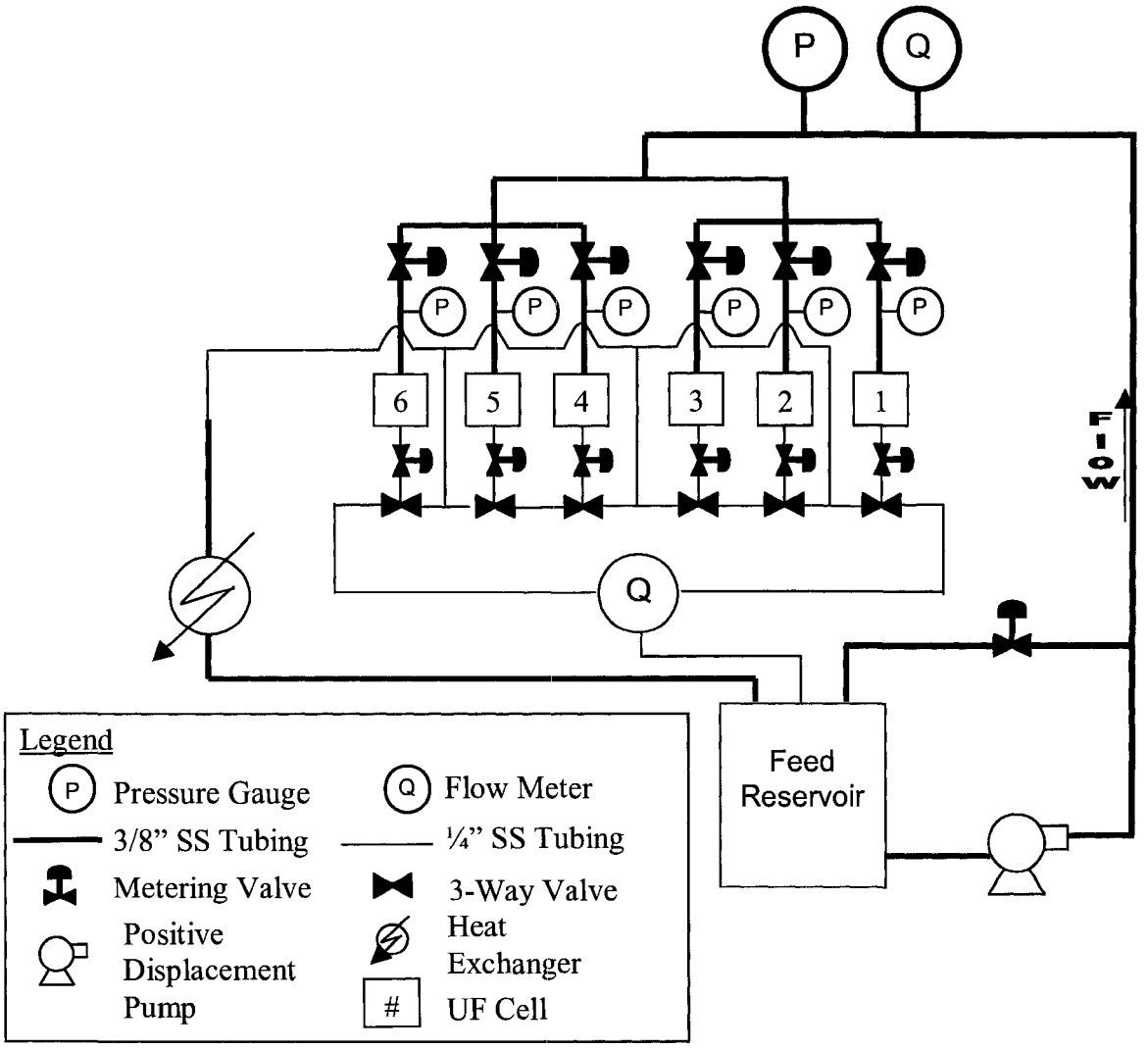


Figure 3.2: Diagram of system set-up (Permeate lines not shown, see Figures 3.3 and 3.4)

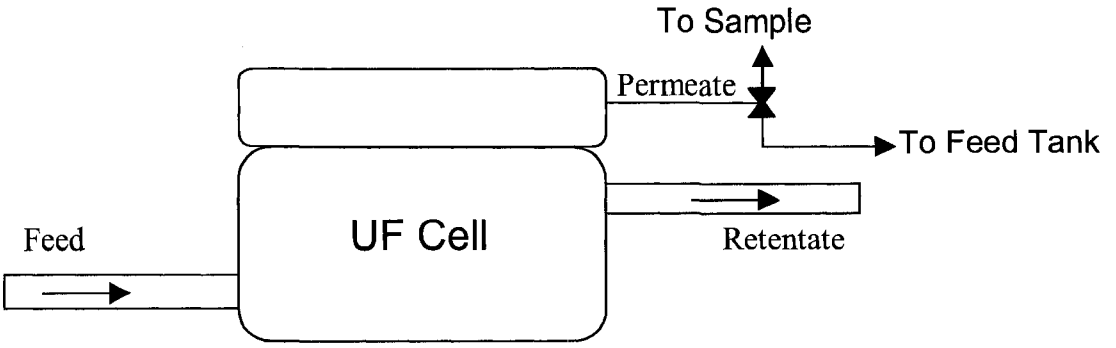
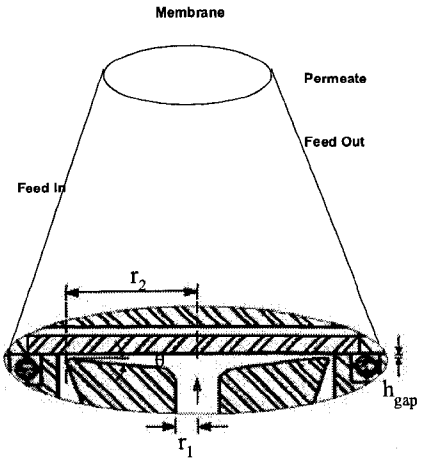


Figure 3.3: Diagram of ultrafiltration cell



r_1	3.175 cm
r_2	25.5 cm
θ	4.5°
h_{gap}	0.6 cm

Figure 3.4: Machine drawing of ultrafiltration cell and dimensions

3.3 Membrane characterization

Membrane characterization consisted of testing for permeability and MWCO followed by filtration tests involving the selected PPCPs and EDCs.

3.3.1 Permeability (PWP) testing

Pure water permeability (PWP) tests indicate the flux of the membrane under ideal conditions using MQ water. Precompaction of the membranes was conducted at cell pressure of 551.58 kPa (80 psig) for 1 hr. Following precompaction, cell pressure was decreased to 344.74 kPa (50 psig) and pure water permeability (PWP) was measured over

a 50 hr period. At various times, permeate samples were collected for a defined amount of time, on average 1 to 5 min. Samples were weighed following collection using an analytical scale (Sartorius, Canada Balances, Mississauga, ON). Flux, J, is the permeate flow per effective membrane area as defined using the following equation:

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

Where J is the flux (L/m^2/h), $Q_{permeate}$ is the permeate flow rate (L/h), $A_{membrane}$ is the membrane area (m^2), $M_{permeate}$ is the mass flowrate of the 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. It was measured as the pure water flux after the 50 h filtration period using the appropriate parameters.

Flux may vary as a result of fluid temperature and operating pressure therefore, in order to properly compare each of the membrane coupons, the results were standardized, resulting in the normalized standard flux (NSF) as follows:

$$J_{sp,20^\circ C} = J_T\left(\frac{\mu_T}{\mu_{sp,20^\circ C}}\right) \tag{3.2}$$

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

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

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).

3.3.2 Molecular weight cut-off determination

Determination of MWCO consisted of conducting a series of filtration runs of single solute solution of compounds, either PEG or PEO with known MW. One solute was tested at a time in recycle mode (i.e., both filtrate and retentate are recycled) for one hour. Permeate and feed samples of known weight were collected to quantify removal and flux. The feed solution was then discarded and replaced with MQ water and run in recycle mode for one hour to clean the system. After each cleaning period, the permeability of the membrane was measured before the next solute solution was tested. Each stock solution was diluted to 8 L using MQ water such that the feed concentration was in the 100 to 200 mg/L range. Samples were collected in pre-weighed total organic carbon (TOC) vials. The samples were weighed following collection and diluted prior to TOC analysis such that there was sufficient sample volume for analysis. It should be noted that each solute test required the pump to be primed using MQ water. The removal results of each test is then used in a pore size model, described in Appendix C. The model is used to determine the MW at which 90 percent removal is achieved (MWCO), the pore size distribution and surface porosity.

3.3.3 PPCP and EDC testing

The PPCP and EDC testing was conducted in a similar fashion as the MWCO evaluation, that is one single solute solution was filtered at a time and each filtration was followed by a MQ cleaning cycle prior to testing the next contaminant. A feed concentration of 10 ppm C was selected as the testing concentration for all solutes so that they could be measured using the available low-level TOC analyzer. Each solute was tested separately,

at concentrations higher than found in the environment since chromatographic analysis at the ηg/L level was unavailable. Table 3.3 contains the actual concentrations of the selected compounds. The feed concentrations are significantly higher than the TOC detection limit; the manufacturer reports a detection limit of 2 ppb, but this was not found experimentally. As previously mentioned, these concentrations are much higher than found in the environment; however, these higher concentrations are assumed to be satisfactory to screen the membranes for performance, properties and removal of the target compounds prior to more in-depth testing and analysis. Assuming high removal by the membranes, the TOC Analyzer would still be able to accurately detect the sample concentration. Contaminants were tested sequentially in order of increasing log K_{OW} to reduce potential carry-over from one contaminant to another and minimize potential site saturation in case of adsorption. The compounds with high log K_{OW} are more likely to adsorb and could therefore, if tested first, yield false results. Single solute solutions also allowed for easier analysis since individual calibration curves for each compound could be prepared.

Table 3.3: Actual concentrations of 10 ppm C feed concentrations

Compound	Concentration (ppm)
SMZ	19.31
Carb	13.11
BPA	12.67
IB	13.21

Four litre (4 L) single solute stock solutions of 20 ppm carbon (ppm C) of each compound (SMZ, Carb, BPA and IB) were prepared using MQ water in glass bottles, mixed with a magnetic stirrer. Solutes were dissolved within 4-48 hrs, with SMZ and

BPA dissolving quickly, followed by IB and Carb. Solutions were transferred to the feed reservoir and diluted with an additional 4 L of MQ water. A 40 mL sample was taken of the stock and diluted samples. The feed tank was then put in place and the feed and return lines re-attached. Once the pump was primed and started, a third feed sample was collected. Permeate samples were collected in 40 mL volumes continuously for a 4 hour period. One feed sample, cell pressures, retentate flow and feed temperature data were collected every 30 minutes. All collection vials were pre-weighed and re-weighed following sample collection along with the collection time such that permeate flow could be determined. Following the filtration of all four compounds, the membranes were removed from the cells. Effective membrane areas were measured using a calliper (Manostat, Precision Plastic Measuring Instruments, Switzerland).

Cleaning of the membrane filtration set-up was conducted between each solute test. Using MQ water, the system was flushed for 20 min in flow through followed by 10 min in recycle mode. Permeate flux was measured after the 30 min cleaning period before filtration of the next solute solution to determine if any membrane fouling had occurred. The feed concentration after cleaning was below 1% of the feed test solution indicating sufficiently thorough cleaning of the membrane filtration set-up.

3.4 Membrane preparation

All membranes were prepared via the phase inversion technique (Matsuura, 1994). CSMMs were developed by Dr. Dipak Rana by modifying the synthesis procedure of SMMs described extensively by Pham et al. (1999) and Rana et al. (2005). The mid-

section was exchanged for a different compound, in this case DEG or PPG. The end-groups, which are the charged portion of the CSMM, is used to terminate the reaction were also selected – HBS or –HBC. Figure 3.5 illustrates the reaction procedure.

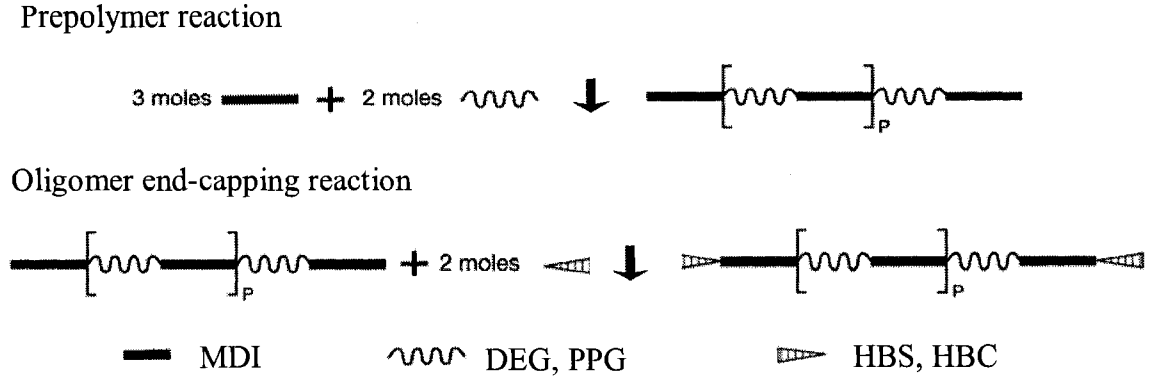


Figure 3.5: Synthesis of CSMMs

Various membrane casting solutions were prepared using different quantities of PES (18 or 20%), the base polymer, a CSMM (3% wt/wt) and NMP, the solvent. The 18% PES was selected according to work by Mosqueda-Jimenez (2003) and the 20% PES was selected to produce tighter membranes. PES was stored in a vacuum dessicator at ambient conditions after being dried for 2 hours at 105°C, NMP was stored in a refrigerator at 4°C. All solutions were prepared in 100 mL bottles with a Teflon lined cap. The mouth of each bottle was lined with Teflon tape to ensure a good seal. First, the NMP is weighed and the appropriate amount of SMM added to ensure full dissolution. The solution was then mixed in an environmental orbital shaker (G24, New Brunswick Scientific Co., Inc., Edison, NJ) for 24 to 48 hrs at 50°C. PES was then added to the solution and remixed in the same shaker for another 24 to 48 hrs at 50°C. Solutions were then pressure filtered through 47 mm Teflon PTFE discs with a pore size of 5.0 μm using

a stainless steel nitrogen gas driven pressure filter (Millipore, Bedford, MA) operated between 69 and 276 kPa (10 to 40 psig), and stored in the refrigerator at 4°C to increase the solution viscosity prior to casting. Increase in solution temperature resulted in pin holes, wrinkles or other defects in the membrane film. Six to ten membrane sheets were produced per solution. Table 3.3 denotes the nomenclature used when referring to the membranes.

Table 3.3: Cast membrane nomenclature

Membrane	Label
Control at 18% condition	PES18
Control at 18% (3min) condition	PES18-3
Control at 20% condition	PES20
DEG-HBS membranes	PES-DEG-HBS
DEG-HBC membranes	PES-DEG-HBC
PPG-HBC membranes	PES-PPG-HBC

All membranes were cast at room temperature in a fume hood using a flat, levelled glass plate, 20.3 cm x 30.5 cm (8" x 12") and a brass machined casting rod. The brass casting rod has two cube-shaped supports and a machined central section to provide a 250 μm gap when the supports are placed on the glass plate. The membrane solution was poured at one end of the glass plate. The casting rod was used to spread the membrane solution along the plate creating a 250 μm nominal thickness film, as shown in Figure 3.6. A gelation bath maintained at 4°C was prepared using distilled water and ice. A Digi-Sense© Type K thermocouple and probe (Cole-Parmer Instruments Company, Montreal, QC) was used to monitor the bath temperature. Casting conditions were either with no migration time (the film and glass plate were immediately submerged in the gelation bath for solidification) or 3 min migration time (the film is kept at room temperature for three minutes prior to being immersed in the gelation bath). The 3 minute migration time was

selected according to work by Garand-Sheridan (2008). Cast membranes were examined on a light box to determine defects and only membranes without defects were selected for testing.

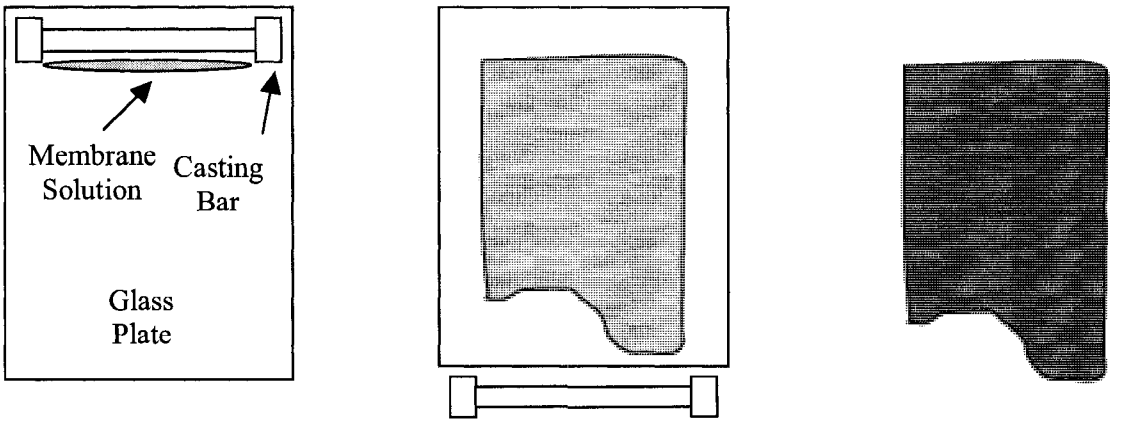


Figure 3.6: Diagram of membrane casting (plan view)

Membranes containing CSMMs were prepared and cast based on a randomized order. CSMM content for each membrane was constant at 3 wt %. Controls were cast prior to the CSMM membranes. Table 3.3 contains the casting order and conditions for all CSMM membranes studied. One or two defect free coupons (surface area: 20 cm^2) were cut from the membrane sheets produced, backed with a 2.5 μm cellulosic filter paper (grade 42, Whatman) for support, and used in subsequent filtration experiments.

Table 3.4: Casting and testing order of CSMM blended membranes

Casting Order	CSMM	% PES	% NMP	3 min Migration Time
1	DEG-HBC	18	79	No
2	DEG-HBS	20	77	No
3	DEG-HBS	18	79	No
4	PPG-HBC	20	77	No
5	PPG-HBC	18	79	No
6	DEG-HBS	18	79	Yes
7	DEG-HBC	20	77	No
8	DEG-HBC	18	79	Yes
9	PPG-HBC	18	79	Yes

PPG=polypropylene glycol, DEG=diethylene glycol, HBC=hydrozyl benzene carbonate, HBS=hydroxyl benzene sulfonate

3.5 Analytical techniques

3.5.1 Total Organic Carbon (TOC) analysis

All calibration curves were prepared using standards of known concentrations of the target compound. They can be found in Appendix D. Calibration curves were subsequently used during sample analysis. All MWCO (PEG and PEO) test samples were analysed in triplicate using a high temperature catalytic oxidation based TOC Analyser (Apollo 9000 Combustion TOC Analyzer, Teledyne Tekmar Company, Cincinnati, OH). Initial and periodic cleanings during analysis were conducted using the built-in cleaning procedure with MQ water. All PPCP and EDC test samples were analyzed in triplicate using a low temperature UV-persulfate based TOC Analyser (Pheonix 8000, Teledyne Tekmar Company, Cincinnati, OH). These two types of analysis are based on Standard Methods 5310B and 5310C, respectively (Standard Methods, 1989).

3.5.2 Contact angle

Membrane sheets were dried for six days prior to slide sample preparation between paper towels. Membrane samples were prepared by adhering randomly chosen rectangular pieces of membrane coupons to glass slides (Fisherfinest, Fisher Scientific, Ottawa, ON) using electrical tape to allow for proper contrast and visualization of the membrane surface. The VCA Optima Contact Angle Analyzer (AST Products Inc., Billerica, MA) used for contact angle measurements is a computerized system with a camera able to zoom in on the membrane surface. Contact angles were measured using the sessile drop method. The slide is placed on the stage and raised to ensure a clear view of the membrane surface to be tested. The stage is then lowered and a 2 μL drop of MQ water is applied to the surface of the membrane. A photo of the drop is captured by the camera and displayed on the computer. Subsequent 0.25 μL drops are administered drop wise and a photo is capture after each additional drop until the drop on the membrane surface shifted – indicating the liquid/solid interface has increased in surface area. The contact angle of the drop prior to this shift is reported as the advancing contact angle using average measurements of the left and right side angles. Three coupons of each membrane type were tested and three readings were taken from each coupon.

3.5.3 Zeta potential

Figure 3.7 shows a flow diagram of the zeta potential (charge) testing system. Electrolyte solutions are prepared by dissolving KCl in MQ water at a concentration of 0.001 M. Dilution of HCl and KOH in MQ water to a concentration of 0.1 M was done to produce acid and base pH adjustment solutions respectively. Silver/silver chloride (Ag/AgCl)

electrodes were prepared by connecting a silver wire electrode probe with an alligator clip to the positive side of a 1.5 V battery. The reference electrode, also silver wire (but much thinner), was attached with a second alligator clip to the negative battery side. Both probes were placed in a solution of 0.0001 M HCl for 24 hrs such that the chloride could deposit on the electrode. Following the 24 hr period, the silver electrode probe is stored in a 0.1 M KCl solution and a second silver electrode probe is attached for another 24 hr period (two probes are required for zeta potential testing).

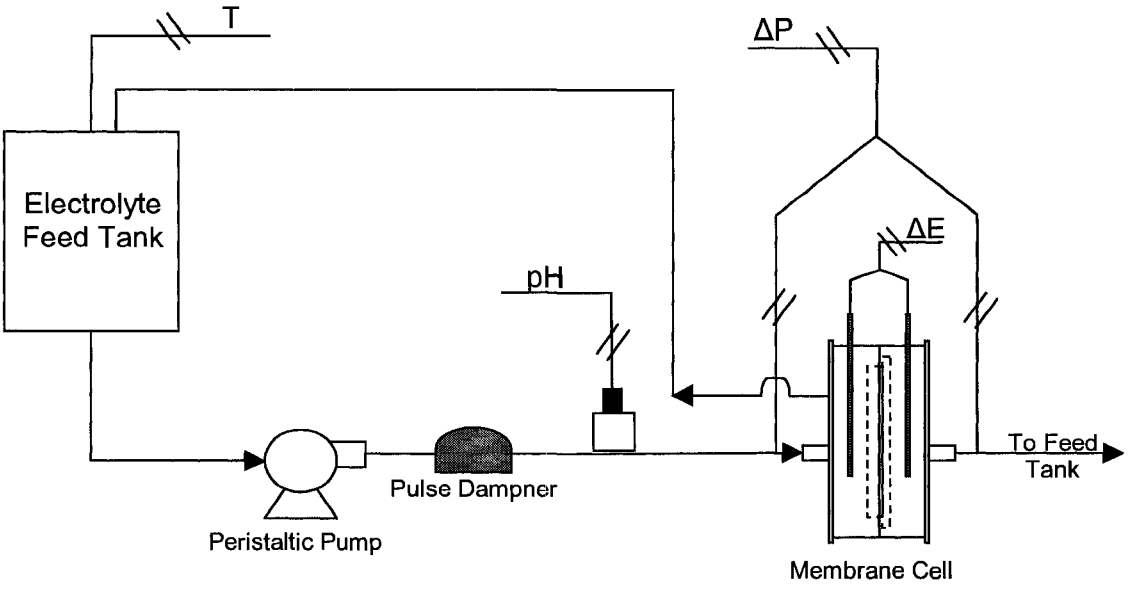


Figure 3.7: Flow diagram of zeta potential test system
T is the temperature, ΔP is the pressure differential and ΔE is the streaming potential

A 20 cm^2 membrane coupon is backed by two superimposed Teflon mesh spacers and placed in a holder. The membrane is secured by sandwiching it between the feed and permeate sides with the use of several screws. The holder is then placed in the zeta potential cell and closed. The electrodes are inserted through their designated holes at the top of the cell such that they are on each of the respective sides of the membrane as

shown in Figure 3.8 below. The pump is turned on such that the trans-membrane pressure may begin to build and the electrolyte (KCl) solution starts to filter until a reading is obtained by the computer (LABView Program, National Instruments, Austin, TX). The pressure is then increased to 10 mbar. Once steady-state is achieved, the temperature, pressure, pH and charge values are recorded using LABView. Pressure is increased by approximately 20 mbar and the system is allowed to achieve steady-state. The values are then recorded. This cycle continues until at least five value sets are collected. The operating pressure range is between 10-150 mbar. The values are plotted and a slope of the line of best fit is used to calculate membrane charge using the Helmholtz-Smoluchowski equation (Nystrom et al., 1994) as follows:

$$\zeta = \frac{\Delta E}{\Delta P} \times \frac{\eta \kappa}{\varepsilon_o \varepsilon_i} \tag{3.4}$$

Where ΔE is the streaming potential variation (mV), ΔP is the trans-membrane pressure variation (mbar), η is the permeate viscosity, κ is the solution conductivity, ε_o is the vacuum permittivity and ε_i is the media dielectric constant.

If the pressure exceeds 150 mbar, a secondary slope may result (Garand-Sheridan, 2008).

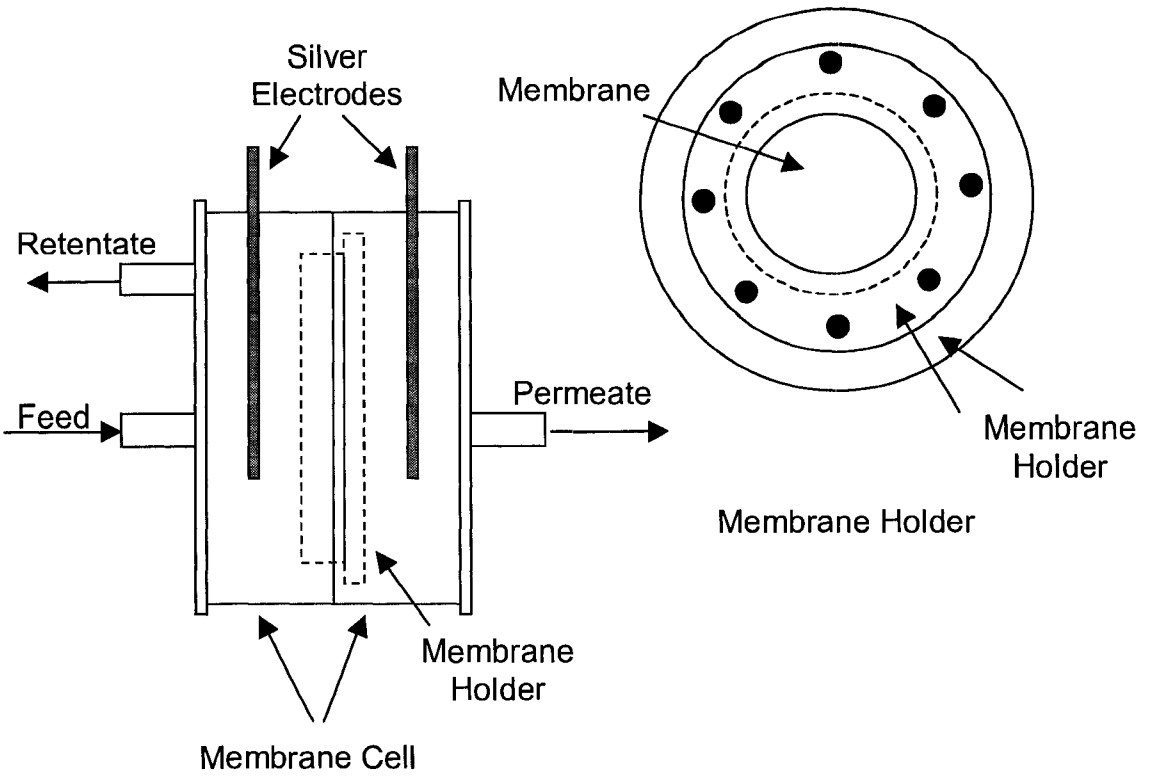


Figure 3.8: Diagram of zeta potential cell and holder

3.5.4 Cleaning

All glassware and TOC vials were cleaned with distilled water and allowed to soak in a solution of lab grade detergent (Contrex, Decon Labs, Inc., King of Prussia, PA) and distilled water for at least two hours. They were then triple rinsed with distilled water before being soaked in acid. TOC vials were soaked in a mixture of chromic and sulphuric acid (Chromerge™) while phosphoric acid (concentration of >1%) was used for other glassware. TOC vials were left to soak for at least one hour and glassware for 24 hrs before being triple rinsed with distilled water and placed in the oven at 105°C to dry. TOC vials were rinsed with MQ water once after the triple rinse prior to drying.

CHAPTER 4

RESULTS AND DISCUSSION

This chapter will discuss the results of the membrane filtration and characterization of the experimental membranes developed in this study, as well as the removals of the four target compounds: SMZ, Carb, BPA and IB. The test system was first characterized for adsorption. Membranes were cast at three conditions: 18% PES, 18% PES with 3 min migration prior to gelation and 20% PES. Controls (PES18, PES18-3 and PES20) and CSMM blended membranes (PES-DEG-HBS, PES-DEG-HBC and PES-PPG-HBC) were cast at these three conditions. Casting solutions of all three PES-PPG-HBC membranes were quite viscous and as a result of the casting method, at times produced very wrinkled membranes. Consequently, due to the variability in visual appearance and visible imperfections (such as holes and wrinkles) in the membrane sheets , only one coupon, if any, could be obtained per membrane sheet, these variations in the membrane characteristics may lead to high performance variability.

Control and CSMM blended membranes were characterized for flux over a 50 hr test period, MWCO, charge and contact angle. Single solute test of the target compounds were then sequentially conducted in order of increasing log K_{OW} over four hour periods.

4.1 Contact angle

Figure 4.1 shows the results of contact angle analysis on control and CSMM membranes. A change in contact angle with respect to the control indicates membrane modification as

a result of incorporation of the CSMM. The manufacturer of VCA Optima claims repeatability of 1^{o} and accuracy of 0.5^{o}. The error bars represent one standard deviation, and are generally considerably larger than 1^{o}, indicating the surface is heterogeneous. This is characterized by variations in contact angle from location to location on any given membrane coupon and between coupons. There are a number of factors affecting contact angle measurements including porosity (Chan, 1994). Higher contact angles can also be attributed to surface roughness (Chan, 1994; Dreilich et al., 1996). Consequently, three readings were taken per sample and each membrane type was tested in triplicate. This indicates SMM migration is not uniform and can significantly affect the performance of a membrane.

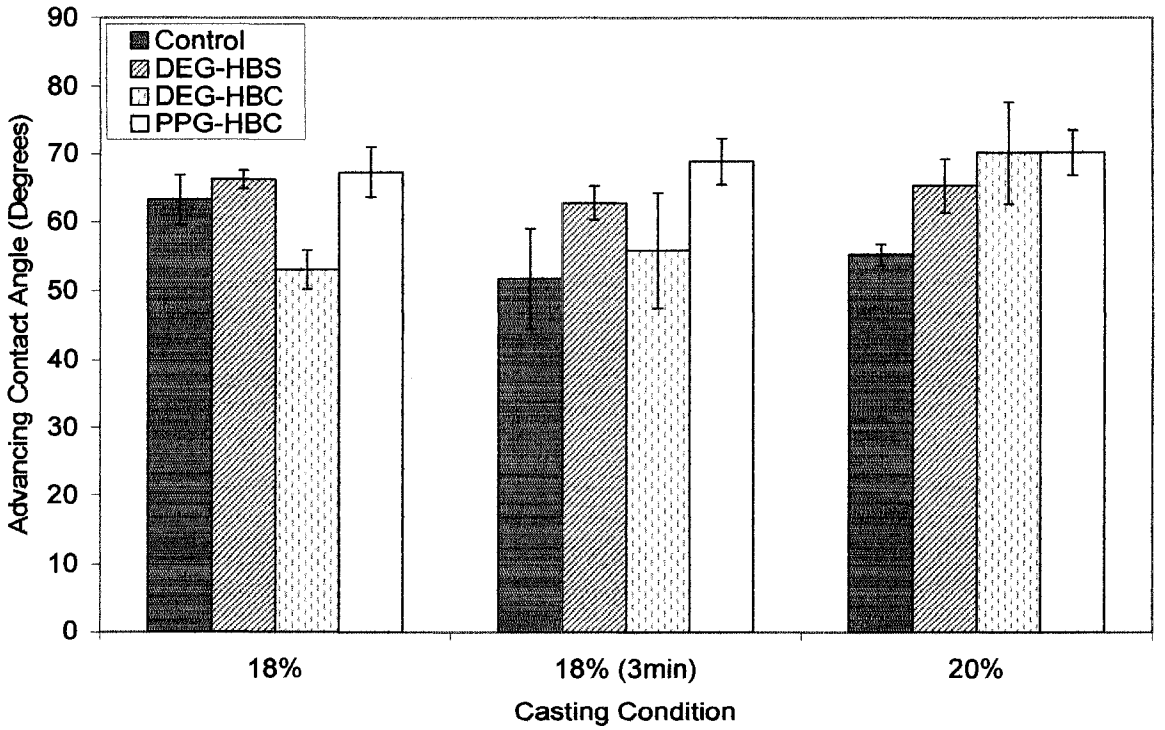


Figure 4.1: Advancing contact angle of tested CSMMs

In terms of PES concentration for membranes containing SMMs, Nguyen (2005) found that PES concentration had no significant effect on contact angle for a membrane containing the same SMM. This was true for the PES-DEG-HBS and PES-PPG-HBC membranes however PES-DEG-HBC saw a 17 degree increase in contact angle with a 2% increase in PES indicating this CSMM, unlike the others, is impacted by PES concentration.

4.1.2 Impact of migration time

It was presumed the incorporation of a three minute migration time prior to gelation would assist CSMM migration. From Figure 4.1, it is clear the CSMM blended membranes showed either no change or an increase in hydrophobicity. Interestingly, the contact angle of the control membranes, PES18 and PES18-3 showed significant decrease, which is unexpected. This appears to indicate variability within the casting technique.

Mosqueda-Jimenez et al. (2004b) concluded the presence of SMM produced no significant effect on membrane modification with migration times of 0 and 3 min. This is comparable to the results found here with the PEG-HBC additive. Suk et al. (2002), using fluorinated end-group SMMs showed at least a 20 min evaporation time was required in order to significantly increase the contact angle. While the hydrophilicity of all the membranes has increased with a 3 min migration time in this study, overlapping confidence limits for the 18% membranes coincide with the lack of effect on contact angle observations noted by Suk et al. (2002).

4.1.3 Effect of additive

The addition of PPG-HBC showed an increase in membrane hydrophobicity with respect to the controls, however, regardless of the PES concentration or incorporation of migration time, the contact angle of the PES-PPG-HBC membranes remained statistically unchanged. A comparison of the PES-DEG-HBS membranes showed, as with the PES-PPG-HBC membranes, there was an increase in membrane hydrophobicity when compared to the control membranes but the different casting conditions had no effect. DEG-HBC, on the other hand, showed a different impact at each of the tested casting conditions. At 18%, the membrane became more hydrophilic than the control, as expected. With a three minute migration time, the membrane increased in hydrophobicity but was statistically the same as the control membrane. At 20%, the membrane has become significantly more hydrophobic and statistically has the same contact angle as the PES20-PPG-HBC membrane. The effect of DEG-HBC may be the result of its higher mobility within the solution (due to its low MW mid-section, DEG) and its higher rigidity, as it does have the highest glass transition temperature (Tg) value.

Due to the nature of the charged end groups, HBS and HBC, it is expected that HBS would have a higher charge than HBC. As PES-DEG-HBS membranes had a lower contact angle than PES-PPG-HBC membranes, and that their confidence limits overlapped, it appears that the charge of the end-group had no significant impact on the contact angle.

As previously stated, all PES-PPG-HBC membranes had an increase in contact angle in comparison to the control membrane and the PES-DEG-HBC membrane increased in contact angle from the 18 to 20% and 18 to 18% (3 min) conditions. A comparison between PES-PPG-HBC and PES-DEG-HBC membranes indicates the PPG segment causes the increase in contact angle within the membrane while the combination of PES solution concentration in combination with DEG produces either an increase or decrease in membrane contact angle. As the contact angle of PPG appears to have remained relatively unchanged and the contact angle of DEG changes significantly based on the casting condition, this suggests the orientation and migration of the bulkier PPG molecule is independent of casting condition while the smaller, more mobile DEG molecules are able to better orient and migrate under different conditions. This trend is expected based on the structure of the CSMMs since migration is a function of CSMM mobility. The variations in contact angle results indicate an impact by the CSMMs on the membranes and this impact may be different at each of the casting conditions.

4.2 Charge

Charge results are shown in Table 4.1. From the control results, it is clear there is change in membrane charge from PES18 to PES18-3 and PES18 to PES20. Prior to gelation, PES18-3 may reach a different membrane equilibrium than PES18 or PES20. More polymer in solution should yield different charge results mainly due to differences in polymerization.

Table 4.1: Surface charge of CSMM blended membranes

	Charge (mV)		
Membrane	**18%**	**18% (3min)**	**20%**
Control	-9.76 ± 1.59	-5.74 ± 0.25	-4.24 ± 1.23
PES-DEG-HBS	-11.36 ± 3.10	-7.16 ± 1.07	-11.17 ± 0.98
PES-DEG-HBC	-6.38 ± 1.66	-8.01 ± 2.05	-16.45 ± 2.33
PES-PPG-HBC	-11.29 ± 1.04	-7.83 ± 1.49	-21.32 ± 0.87

Note: Charge variation is represented by one standard deviation

Figure 4.2 contains a comparison of the charge results at each of the casting conditions and their respective confidence intervals. In Figures 4.2-A and 4.2-B, it is interesting to note all the CSMM blended membranes overlap the charge results of the control, indicating their change in charge is statistically insignificant. It is interesting to note that, given a migration time, all CSMM blended membranes indicated charges comparable to one another. The migration time may have allowed the CSMM membranes to reach a different equilibrium (in terms or orientation and position within the film) than the membranes without migration time. Figure 4.2-C, with a PES concentration of 20%, shows change in charge from the control by the modified membranes. The addition of the CSMM has modified the membrane and has changed the membrane charge.

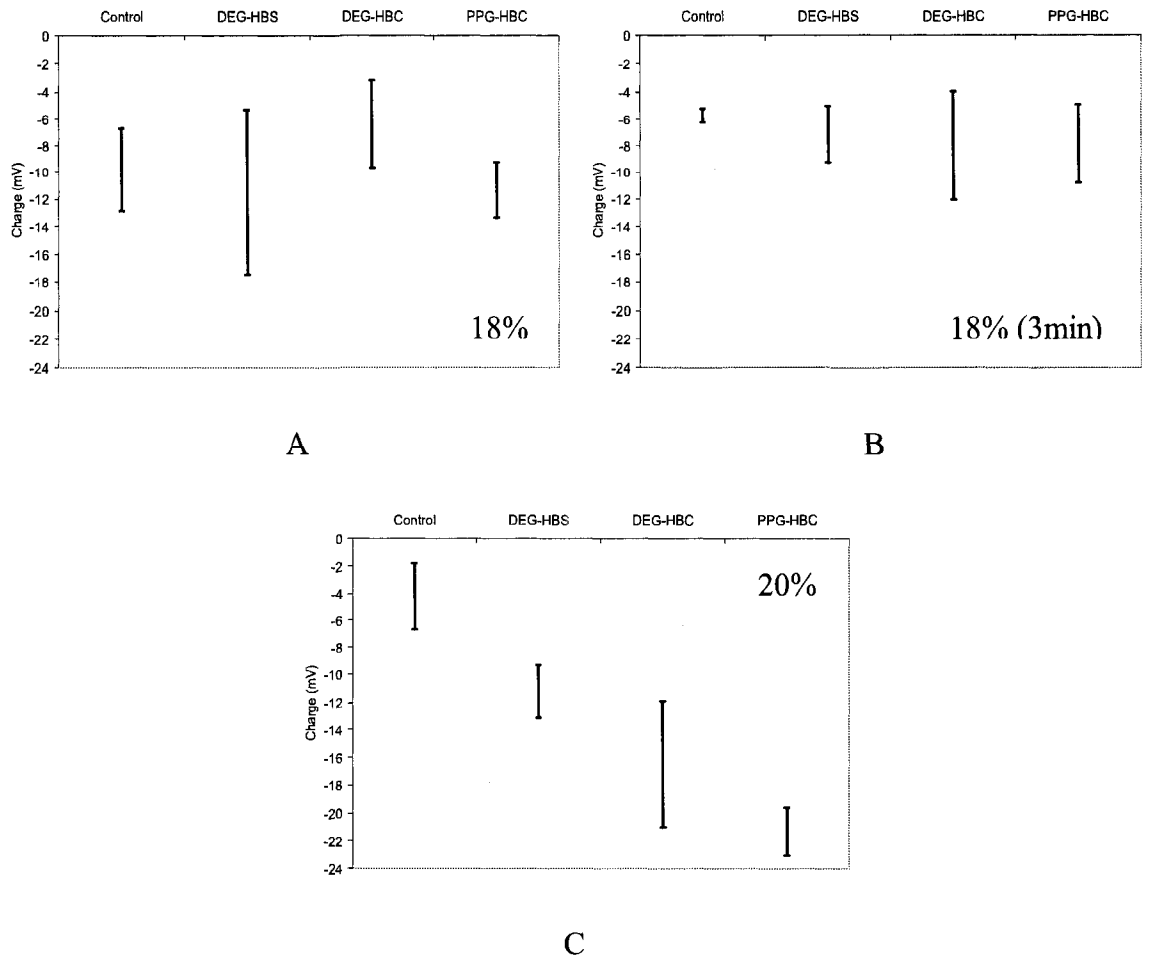


Figure 4.2: Charge confidence limits (95%) for CSMM blended membranes at the different casting conditions

Charge results, shown in Table 4.1, indicate a decrease in membrane surface charge (i.e., more negative) with the presence of CSMMs with the exception of PES-DEG-HBC membrane at 18%. At this casting condition, the surface charge has decreased and is similar to those membranes at the 18% (3 min) condition, reinforcing the increased hydrophilicity of this membrane (as shown by the contact angle findings). Conversely, both the PES-DEG-HBS and PES-PPG-HBC membranes, had an increase in hydrophobicity in comparison to PES18 control membrane. At 18% (3 min) the surface charge has increased for all CSMMs in comparison to PES18-3 but all four membranes

have a value larger than PES18. Based on the increase in negative charge it appears to indicate all the membranes have become more hydrophilic; however, the contact angle measurements appear to indicate otherwise. Therefore, it appears contact angle measurements are impacted by other factors. At 20% PES, the PES-DEG-HBS membrane charge is similar to the charges at 18%. On the other hand, the surface charge of PES-DEG-HBC has more than doubled indicating, as with contact angle, the concentration of PES in the membrane solution has a significant impact on the properties of the resulting membrane for this CSMM. Similar to the PES-DEG-HBC membrane, the charge of the PES-PPG-HBC membrane shows a near doubling of the charge compared to the control. It is expected the sulfonated end-group would result in a higher charge than the carbonated end-group based on the chemical structure; however, results indicate the opposite trend is true. Membranes prepared with both additives containing HBC end-groups have shown an increase in surface charge. This may be the result of better orientation of the HBC end groups at the surface either due to higher mobility (DEG-HBC), more flexibility (PPG-HBC) or the interaction of HBC and PES concentration. Given a migration time, all CSMM blended membranes indicated charges comparable to one another. The increase in migration time may have allowed for the CSMM to have reached a better equilibrium (in terms of orientation and migration) within the membrane film and therefore a different orientation than without migration time.

4.3 Charge and contact angle comparison

A comparison between the charge and contact angle results for the different CSMMs is shown in Figure 4.3. These two properties can theoretically be related since the SMMs used contain a charge. The more hydrophilic the CSMM the higher the negative charge should be such that hydrogen bonding may occur. Experimental data seems to indicate a slight increase in hydrophobicity with increasing membrane negative charge. This may be caused by the CSMMs not migrating entirely to the surface and rather modifying the bulk of the membrane and/or possible inaccuracies in the contact angle and surface charge measurements.

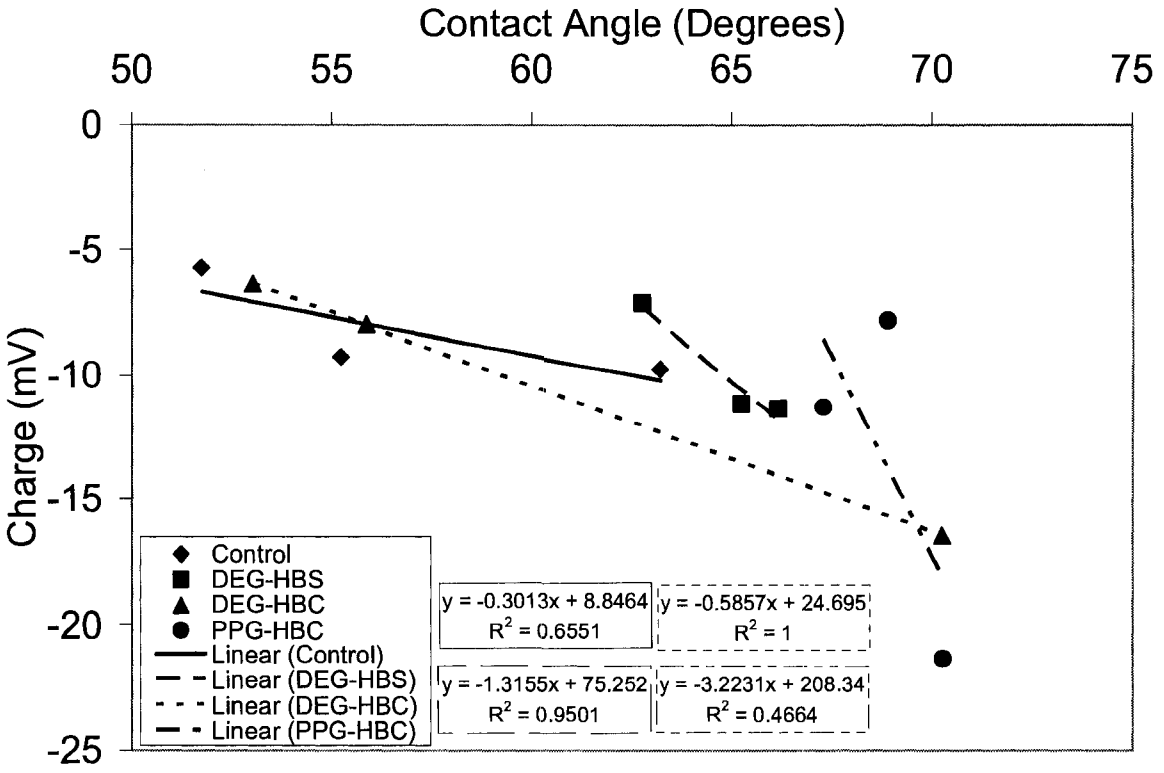


Figure 4.3: Comparison of charge and contact angle for all studied CSMMs

4.4 Membrane permeability

Pure water permeability (PWP) tests indicate the flux of the membrane under ideal conditions. The system was operated in recycle mode using MQ water. All six cells were used simultaneously to test three coupons of two different membranes. Flux may vary as a result of fluid temperature and cell pressure; therefore, in order to properly compare each of the membrane coupons, the results were standardized to eliminate these variables, resulting in the normalized standard flux (NSF) (Equations 3.2 and 3.3).

Figure 4.4 shows the NSF for all the membranes at the three casting conditions. In all cases, membranes were tested in triplicate. In some cases, coupons of the same membrane exhibited high variability; significant outliers were subsequently removed from the analysis using the Dixon method. Other membranes had a wide variability in NSF, as evidenced by the span of the error bars, representing the standard deviation, indicating poor reproducibility of the membrane.

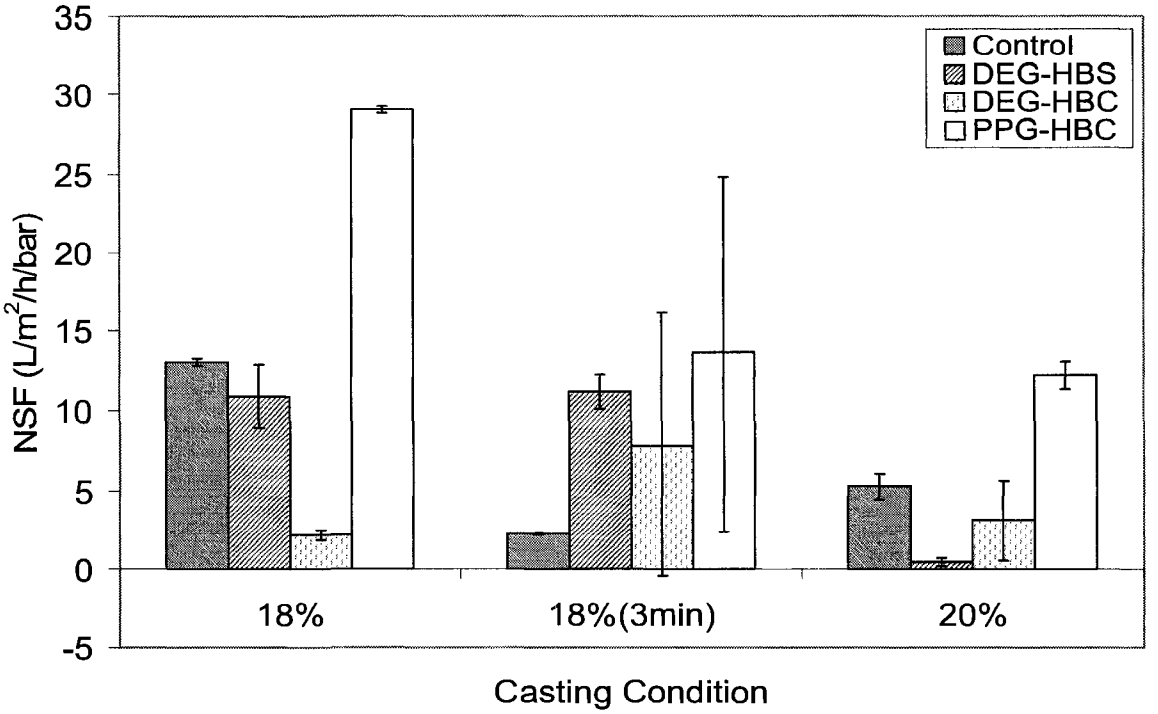


Figure 4.4: Comparison of normalized standard flux with casting condition for CSMM blended membranes

4.4.1 Flux evaluation of control membranes

In the case of the control membranes, the NSF was lower for both PES18-3 and PES20 membranes when compared to the PES18 membrane. It is expected the PES20 membrane would be tighter as there is more polymer in solution and should therefore yield a denser membrane. The PES18-3 membrane, on the other hand, should remain the same as the PES18 membrane since there is no CSMM in solution. The decrease in flux may be a result of the PES reaching a different equilibrium within the film prior to polymerization than at the 18% condition. A study by Nguyen (2005) found the flux of control membranes to be approximately four times higher than what was achieved in this study using the same casting method. However Dang et al. (2008), using the same casting conditions, reported PWP flux values approximately half the magnitude of those

reported by Nguyen (2005), indicating large variations between studies. Additional possibilities that may account for the difference in results in this study is the different system configuration used (series versus parallel) or other extraneous factors during the casting process.

4.4.2 Effect of base polymer concentration

When increasing the PES concentration from 18 to 20%, the membranes incorporating PES-DEG-HBS and PES-PPG-HBC membranes both had a significant decrease in flux, similar to that observed with the control. This is expected since the membrane is denser due to the increase in polymer concentration. As expected, the flux results from all of the membranes at the 20% condition have the same trend as at the 18% condition; the flux has simply decreased by the same proportion. This would indicate the concentration of base polymer directly affects the membrane porosity (Section 4.6.3) and hence the NSF. PES-DEG-HBC membranes, however, showed an increase in flux. However, given the wide confidence interval which overlaps both the results from the other two CSMM blended membranes, statistically, their fluxes are the same.

4.4.3 Effect of migration time

When CSMMs are incorporated into the membranes, the total polymer concentration has increased (+3 wt%) when compared to the control; this results in a denser membrane which should have lowered flux. PES-DEG-HBS and PES-DEG-HBC membranes, however, showed an increase in the flux for membranes at the 18% (3 min) condition. This indicates the CSMM had modified the membrane to increase water migration across

the membrane. This suggests the membrane may be hydrophilic; however, this could not be confirmed by the contact angle results. The increased flux may also be due to higher porosity of the membrane (see Section 4.6.3). Only PES-PPG-HBC membranes followed a decrease in flux similar to that observed for the control membranes.

4.4.4 Effect of CSMM addition

The different CSMM blended membranes are compared at the different casting conditions in Figure 4.4. As shown by the first four bars, it is clear that at 18% the CSMMs are hindering flux with the exception of PPG-HBC which has significantly higher NSF than the control. Given the 18% PES membranes with a 3 min migration time (columns five to eight) the CSMMs appear to significantly be helping the membrane flux. When the membranes contained 20% PES, the addition of the CSMMs has mixed impact on the membrane NSF. One has a significantly lower NSF (PES-DEG-HBS), one has about the same NSF (PES-DEG-HBC) and the last is significantly higher (PES-PPG-HBC). The PES-DEG-HBS membrane flux dropped from 10.888 to 0.438 $L/m^2/h/bar$ (at the 18% condition), a 96% decline. The addition of the CSMM has also increased the total polymer concentration within the membrane solution. It is expected that this should result in even lower fluxes since the resulting membrane should be denser; however, at 18% (3 min), the DEG containing additives show a marked effect on the flux of the membrane. Therefore, despite these observations, there appears to be no clear trend in the data when comparing the casting conditions of the different CSMMs – each modified membrane behaves differently.

4.5 Comparison of NSF to membrane charge

Figure 4.5 shows the relationship between flux and membrane charge. It is interesting to note that only the PES-DEG-HBC membrane shows a distinct correlation between these two properties. All of the other membranes, including the controls, show no relationship. This indicates that the DEG-HBC CSMM has migrated to the surface and is assisting the flux of the membrane. This trend is in the same direction as the control but is opposite to those of the DEG-HBS and PPG-HBC CSMMs. From the Tg values, DEG-HBS and PPG-HBC are more flexible than DEG-HBC; the lack of trend could be attributed to the orientation of the CSMM at the membrane surface.

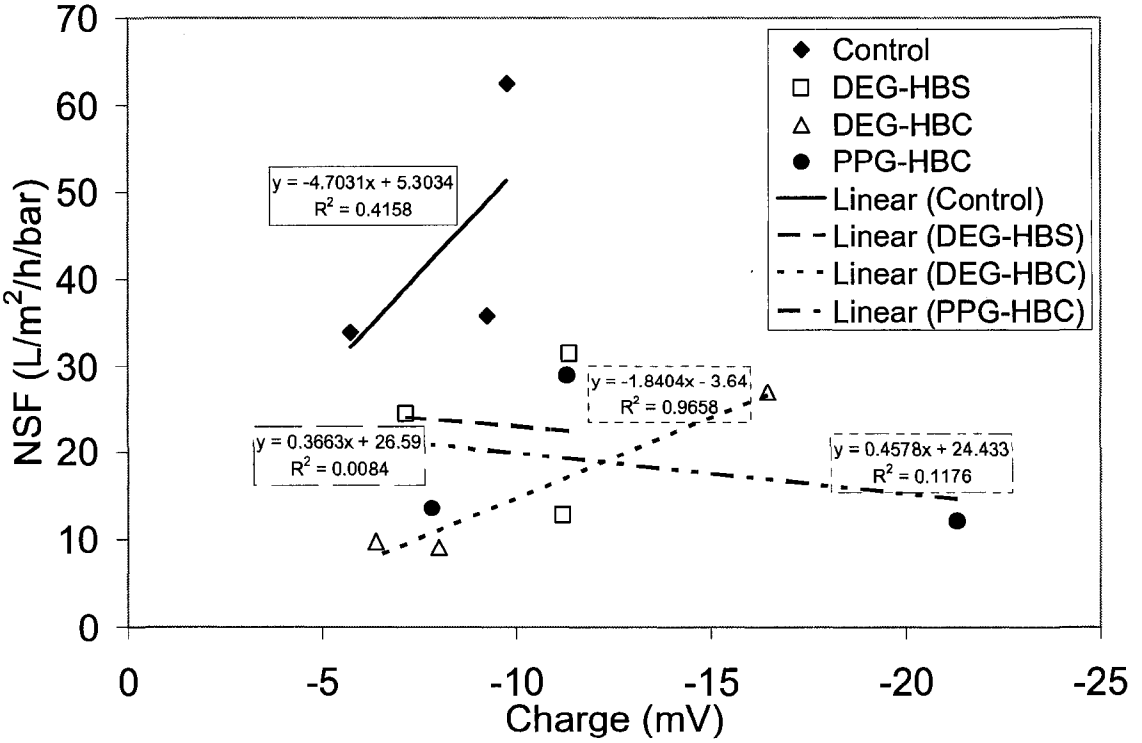


Figure 4.5: Relation between NSF and membrane surface charge

4.6 Membrane characteristics

4.6.1 MWCO

MWCO is used to determine the nominal size range of the membrane pores at which 90% rejection will occur. This is based on solute transport tests, in this case, involving varying molecular weight of PEG and PEO solutes. Development of the equations used in calculating MWCO and the associated properties (pore distribution, porosity and pore density) can be found in Appendix C. MWCO is important since the target compounds used in this study are quite small and therefore the MWCO will determine whether size exclusion of PPCPs and EDCs is feasible or if another removal mechanism is required (i.e., charge repulsion). This test only provides a general idea of whether or not the removal of the actual target compound will be successful.

Figure 4.6 shows the MWCO for each of the CSMMs at the three casting conditions. Comparison of the control membranes show the PES18-3 and PES20 membranes have smaller pores. It is expected that with an increase in base polymer (18 to 20%) that the membrane pores should be tighter as the membrane is denser. With the incorporation of the three minute migration time, the decrease in MW may be the result of more closely approaching equilibrium (prior to gelation) within the membrane causing different distribution or orientation of PES and NMP.

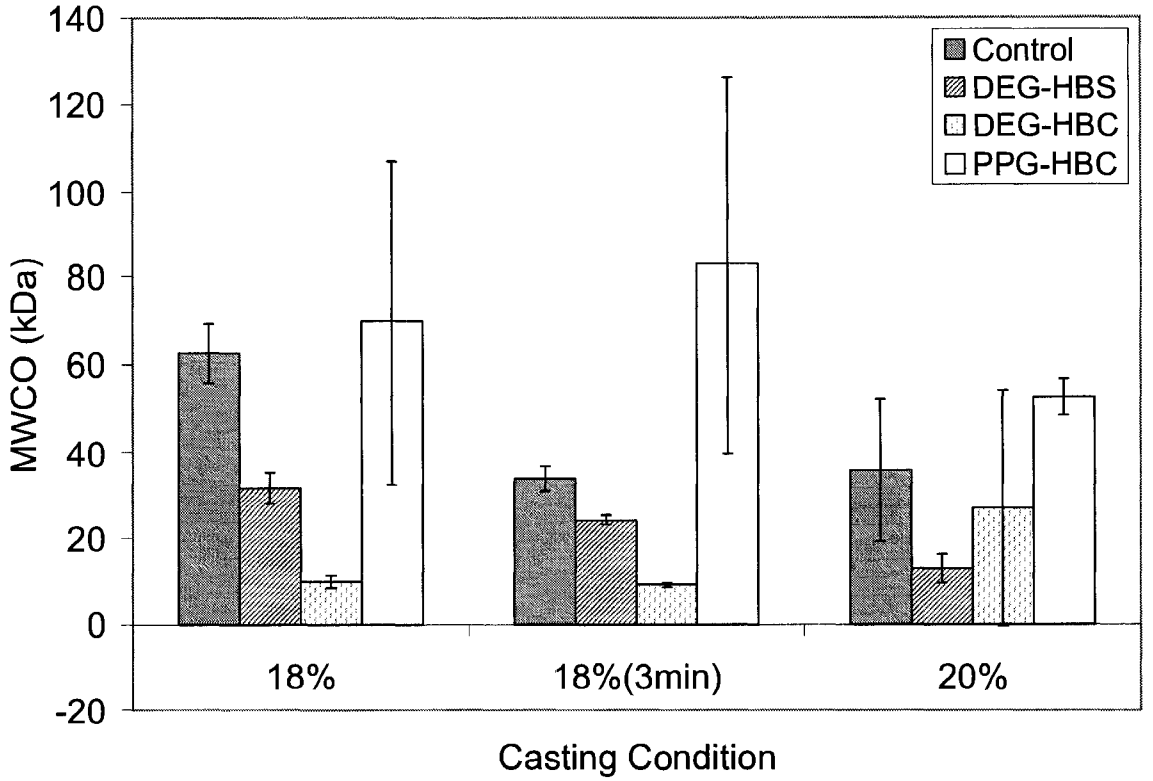


Figure 4.6: Comparison of MWCO and casting conditions for different CSMM membranes

It is interesting to note that at the 18% condition the control membrane (PES18) has a higher MWCO than the PES-DEG-HBS or PES-DEG-HBC membranes, similar to the NSF trend. This is not surprising as the two properties can be related. Similarly, at the same condition PES-PPG-HBC does show a higher MWCO than PES18, as it did with the NSF results. With the membranes cast at the 18% (3 min) condition, however, the pattern is only partially repeated. While there was a significant increase in flux for all the membranes containing CSMMs, only the PES-PPG-HBC membrane showed an increase in MWCO. This seems to indicate that the membrane pores have increased in size. The membranes containing a DEG bodied additive decreased in MWCO. This seems to indicate that the presence of DEG CSMMs created smaller but more pores given their

larger flux. At the 20% condition, the MWCO of PES20 has remained the same as PES18-3, however, the confidence limits have increased. Interestingly, PES-DEG-HBS and PES-PPG-HBC membranes at 20% have decreased in MWCO while the MWCO of PES-DEG-HBC has increased when compared to both 18 and 18% (3 min) conditions. This suggests the increase in PES in solution has compressed or changed the orientation of the DEG-HBS and PPG-HBC additives as they are more flexible than DEG-HBC. The increase in MWCO caused by DEG-HBC appears to be the result of the higher rigidity of this CSMM and may also be the result of a different orientation within the casting film. Despite notable modification to the membrane, the MWCO of the membrane is insufficiently small compared to the target compounds.

PES-PPG-HBC membranes cast at 18 and 18% (3 min) and PES-DEG-HBC at 20% showed significant error as a result of poor reproducibility. Despite removing an outlier for PPG, the membrane performance varied significantly as is evident from the standard deviation in Figure 4.6. This indicates PES membranes blended with HBC end-capped CSMMs have high variability and therefore poor reproducibility. These solutions were more viscous and many of the membrane sheets produced only provided one coupon, if any and at times, were quite wrinkled. The imperfections observed with membrane sheets are likely the cause of the high variability.

Figure 4.7 shows the relationship between membrane flux and MWCO of the control and CSMM blended membranes. It is interesting to note that for the PES-DEG-HBC membrane that the data trend is the inverse of the other membranes meaning that as the

MWCO increases, the flux of the membrane decreases. As it is desired to have a membrane with high flux and low MWCO, the trend of the PES-DEG-HBC membranes appears most promising of the cast membranes tested.

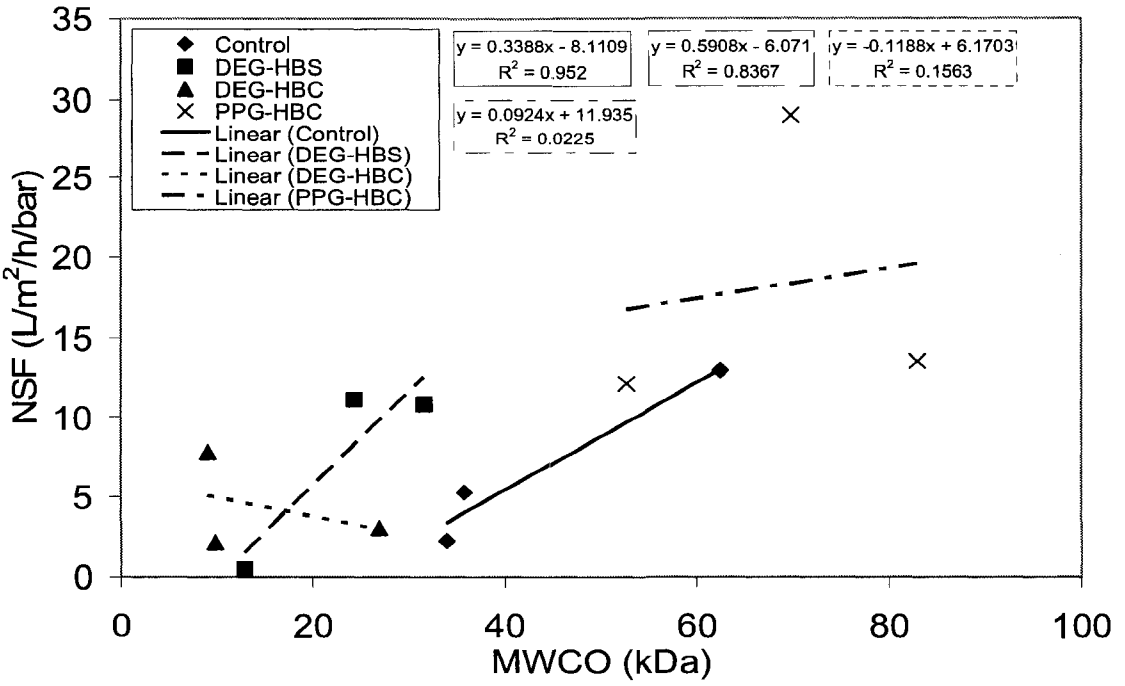


Figure 4.7: Flux vs. MWCO for control and CSMM blended membranes

Figure 4.8 shows the relationship between the change in flux and MWCO compared to the control. It can be seen that PES-DEG-HBS and PES-PPG-HBC membranes both have a linear correlation. The PES-PPG-HBC membranes saw both an increase in flux and MWCO with incorporation of the PPG-HBC additive. PES-DEG-HBS membranes showed a slight decrease in MWCO and a slight change in flux – when there was a significant increase in the flux, the change in MWCO was low. PES-DEG-HBC membranes, on the other hand, had a more significant decrease in MWCO for two conditions with one having a significant increase in flux when compared to the control.

Based on the low MWCO and the high flux, DEG-HBC appears to be the most promising additive.

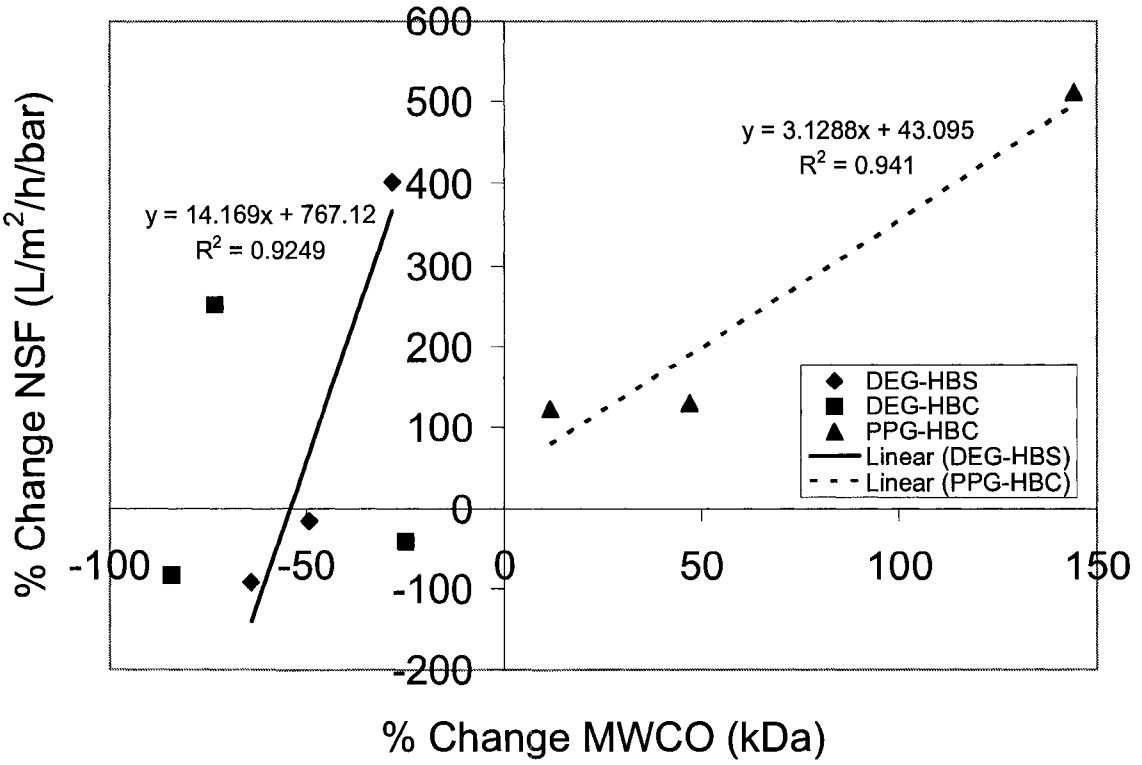


Figure 4.8: Change in flux and MWCO of all CSMM membranes in comparison to control membranes

4.6.2 Pore size distribution

Pore size distribution is determined from the solute tests conducted to determine MWCO. This allows for a better idea of the physical properties of the membrane and may give insight to solute removal during filtration tests. Despite using solutes of known MW, the curves generated (sieving, distribution) do not always fit the data very well. The fit on the graph attempts to use a distribution model to best fit the input parameters. The parameters used and the graphs generated can be found in Appendix C.

Figure 4.9 shows the simulated pore size distribution for the membranes tested. Among the control membranes the PES18 membrane has the widest pore size distribution while the PES18-3 and PES20 membranes had much narrower and fairly similar distributions and modes (Figure 4.9-A). PES-DEG-HBS membranes shown in Figure 4.9-B, indicated the simulated pore distributions of the membranes cast at the 18% PES and 20% PES conditions were more heavily weighted towards the smaller pore sizes. In comparison to the control, the increased probability of smaller pore sizes is consistent with lower flux and MWCO. At 18% (3 min), however, a wider pore distribution and larger pore size than observed with the control is consistent with the increase in NSF.

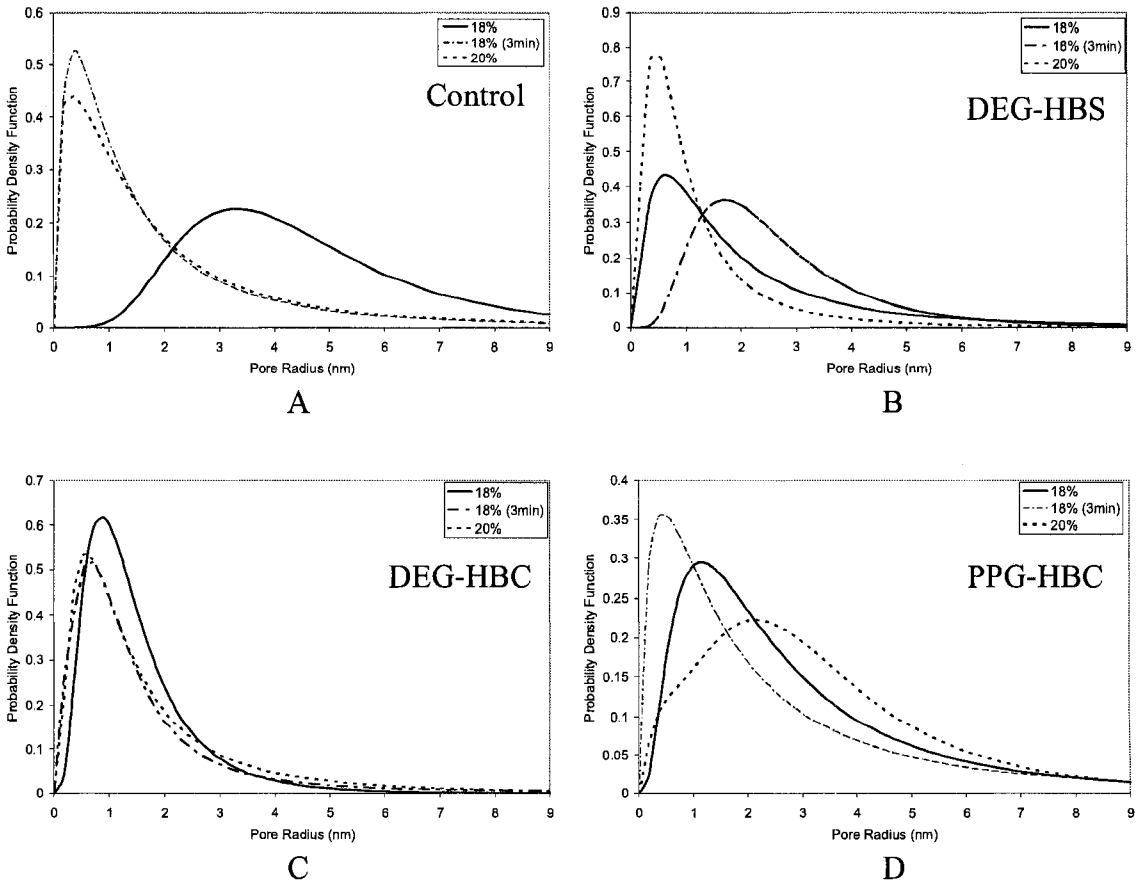


Figure 4.9: Pore radius probability density functions for tested membranes

PES-DEG-HBC membranes showed the pore size distribution at 18%, 18% (3 min) and 20% had a higher weighting towards the smaller size pores indicating the membrane became tighter (Figure 4.9-C). MWCO for the PES-DEG-HBC membrane was quite low but showed a high flux at 18% (3 min).

PES-PPG-HBC membranes had a wide pore distribution for all three casting conditions, shown in Figure 4.9-D, and was reflected in both higher MWCO and NSF. Only the distribution of PES18-3-PPG-HBC membrane was more heavily weighted towards the smaller pore sizes. Both the NSF and MWCO results were significantly higher than the PES18-3 membrane. Compared to the 18% casting condition, the NSF was lower while the MWCO was higher. These significant changes in performance parameters can therefore be attributed to PPG-HBC membrane modification.

4.6.3 Porosity

Pore density (N) and surface porosity (S_p) were calculated for each of the cast membranes following the procedure described in Appendix C which uses solute transport data and flux results. Figure 4.10 shows the results of the porosity for the various membranes. The 18 and 20% membranes followed the same trend as their respective NSF (Figure 4.4) and MWCO (Figure 4.5) results. This is not surprising as the surface porosity will directly influence the flux of the membrane. Again, it is interesting to note the reproducibility of the membranes decreases significantly when using HBC end-grouped CSMMs.

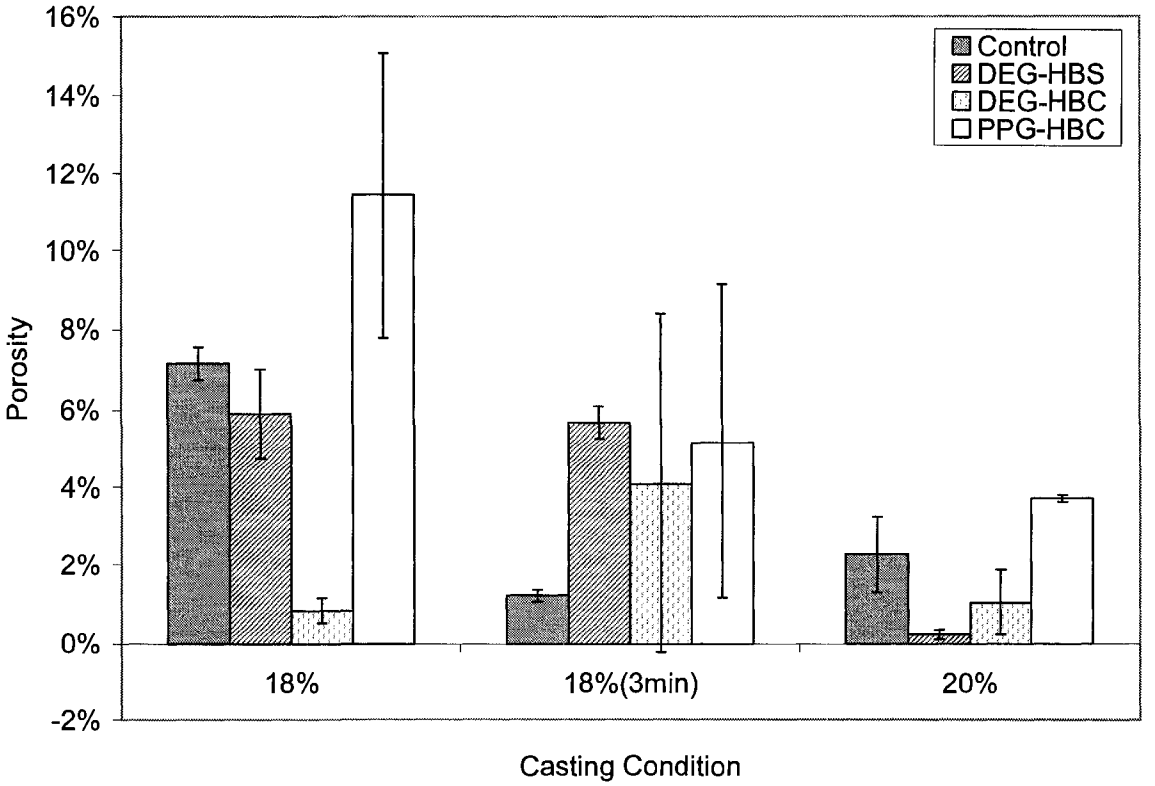


Figure 4.10: Comparison of porosity and casting conditions of different CSMM membranes

Figure 4.11 shows the relationship between flux and porosity. Regardless of the CSMM blended in the membrane, there is a direct correlation between the two variables which is expected since they are linked (flux is involved in the estimation of porosity). One interesting note is the close grouping of the control and DEG containing membranes. This appears to indicate that the flux of the membrane and its associated porosity is hardly influenced by the presence of the CSMM. PES-PPG-HBC, on the other hand, shows significant deviation from the control. The addition of PPG-HBC showed significant increase in porosity and NSF when compared to the respective controls. As the membranes are desired to be tight for removal of PPCPs and EDCs, this modification is not favourable. This may be a result of the higher MW of the PPG body compared to

the DEG bodied CSMMs and the increased bulkiness of this CSMM and its orientation within the membrane directly affects the pores of those membranes. DEG is quite small and presumed more mobile and therefore is expected to have a lower impact on the pore size and consequently its porosity.

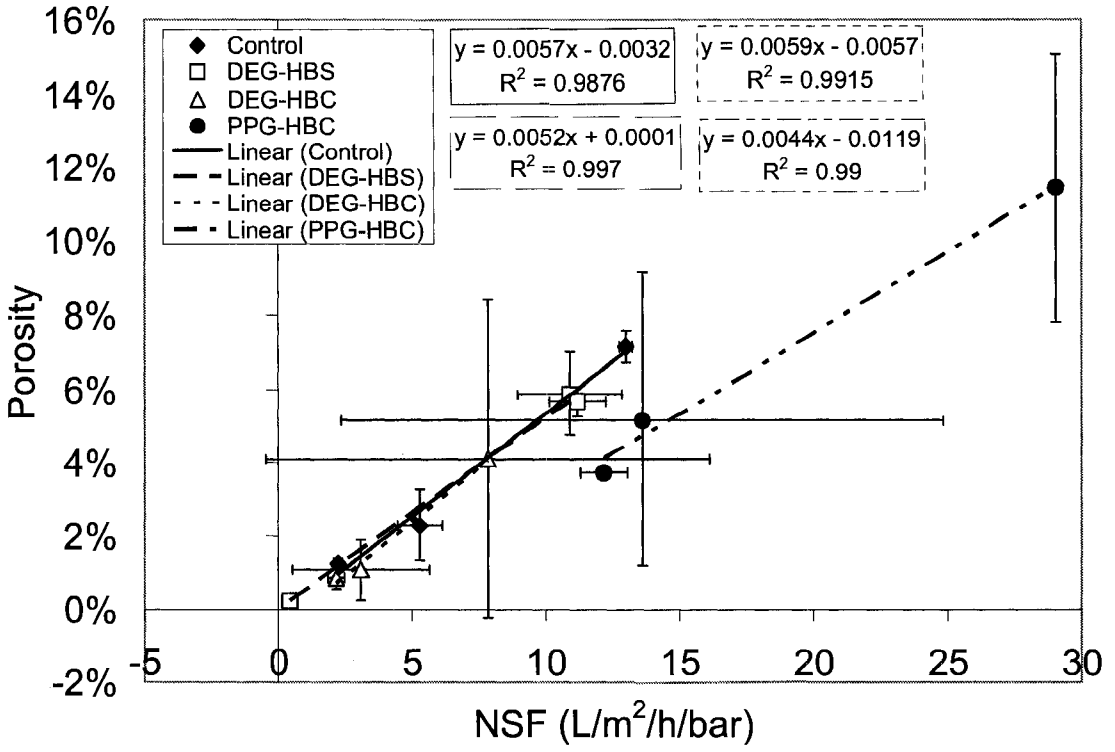


Figure 4.11: Comparison of membrane porosity and flux of different CSMMs

4.7 Removal of target compounds

Removals of the target compounds, SMZ, Carb, BPA and IB were quite varied. Depending on the flux of the membrane, the number of samples collected during solute removal varied significantly. For some membranes up to 20 samples were collected over the four hour run while other membranes were quite tight and only produced sufficient permeate for one sample, at times requiring dilution to have sufficient volume for analysis. Similar to the NSF and MWCO results, the membrane coupons determined to

be outliers were also excluded from removal analysis. An example of the removal achieved by PES-DEG-HBC membrane cast under the 18% (3 min) condition is shown in Figure 4.12. Note the number in parentheses within the legend refers to the coupon number. Removal results of all other tested experimental membranes can be found in Appendix E.

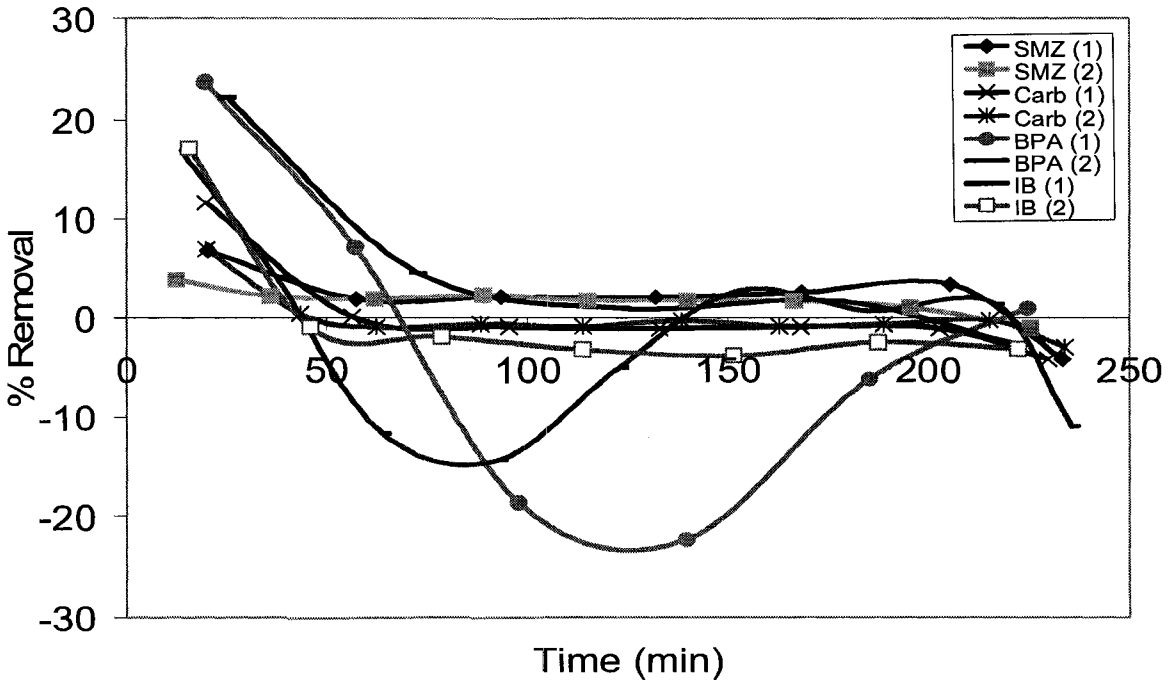


Figure 4.12: Removal of target compounds by PES-DEG-HBS (in duplicate) with time

From the removal graphs, the high initial removal decreased to a lower, steadier removal consistent with an adsorption trend. A study by Yoon et al. (2007) also concluded that the removal mechanism of compounds with higher polarity and lower hydrophobicity was adsorption.

Negative removals were also observed over the collection period, consistent with desorption trends. Desorption may be the result of site saturation within the membrane.

As a result of the high concentration and the permeation rate, the target compound desorbs, resulting in a high concentration in the permeate. Removals after four hours were also found to be minimal indicating all of the membranes were inefficient in removal of the target compounds. MWCO for all of the membranes was far too large (i.e., MWCO >10 000 kDa) for any removal by size exclusion to be observed. For comparison purposes, initial removals will be compared, as shown in Figure 4.13.

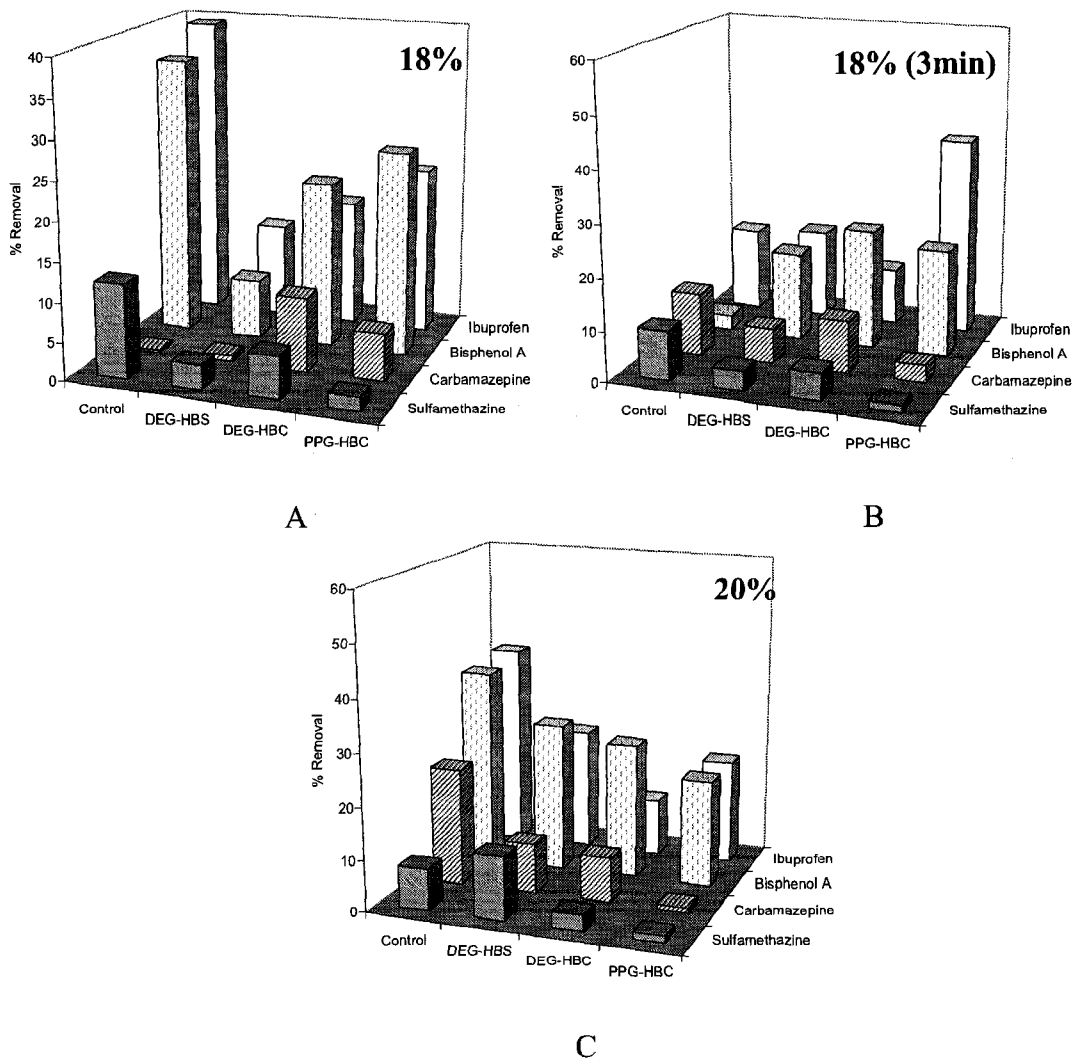


Figure 4.13: Initial removal of SMZ, Carb, BPA and IB using CSMM blended membranes and unmodified membranes at the three different casting conditions

Under the 18% casting condition (Figure 4.13-A), the control membrane shows the best removal for all of the target compounds, particularly for BPA and IB indicating the presence of CSMM may hinder removal at this condition. Both the control and PES-DEG-HBS membranes show removals increasing with an increase in compound log K_{OW}. The membranes containing CSMMs with an HBC end group, however, show a maximum removal for BPA. All the CSMM membranes showed their highest removal for BPA; however, in general, removal was reflective of increasing log K_{OW} (see Section 4.8.2). The presence of CSMM in membranes cast at 18% (3 min) (Figure 4.13-B) does indicate modification to the membrane as the initial removals of the target compounds have shifted, particularly with the higher charged compounds BPA and IB. The PES18-3 membrane shows better removal for SMZ and Carb than the CSMM membranes but worse removal for BPA. With IB as the solute, only the PES-PPG-HBC membrane showed better removal. The removal of IB by PES-DEG-HBS membranes remains the same while for PES-DEG-HBC membranes removal declines. PPG is a longer bodied segment compared to DEG, meaning the mobility of PPG-HBC will be lower and will not migrate as well. The presence of the CSMMs has helped increase the initial removal of the target compound, particularly the addition of PPG-HBC; however, once again, the membranes were unable to sustain removal over the entire four hour run.

With an increase in PES concentration from 18 to 20%, the membranes have become denser and therefore tighter. As a result, the removal of the target compounds increased, as shown in Figure 4.13-C however, the MWCO is still significantly greater than the target compounds. Like with the 18% casting conditions, the initial removal by the

PES20 membrane is higher than the CSMM blended membranes and maximum initial removal is achieved with BPA as the target compound.

In relation to the membrane charge, the control consistently had the lowest charge with the exception of the PES-DEG-HBC membrane at 18%. Both the PES18 and PES20 membranes had superior target compound removals than any of the CSMM blended membranes. Initial removal was compared to membrane charge (see Appendix F). The control membranes showed a correlation between the membrane charge and removal of BPA and IB. Only DEG-HBC showed a correlation between the membrane charge and removal of SMZ and BPA. There were no correlations between any of the other membranes and their surface charge. As there was no consistent relationship between the removal of the target compounds and surface charge and removal could not be sustained, it is not possible to conclude the initial removal mechanism is charge repulsion

With migration time, the blended membranes were comparable to the control for the removal of the target compounds. The charge of all blended membranes at the 18% (3 min) condition increased between 1.5-2.2 mV, indicating migration of the CSMM to the membrane surface. Despite migration to varying degrees for all three casting conditions, these increases were not sufficient to improve the removal of the target compounds via charge repulsion as the removal levels could not be sustained for the length of the experimental run.

4.8 Adsorption analysis

4.8.1 System characterization

Prior to the filtration experiments, single solute solutions of SMZ, Carb, BPA and IB were used to characterize the system for potential losses due to adsorption. The system was run in recycle mode (i.e., the retentate and permeate were recycled to the feed reservoir) as shown in Figure 3.2. No physical barrier was used in place of the membranes so the solution circulated freely through the permeate side of the six cells. Feed samples for each of the solutes were collected over a two day period. Concentration of the feed reservoir samples for the four runs are shown in Figures 4.14 to 4.17, the units of concentration are mg/L C as the concentration of these target solutes were quantified using a TOC analyzer. Figures 4.14 and 4.15 show no decrease in feed concentration indicating no adsorption on the system of SMZ and Carb, respectively. However, Figures 4.16 and 4.17 show a notable decrease in the feed concentration of BPA and IB, respectively, indicating adsorption on to the various components of the system. The materials of the system components were stainless steel (pipes, valves, fittings), glass (feed reservoir and rotameter casing), polypropylene (pump diaphragm) and Teflon wrapped O-Rings. These particular materials were chosen to minimize adsorption. It is expected that any adsorption that will occur can be directly related to system adsorption – volatilization of the compounds is expected to be insignificant as stated by Kimura et al. (2004). The decrease in system concentration was found to be 13.2% (1.37 mg/L C) and 29.8% (2.98 mg/L C) for BPA and IB, respectively. It is important to note that after 48 hours, the adsorption of IB had not reached equilibrium and given more time, system adsorption of this compound could continue.

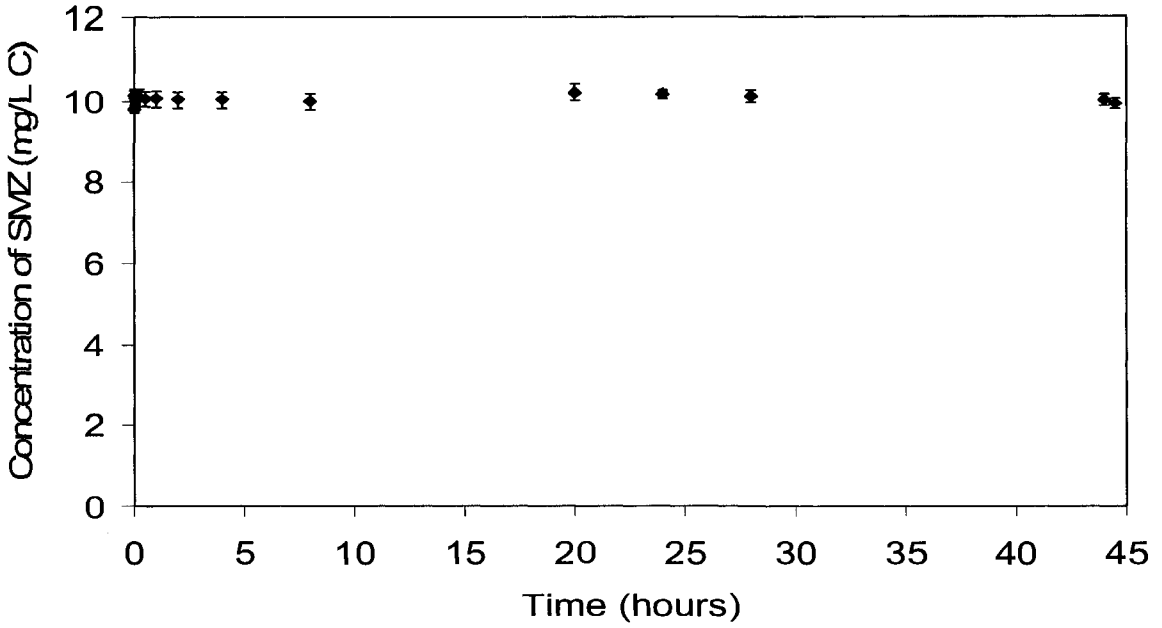


Figure 4.14: System adsorption of sulfamethazine (SMZ)

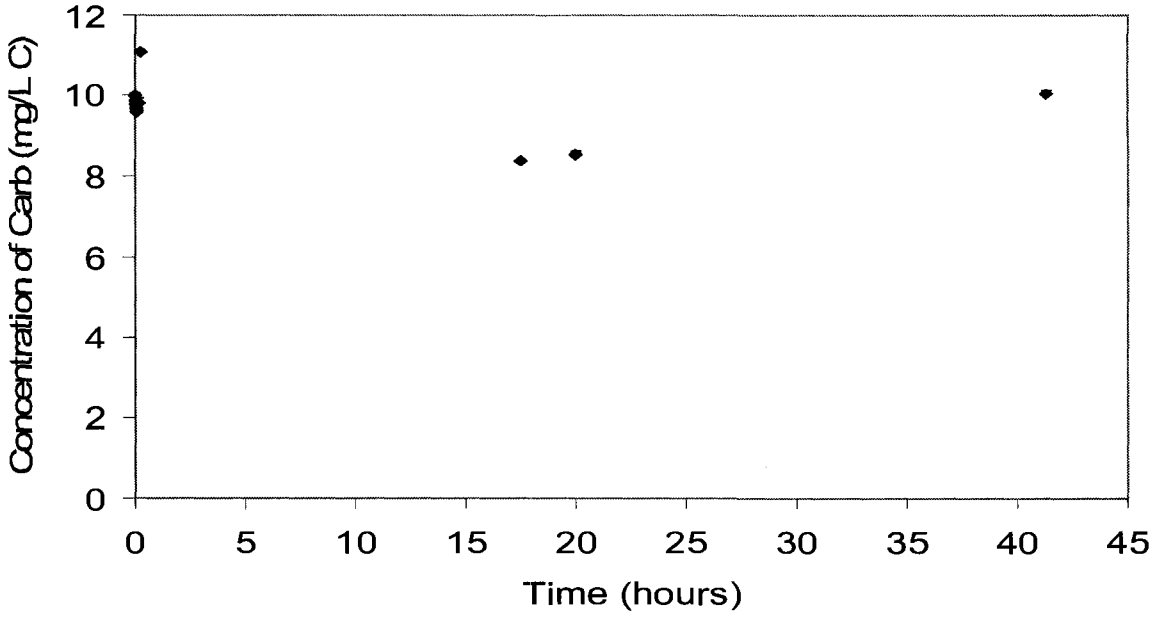


Figure 4.15: System adsorption of carbamazepine (Carb)

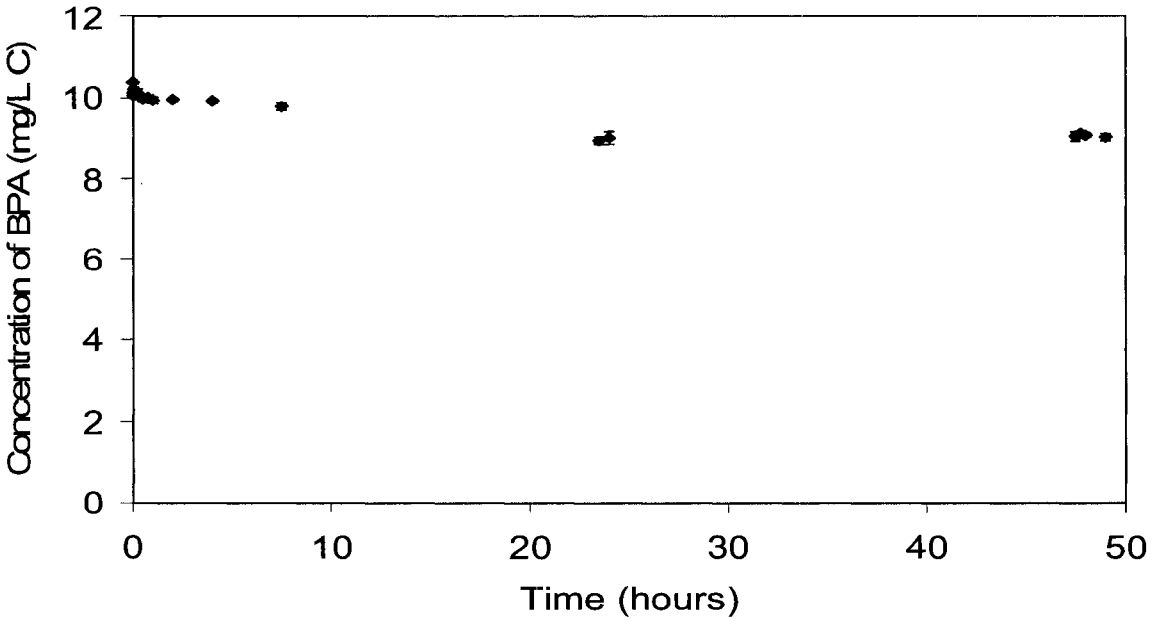


Figure 4.16: System adsorption of bisphenol A (BPA)

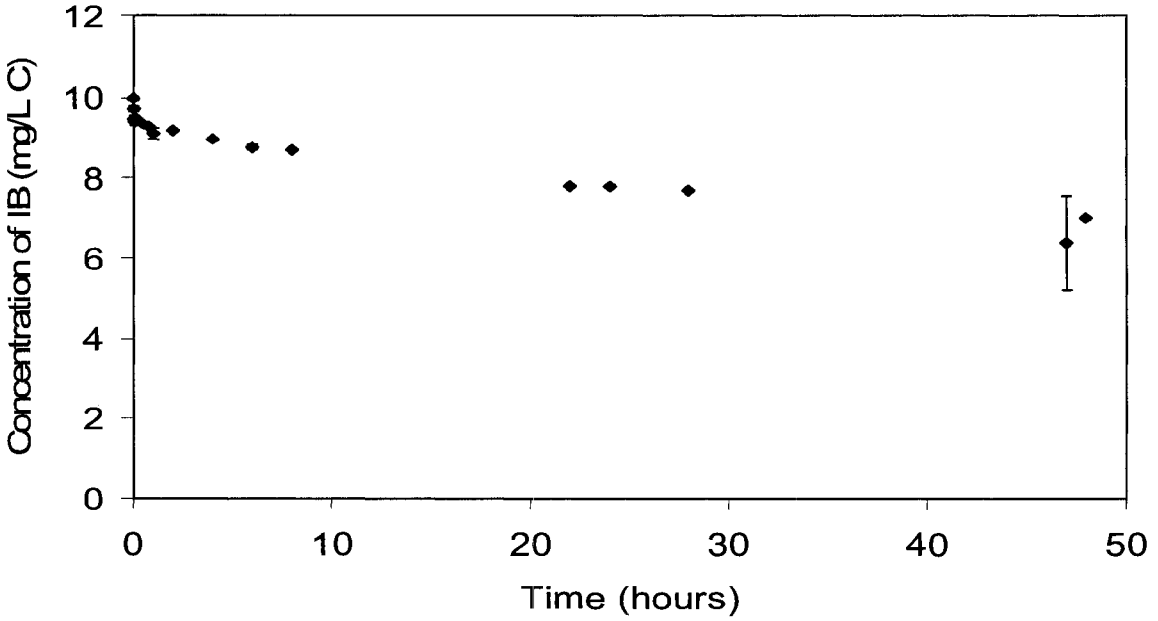


Figure 4.17: System adsorption of ibuprofen (IB)

4.8.2 Adsorption of target solutes onto membranes

Figure 4.18 shows an example of initial removal with increasing log K_{OW}. All membranes exhibited this general trend at their respective casting conditions. This corresponds to the results of Yoon et al. (2007) who found increased solute hydrophobicity generally increased solute sorption potential, indicating initial removal of the target compounds tested is likely adsorption.

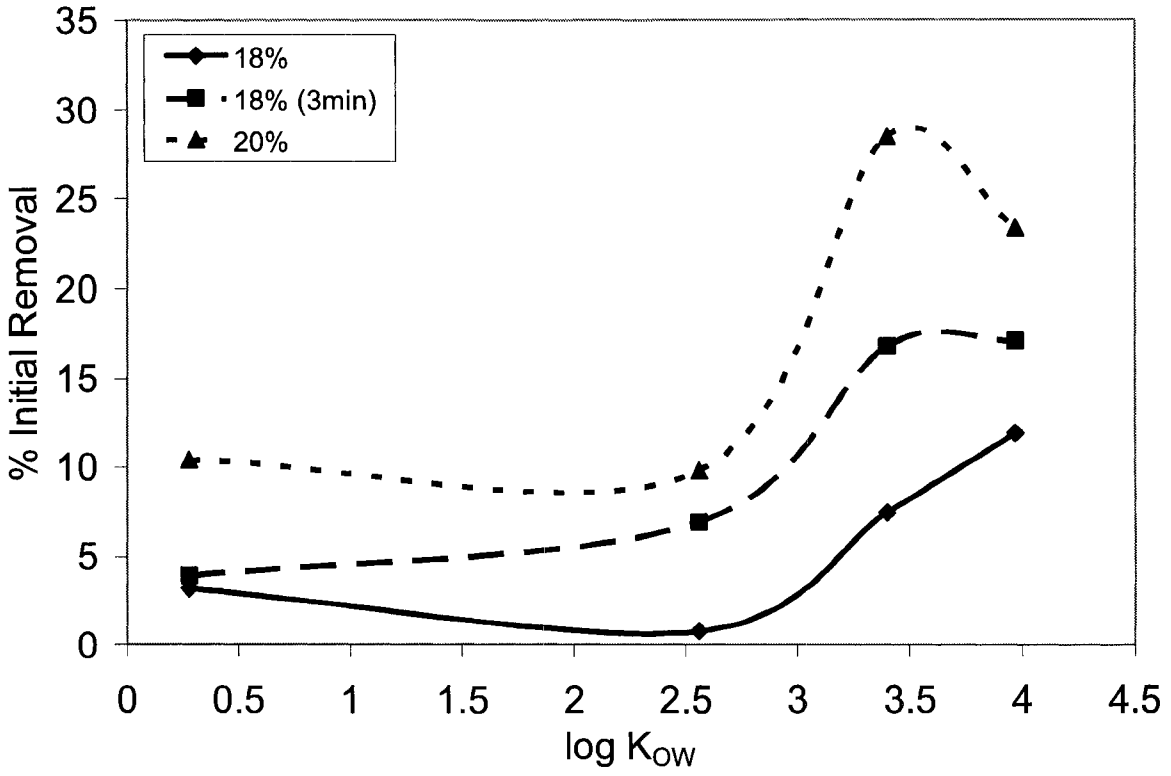


Figure 4.18: Comparison of the initial removal by PES-DEG-HBS membranes based on the log K_{OW} of the target compounds

As previously proposed, removal curves presented follow the same removal trend as is common when adsorption is the dominant removal mechanism. Further analysis of the change in feed concentration with time was conducted for each of the six coupon tests and their feed concentrations compared against that of the system baseline

characterization. Development of the equations used for this analysis can be found in Appendix G. Figures 4.19 and 4.20 show the results of the calculated mass adsorbed during the membrane filtration tests in comparison to the system characterization (baseline), described in Section 4.8.1.

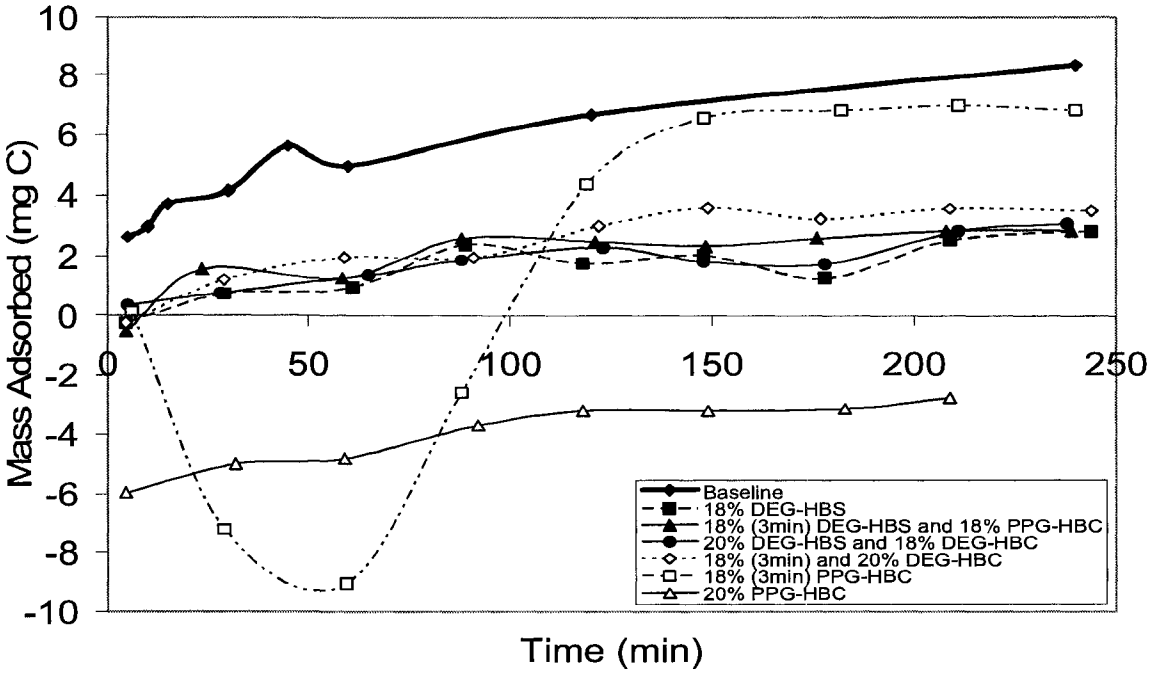


Figure 4.19: BPA adsorption by all CSMM blended membranes

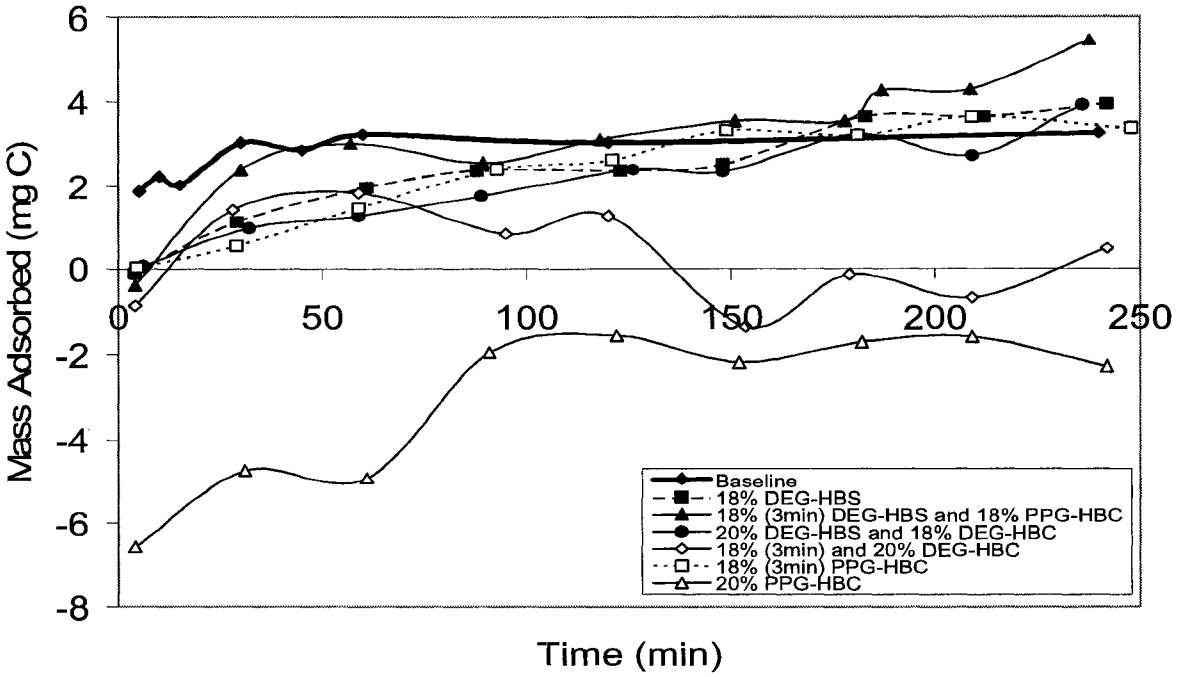


Figure 4.20: IB adsorption by all CSMM blended membranes

From Figures 4.19 and 4.20, it is clear that adsorption cannot be attributed as the main removal mechanism since, in the majority of cases, the membrane adsorption curves are below the baseline (system adsorption). With IB as the solute, only a couple samples showed adsorption greater than the baseline however this may be the result of variability and cannot be conclusively determined to be adsorption. It is expected the adsorption with the membrane in the system would be higher than the baseline as there is more surface available for adsorption. The lower adsorption observed during the filtration tests may be the result of the permeate return lines (back to the feed tank) no longer being part of the total system since permeate samples were collected instead.

One other note is the testing of two different membranes in triplicate at the same time. As the retentates from two different membranes are mixed in the common feed reservoir,

it is impossible to distinguish potential adsorption onto one set of membranes from another. Thus, it is recommended that future testing should be limited to one membrane type or that sample ports on the retentate side of each membrane cell be installed.

4.9 Comparison to commercial membrane (NF270)

Solute removal tests were also conducted using a commercial nanofiltration thin film composite membrane, NF270 (DOW/Filmtec). Figure 4.21 shows the removal by NF270 following the same testing protocol as the experimental membranes. Higher, consistent removals were achieved with SMZ and Carb which have lower log K_{OW}. This indicates that adsorption is not the dominant removal mechanism for the experimental membranes. There was a decrease in removal with time for both BPA and IB, perhaps partially due to adsorption and site saturation. A study by Nghiem et al. (2005b) showed rejection of Carb by various NF membranes (NF270, NF90) was solely via size exclusion. They also found that for other tested compounds, such as IB, had a higher, consistent rejection with time in comparison to Carb (none was detected in the permeate), but the rejection mechanism in this case was charge repulsion. Higher removals in the first collected sample of BPA and IB may have been the result of adsorption to the membrane. As the trend for the membranes developed in this study is the opposite of the one observed by Nghiem et al. (2005b) with the NF270, this further suggests the removal mechanism of the experimental membranes was neither size exclusion nor charge repulsion but rather adsorption.

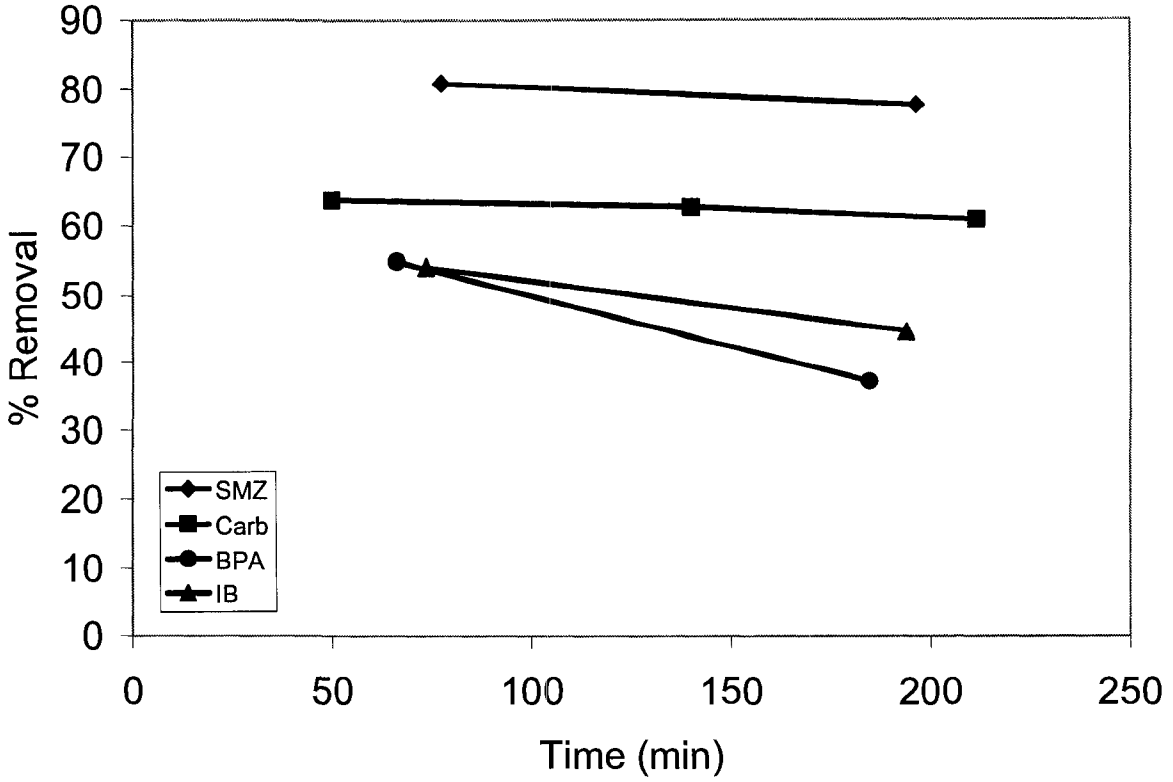


Figure 4.21: Removal by commercial membrane, NF270

One interesting observation is, due to the tightness of the NF270 membrane, only 2-3 samples were collected over four hours which was the run time for the experimental membranes. To be able to further quantify removal by this membrane, the run should have been continued for a longer period of time. Many of the CSMM blended membranes proved to be as tight or tighter than the NF270 (based on flux) and were the ones to achieve higher removal in comparison to looser CSMM blended membranes. In those cases, it is possible that size exclusion began to become a factor in removal; however with few samples collected, it is not possible to draw a conclusion.

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 DEG-bodied CSMMs within experimental PES ultrafiltration membranes increased membrane charge and tightness when compared to the control membranes. Despite these modifications, however, the membranes were relatively unsuccessful for the removal of SMZ, Carb, BPA and IB. A membrane material with tighter pores and possibly a stronger charge is required for this application.
2. The membranes with the PPG-bodied CSMM had larger pores, higher fluxes, and poor removal of the target compounds. Due to their poor reproducibility membranes incorporating this CSMM should not be further investigated.
3. The temporary initial removal of the target compounds by the experimental membranes was a function of their increasing octanol-water coefficient (log K_{OW}), indicating initial removal was via adsorption. Initial removal could not be linked to any other solute or membrane properties evaluated.
4. DEG-HBC is the most promising CSMM based on flux and MWCO, especially at 18% (3 min). The presence of this CSMM caused an increase in NSF while decreasing MWCO. It also achieves the highest removal at the 18% (3 min) condition. Though this modification was insufficient for successful removal of the target compounds, it may be worthwhile investigating other applications for these membranes and further development of these membranes for this application.

5. DEG-HBS and PPG-HBC CSMMs produced membrane surfaces with higher contact angles than the unmodified membranes at all three casting conditions. Based on the end groups of the CSMMs, it is expected the membranes would become more hydrophilic. The increase in contact angles of these membranes is presumably due to increased surface roughness. DEG-HBC, on the other hand, increased the membrane contact angle from the 18 to 20% condition and from the 18 to 18% (3 min) condition.
6. Membrane charge was unchanged with respect to the control for 18 and 18% (3 min) membranes, however decreased for 20% PES membranes. The CSMMs developed for this study did not significantly vary the charge of the membranes.
7. The removal mechanism for CSMM blended membranes could not be determined. MWCO of the all the membranes was significantly larger than the target compounds, hence the mechanism could not be size exclusion. A comparison of removal with membrane charge revealed there was no consistent correlation and therefore removal could not be attributed to charge repulsion. Adsorption analysis showed no significant removal when compared to the baseline adsorption despite the removal with time plots following an adsorption trend. Slight differences between the adsorption and solute tests may have resulted in higher baseline adsorption levels.

5.1.1 Minor Conclusions

1. No relationship between flux and surface charge was found, with the exception of PES-DEG-HBC.
2. Solutes with high log K_{OW} (i.e., BPA and IB) were found to adsorb to the filtration system.

3. Initial removal by the membranes increased with an increase in log K_{OW}.

5.2 Recommendations

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

1. From the results of the literature review and this study, there is still no one process that effectively removes all PPCPs and EDCs. This indicates that either a) further refining of the existing membrane process or b) the combination with other advanced technologies such as ozonation or other advanced oxidation processes is required.
2. Further optimization of DEG-HBC is warranted. The addition of migration time produced membranes that had high flux and lower MWCO however, this was insufficient to successfully remove the target compounds. Incorporation of migration time at higher PES concentration (20%+) could result in a tighter membranes which may achieve higher removals while still maintaining sufficient flux.
3. To more conclusively correlate trends to the membrane casting parameters (base polymer concentration, migration time or CSMM), an experimental design approach should be incorporated at various casting conditions. Distinction between removals as a result of increased PES concentration or the pronounced effect of the CSMM can then be determined.
4. Other analysis methods, such as gas chromatography, should be used in place of TOC for analysis. These would allow for better indication of carry-over within the system (particularly in the case of desorption).

5. Modification to the test system should be made such that retentate samples for each membrane cell can be collected prior to recycle and measured in order to carry out mass balance calculations for each coupon tested and more definitive adsorption and removal result attributions may be made.
6. Due to high membrane variability, more replicates are warranted to better determine membrane performance and reproducibility. As a result of the high variability of membranes cast containing PPG-HBC, this CSMM should not be further investigated for the removal of PPCPs and EDCs.
7. Static adsorption tests (jar tests) could be carried out on membrane coupons to determine the extent of membrane adsorption.
8. A suitable membrane substitute has to be found in order to make the baseline adsorption tests be more comparable to the filtration tests.
9. Negative removals indicated competitive adsorption during the filtration run. Other cleaning methods should be investigated – either a longer cleaning period and/or a method which would promote desorption of the target compounds (i.e., by allowing the membranes to soak in MQ water).
10. Investigate the development of higher charged CSMMs.
11. Further characterize the CSMMs in terms of measuring the end-group charge and their molecular weight.
12. Automation of the flow within the system would reduce the pressure and flow variability.
13. If the development of a suitable membrane is achieved, further investigation into the feasibility of implementing the membrane for drinking water applications is

warranted. Investigation into its interaction and performance with real waters (in the presence of NOM), the removal of a mixture of PPCPs and EDCs and sufficient product water production should be conducted prior to implementation.

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APPENDIX A

Removal of PPCPs and EDCs by commercial membranes

Removal of PPCPs and EDCs has been extensively investigated using commercial membranes. Table A.1 contains the removal results from those studies and Table A.2 some compound groups used in the studies contained in Table A.1.

Table A.1: Removal of PPCPs and EDCs from various membrane studies

Types	Membrane	Set-up Type	Compounds Removed	% Retention	Adsorption	Reference
UF	GM	Dead-End Stirred Cell	Group 1, Group 2 (see Table A.2)	Group 1: less than 40% retention except triclosan (87%), oxybenzone (77%), progesterone (56%); Group 2: high degree of retention by both NF and UF membranes except a few compounds (α- and β-BHC, fluoranthene, hydrocodone, metolachlor, and musk ketone) were poorly removed	Greater mass recovery, >50% includes 14/25 compounds	1
	GM	Dead-End Stirred Cell	17β-Estradiol, Fluoranthene	95%+ in absence of NOM, E2 removal in absence of NOM removal decreased from 60 to 95% to 10 to 20% in presence of NOM	Fluoranthene 15 to 25%	2
	GM	Cross Flow	Ibuprofen	High rejection (~98-99% Fig1, no NOM) at low pump pressure (electrostatic repulsion)		3
NF	NF-270	Cross Flow, Plate and Frame	Nonylphenol, Tertbutylphenol, Bisphenol A	~45% BPA, ~50% tertbutylphenol ~55% BPA, ~65% tertbutylphenol	No adsorption for BPA	4
	NF-270	Cross Flow	Sulfamethoxazole, Carbamazepine, Ibuprofen	~96% sulfamethoxazole, ~84% sarbamazepine and ~99% ibuprofen	No adsorption	5
	NF-270	Cross Flow	Estradiol, Estrone, Testosterone, Progesterone	Initial high rejection at 100% (due to adsorption) decreases until equilibrium is achieved; NaCl rejection 40%	100% rejection due to adsorption at start of experiment	9
	NF-200	Bench-scale Flat-sheet Tests and Lab-scale 2540 Spiral Wound Elements	Group 5 (see Table A.2)	Rejection of ionic pharmaceutical residues and pesticides exceeded 89%		6
	NF-200	Spiral wound membrane element	Group 3 (see Table A.2)	Rejection of ionic pharmaceutical residues and pesticides exceeded 89%; in the presence of NOM, rejection negatively charged compounds 93.5% +- 2.3% to 97.7 +-1.0%	Adsorption pore clogs and enhances steric and electrostatic exclusion	7

Types	Membrane	Set-up Type	Compounds Removed	% Retention	Adsorption	Reference
NF	NF-90	Cross Flow, Plate and Frame	Nonylphenol, Tertbutylphenol, Bisphenol A	>90% BPA and tertbutylphenol	No adsorption for BPA	4
	NF-90	Cross Flow	Sulfamethoxazole, Carbamazepine, Ibuprofen	100% sulfamethoxazole, 96$ carbamazepine and 100% ibuprofen	No adsorption	5
	NF-90	Bench-scale Flat-sheet Tests and Lab-scale 2540 Spiral Wound Elements	Group 5 (see Table A.2)	Rejection of ionic pharmaceutical residues and pesticides exceeded 95%		6
	NF-90	Spiral wound membrane element	Group 3 (see Table A.2)	Rejection of ionic pharmaceutical residues and pesticides exceeded 95%; in the presence of NOM, rejection negatively charged compounds 97.1% +- 1.4% to 99.3 +-0.3%	Adsorption pore clogs and enhances steric and electrostatic exclusion	7
	NF-90	Cross Flow	Estradiol, Estrone, Testosterone, Progesterone	Initial high adsorption at 100% (due to adsorption) decreases until equilibrium is achieved; NaCl rejection 85%		9
	ESNA	Dead-End Stirred Cell	Group 1, Group 2 (see Table A.2)	Group 1: 44-93% except naproxen of no retention; Group 2: high degree of retention by both NF and UF membranes except a few compounds (α- and β-BHC, fluoranthene, hydrocodone, metolachlor, and musk ketone) were poorly removed	Group 1: less than 100% recovery (androstenedione, oxybenzone, progesterone, testosterone, triclosan;, less than 40% recovery except gemfibrozil and ibuprofen; >50% for 7/25 compounds	1
	ESNA	Dead-End Stirred Cell	17β-Estradiol, Fluoranthene	95%+ in absence of NOM, increase from 15 to 70% DI water in presence of NOM (E2); increase from 77 to 95% DI water in presence of NOM (Fluoranthene)	Fluoranthene 10 to 20%;	2

Types	Membrane	Set-up Type	Compounds Removed	% Retention	Adsorption	Reference
NF	RF	Cross Flow	Ibuprofen	Rejection over 90%		3
	TFC-S	Cross Flow, Dead end stirred cell	Estrone, Estradiol	~78% (estrone) and ~82% (estradiol)	Retention decreases as adsorption decreases	8
	TFC-S	Cross Flow (stirred cell)	Estrone	Initially high (adsorption); decreases to about 55%	Apparent breakthrough; pore size same order of magnitude as estrone molecule - log scale linear (stirred ceel w/ convection)	10
	TFC-S	Magnetically stirred batch cells	Estrone	High (95-99%)		11
	TFC-SR2	Spiral wound membrane element	Group 3 (see Table A.2)	Poor rejection of ionic solutes (declined from 41.2 +-15.6% to 32.6 +-23.1% only diclofenac increased by 11.5% in presence of NOM)	Adsorption pore clogs and enhances steric and electrostatic exclusion	7
	TFC-SR2	Cross Flow, Dead end stirred cell	Estrone, Estradiol	Retention decreased to 13% when equilibrium between estrone and the membrane has been established; NaCl retention 2-17%	Retention decreases as adsorption decreases	10
	TFC-SR2	Cross Flow (stirred cell)	Estrone	High initial retention (above 90%) at low pH and low estrone retention (about 55%) clearly indicate that retention in this case governed by adsorption (direct from article)	Initially high	10
	TFC-SR2	Magnetically stirred batch cells	Estrone	High (95-99%)		11
NF/RO	ACM-4	Cross Flow, Dead end stirred cell	Estrone, Estradiol	Diffusion does not affect retention of estrone	Retention decreases as adsorption decreases	10
	ACM-4	Magnetically stirred batch cells	Estrone	High (95-99%)		11

Types	Membrane	Set-up Type	Compounds Removed	% Retention	Adsorption	Reference
NF/RO	TFC-SR1	Cross Flow, Dead end stirred cell	Estrone, Estradiol	Retention decreased to 34% when equilibrium between estrone and the membrane has been established; NaCl retention 24-32%	Retention decreases as adsorption decreases	10
	TFC-SR1	Magnetically stirred batch cells	Estrone	High (95-99%)		11
NF/RO	TFC-ULP	Cross Flow, Dead end stirred cell	Estrone, Estradiol	Diffusion has very weak affect retention of estrone	Retention decreases as adsorption decreases	10
	TFC-ULP	Magnetically stirred batch cells	Estrone	High (95-99%)		11
	TS-80	Cross Flow, Dead end stirred cell	Estrone, Estradiol	Diffusion does not affect retention of estrone (may underestimate long term retention)	Retention decreases as adsorption decreases	10
	TS-80	Magnetically stirred batch cells	Estrone	High (95-99%)		11
	XN-40	Cross Flow, Dead end stirred cell (may underestimate long term retention)	Estrone, Estradiol	Retention decreased to 43% when equilibrium between estrone and the membrane has been established; NaCl retention 21-34%; lowest rejection efficiency; removal 20-25% for chloroform; 35-45% bromoform	Retention decreases as adsorption decreases	10
	XN-40	Magnetically stirred batch cells	Estrone	Lower (80%); exibited lowest sodium rejection		11
ULPRO	XLE spiral membrane elements	Spiral wound membrane element	Group 3 (see Table A.2)	Rejection of ionic pharmaceutical residues and pesticides exceeded 95%; in the presence of NOM, rejection negatively charged compounds 93.5% +- 1.0% to 97.2 +-0.6%; removal 20-25% for chloroform; 35-45% bromoform	Adsorption pore clogs and enhances steric and electrostatic exclusion	7

Types	Membrane	Set-up Type	Compounds Removed	% Retention	Adsorption	Reference
ULPRO	XLE	Cross Flow Membrane Unit with flat sheet membrane cell	Group 4 (see Table A.2)	%rejection range from 57-91% specific table 3 p.75, molecular size dominant rejection factor, molc with high dipole moment = poor rejection; salt rejection 90%		11
	XLE	Bench-scale Flat-sheet Tests and Lab-scale 2540 Spiral Wound Elements	Group 5 (see Table A.2)	Rejection of ionic pharmaceutical residues and pesticides exceeded 95%		6
RO	CTA	Bench-scale Flat-sheet Tests and Lab-scale 2540 Spiral Wound Elements	Group 5 (see Table A.2)	Membrane fouling on cellulose Triacetate membranes resylts in elevated concentrations of target solutes in the permeate		6
	D2731		Carbadox, Sulfachlorpyridazine, Sulfadimethoxine, Sulfamerazine, Sulfamethazine, Sulfathiazole, Trimethoprim	TDS rejection 86%, rejection of antibiotics 90.2% from DD water and 90.3% MRW; 99 to 99.9% rejection with 2-3 RO units in series		12
	SC-3100	Cross Flow Membrane Unit with flat sheet membrane cell	Group 4 (see Table A.2)	% rejection range from 0-85% specific table3 with % p.75 molecular size dominant rejection factor, rejection dependent on polarity (low logKow = higher dipole moment); salt rejection 94%		9
	TCF-HR	Bench-scale Flat-sheet Tests and Lab-scale 2540 Spiral Wound Elements	Group 5 (see Table A.2)	Rejection of ionic pharmaceutical residues and pesticides exceeded 95%		6

Types	Membrane	Set-up Type	Compounds Removed	% Retention	Adsorption	Reference
RO	TFC-HR	Spiral wound membrane element	Group 3 (see Table A.2)	rejection of ionic pharmaceutical residues and pesticides exceeded 95%;in the presence of NOM, rejection negatively charged compounds 95.8% +- 2.8% to 98.6 +-0.5%; removal 20-25% for chloroform; 35-45% bromoform	Adsorption pore clogs and enhances steric and electrostatic exclusion	7
	X-20	Cross Flow, Dead end stirred cell	Estrone, Estradiol	Diffusion does not affect retention of estrone	Retention decreases as adsorption decreases	10
	X-20	Cross Flow (Dead End)	Estrone	Diffusion controlled for tight membranes - sieving mechanism		11
	X-20	Magnetically stirred batch cells	Estrone	High (95-99%)		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](Drewes et al., 2005), [7](Xu et al., 2005), [8](Nghiem et al., 2004a), [9](Nghiem et al., 2004b), [10](Nghiem et al., 2002a), [11](Nghiem et al., 2002b), and [12](Adams et al., 2002)

Table A.2: Compound groups from various PPCP and EDC removal studies

Group 1	Group 2	Group 3	Group 4	Group 5
Gemfibrozil	Benzo[a]pyrene	Ibuprofen	2-Naphthol	**Hydrophilic Ionic**
Triclosan	benzo[k]fluoranthene	Diclofenac	4-Phenylphenol	Ibuprofen
Estradiol	α-Chlordane	Ketoprofen	Phenacetine	Diclofenac
Ibuprofen	Heptachlor	Naproxen	Caffeine	Ketoprofen
Progesterone	DDD	Gemfibrozil	NAC standard	Naproxen
Oxybenzone	Galaxolide	Mecoprop	Primidone	Gemfibrozil
Ethynylestradiol	Chrysene	Primidone	Bisphenol A	Mecoprop
Testosterone	Benzo[b]fluoranthene	Bromoforn	Isopropylantipyrine	Propyphenazone
Naproxen	Benz[a]anthracene	Chloroform	Carbamazepine	Dichloprop
Estrone	Dieldrin		Sulfamethoxazole	2,4-dihdroxybenzoic acid
Erythromyein-H_2O	Endrin		17β-Estradiol	2-Naphthalenesulfonic acid
Diazepam	Fluoranthene			1,5-naphthalenedisulfonic acid
Androstenedione	Methoxychlor			Glutaric acid
Atrazine	Pyrene			Acetic acid
Diantin	Phenanthrene			**Hydrophilic Non-Ionic**
Carbamazepine	Anthracene			Primidone
Estriol	Musk Ketone			Phenacetine
DEET	Fluorene			Caffeine
TCEP	Ancenapthylene			Tris(2-chloroethyl-phosphate
Trimethoprim	Acenaphtlene			Tris(2-Chlorosiopropyl)-phosphate
Sulfamethoxazole	α-BHC			Sucrose
Diclofenac	β-BHC			Glucose
Meprobamate	Naphthalene			Urea
Acetaminophen	Metolachlor			**Hydrophobic Non-Ionic**
Pentoxifylline	Hydrocodone			Bromoform
Caffeine				Chloroform
Iopromide				Trichloroethylene
				17beta-estradiol
				Estriol
				Testosterone
				2-Naphthol
				Carbamazepine
				Naphthalene

APPENDIX B

NSF vs. MWCO results for CSMM membranes at the different casting conditions

The relationship between NSF and MWCO is important in the measure of success of the CSMM membranes. Figure 4.10 presented the change of NSF and MWCO compared to the control. Figures B.1 to B.4 show the relation between NSF and MWCO for each of the control and CSMM blended membranes at the three casting conditions.

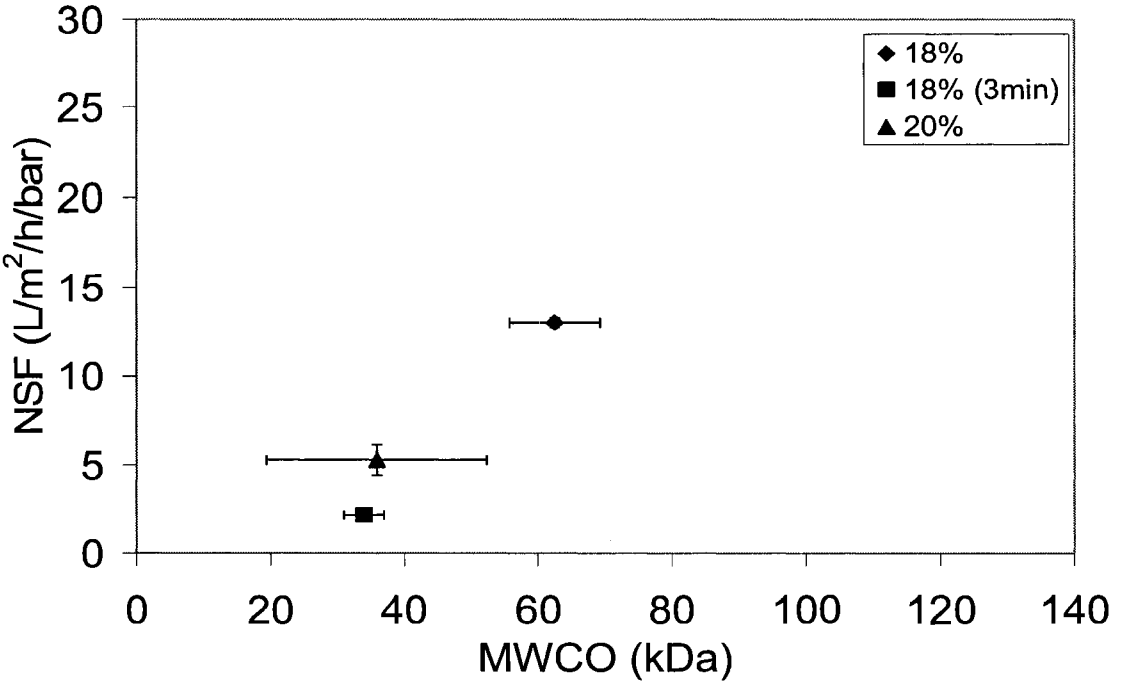

Figure B.1: Relation of NSF and MWCO for control membranes

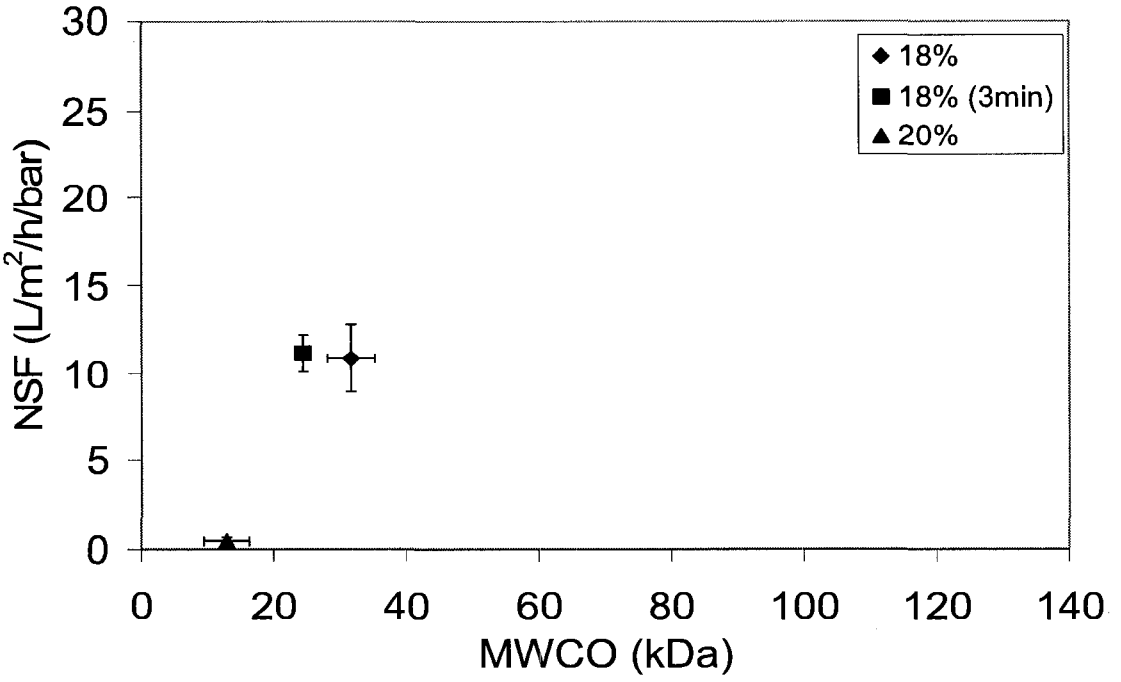

Figure B.2: Relation of NSF and MWCO for PES-DEG-HBS membranes

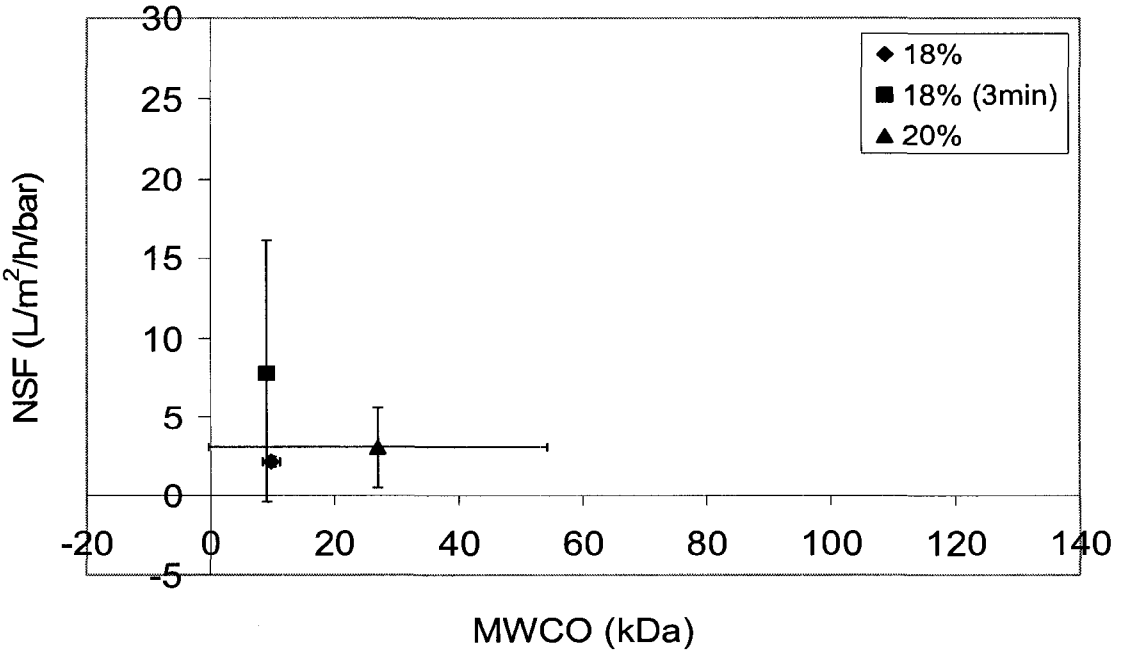

Figure B.3: Relation of NSF and MWCO for PES-DEG-HBC membranes

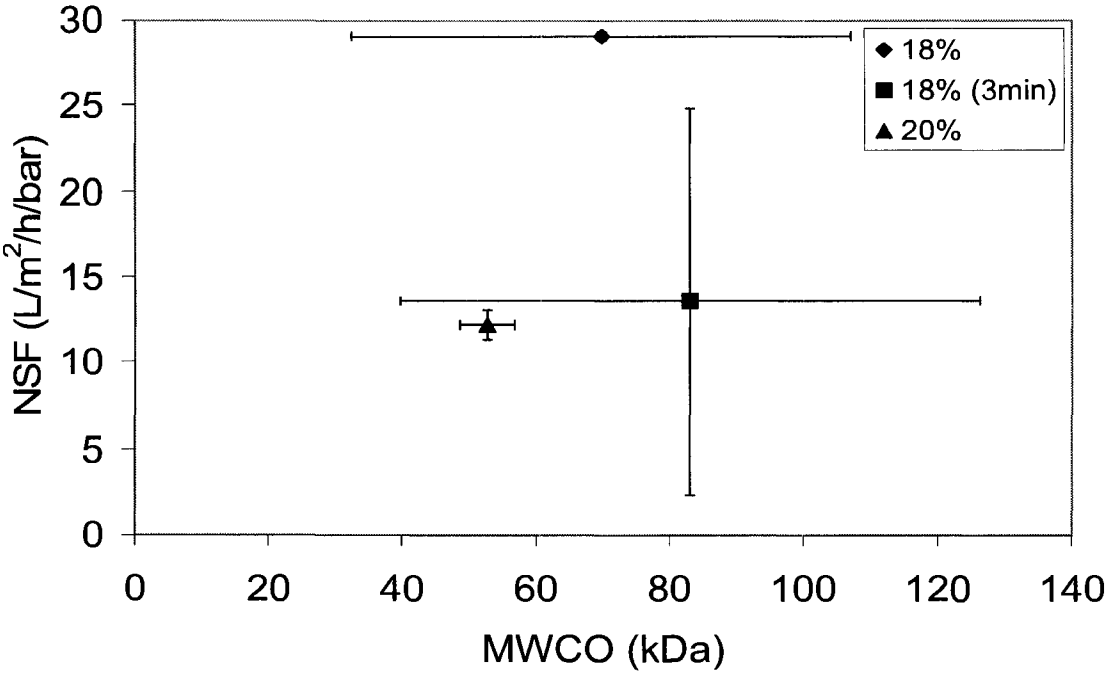

Figure B.4: Relation of NSF and MWCO for PES-PPG-HBC membranes

APPENDIX C

Development of solute transport equations

The solute is defined as the compound in a solution in lower quantity while the solvent is the compound in higher quantity. MWCO is determined using solute separation data generated from the sequential filtration of PEG and PEO solutions of different molecular weights. The solutions are tested in order of increasing molecular weight and in between each solution the feed is changed to distilled water to clean the system. As it is desired to determine what solute size will be retained by the membrane, for each selected solute size (typically five) the permeate (one) and feed (two) samples from each cell are collected and analyzed. For a UF membrane, the MWCO is the size of solute at which 90% is retained. The solute transport data is generally presented as the percent removal versus solute particle size.

The Stokes radius is the radius of a particle assuming the particle is a sphere and will behave as such when studied. The Stokes radius (a) of PEG and PEO were calculated using the molecular weight of the solute (MW), equations (C.1 and C.2).

$$a_{PEG} = 16.73 \times 10^{-10} MW^{0.557} \qquad \text{(C.1)}$$

$$a_{PEO} = 10.44 \times 10^{-10} MW^{0.587} \qquad \text{(C.2)}$$

The above expressions were derived by Singh et al. (1998) based on empirical expressions of the intrinsic viscosities and the Stokes-Einstein diffusivity expressions. Based on the separation data of PEG and PEO, the pore size distribution of the membrane was calculated using the log-normal probability function stated (using equation C.3). Michaels (1980) states this to be an accurate method to describe UF membrane sieving

curves. Inherent to this type of analysis is that one can equate the membrane pore size distribution to the particle size of the solutes passing through the membrane.

$$\frac{\partial f(d_p)}{\partial d_p} = \frac{1}{d_p \ln \sigma_p \sqrt{2\pi}} \exp\left[-\frac{1}{2}\left(\frac{\ln(d_p / \mu_p)}{\ln \sigma_p} \right)^2 \right] \qquad \text{(C.3)}$$

where d_p is the pore diameter, μ_p is the geometric mean of the pore diameter and σ_p is the geometric standard deviation of the pore diameter. These parameters are denominated geometric since they correspond to a *log-normal* distribution. When the solute separation, f=50%, $\mu_p = d_p$,, which corresponds to the solute diameter at which 50% separation occurs. The pore diameter geometric standard deviation, σ_p is calculated by equation C.4.

$$\sigma_p = \frac{d_p @ f = 84.13\%}{d_p @ f = 50\%} \qquad \text{(C.4)}$$

The standard normal distribution and base10 logarithm (NORMSINV and LOG10 functions in MS Excel, respectively) were used to compute the solute separation, f(%) for a predetermined pore size based on the PEG and PEO separation data. The calculated f values with the μ_p and σ_p values obtained from equation C.4 were used to determine the pore size of the membrane using equation C.3. It is assumed the solute diameter is equivalent to the pore diameter and their geometric standard deviations are the same.

Pore density, the number of pores per unit area (N) and the surface porosity (S_p), the ratio of pore area to the total membrane area are based on the Hagen-Poiseuille equation (Singh et al., 1998) which has been modified for a porous membrane, as shown in equation C.5.

$$J_i = \frac{N_i \pi d_i^4 \Delta P}{128 \eta \delta} \tag{C.5}$$

where J_i is the solvent flux of the pores with diameter d_i (m^3/m^2 s), N_i is the density of the pores with diameter d_i (dimensionless), ΔP is the pressure difference across the pore (Pa), η is the solvent viscosity (N.s/m^2) and δ is the length of the pore (considered equivalent to the skin layer thickness). Therefore the total flux, J, can be defined as:

$$J = \sum J_i = \frac{\pi \Delta P}{128 \eta \delta} \sum N_i d_i^4 = \frac{\pi \Delta P N}{128 \eta \delta} \sum_{d_{min}}^{d_{max}} f d_i^4 \tag{C.6}$$

where f is the fraction of pores of diameter d_i. Equation C.6 can then be re-arranged to:

$$N = \frac{128 \eta \delta J}{\pi \Delta P \sum_{d_{min}}^{d_{max}} f_i d_i^4} \tag{C.7}$$

Surface porosity (S_p), the void volume of the membrane is calculated using equation C.8.

$$S_p(\%) = \left(\frac{\pi}{4} \sum_{d_{min}}^{d_{max}} N d_i^2 \right) \times 100 = \left(\frac{N \pi}{4} \sum_{d_{min}}^{d_{max}} f_i d_i^2 \right) \times 100 \tag{C.8}$$

Plots of the MWCO sieving curves for each of the membranes studied, each containing a different CSMM, cast at each of the different conditions (18%, 18% (3 min) or 20%) are shown in Figures C.1-C.4.

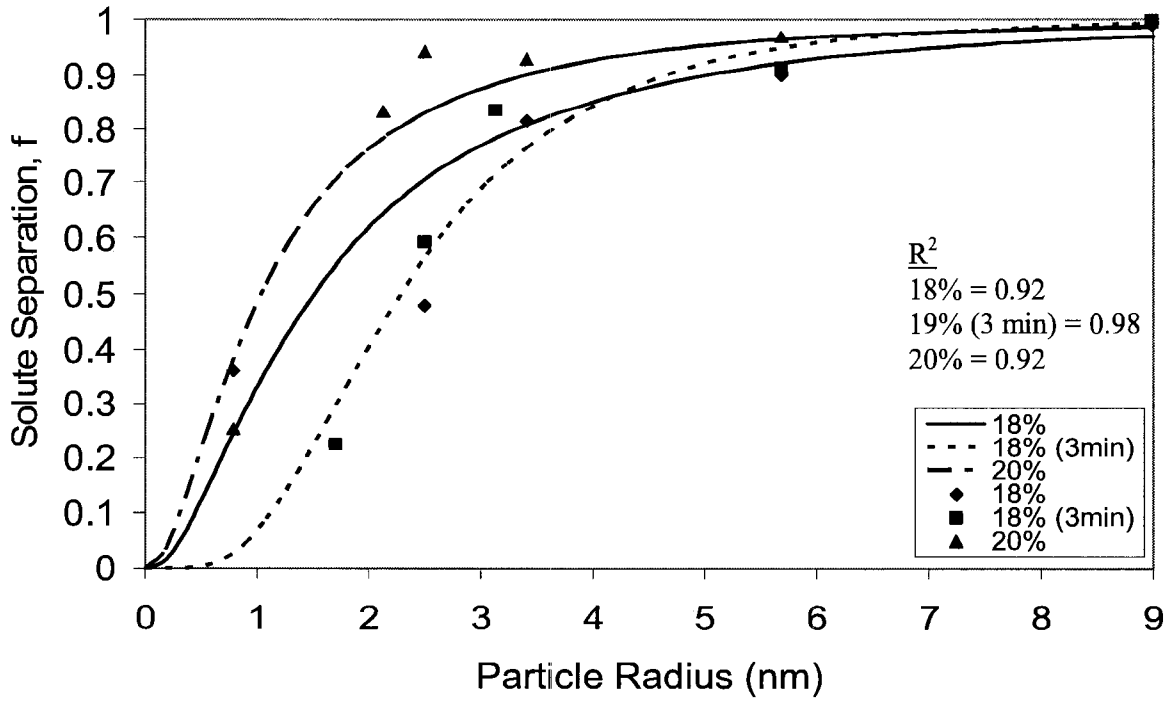

Figure C.1: Solute separation and particle radius for PES-DEG-HBS membranes

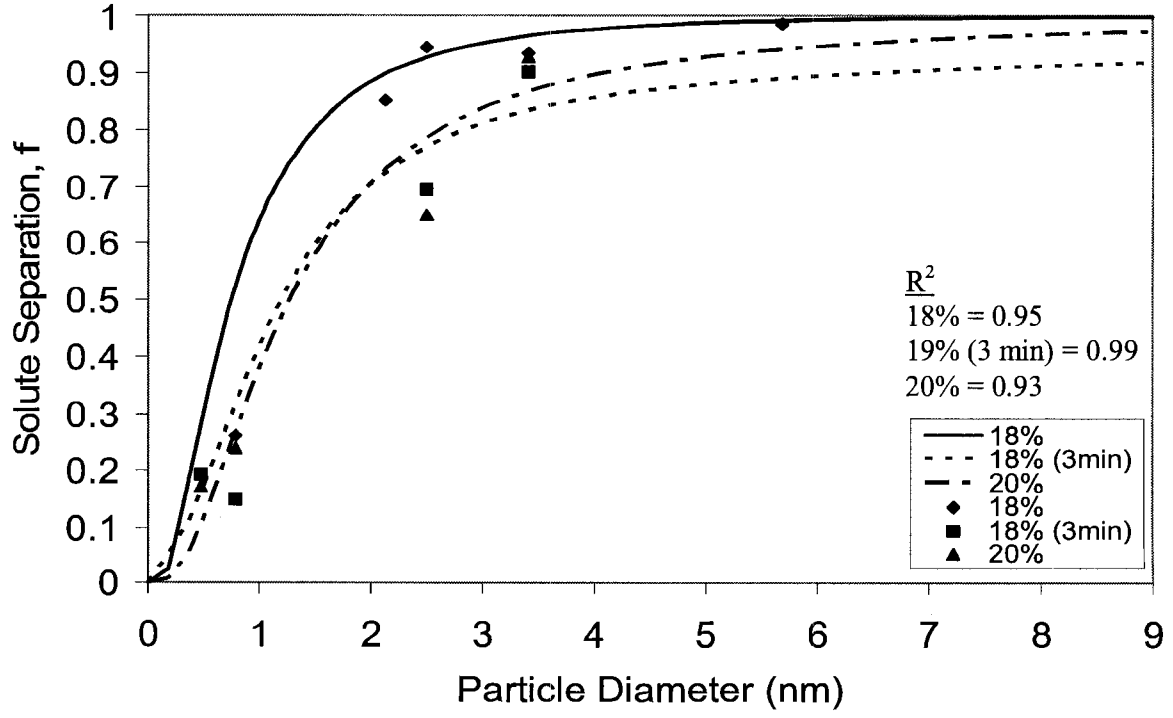

Figure C.2: Solute separation and particle radius for PES-DEG-HBC membranes

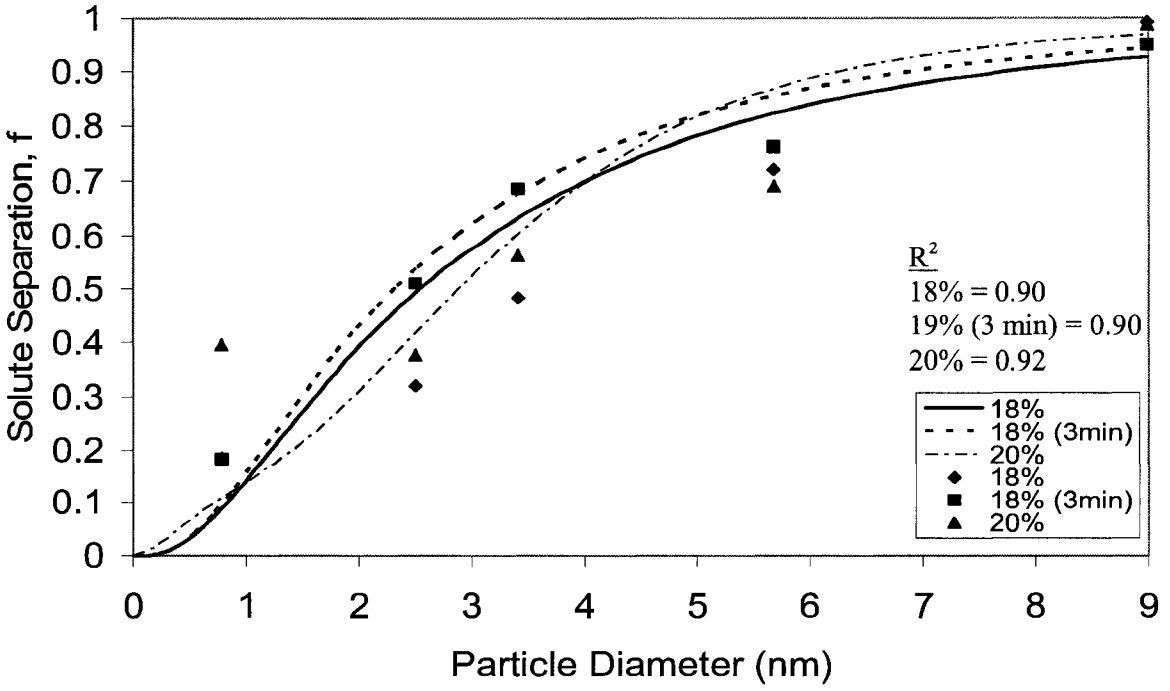

Figure C.3: Solute separation and particle radius for PES-PPG-HBC membranes

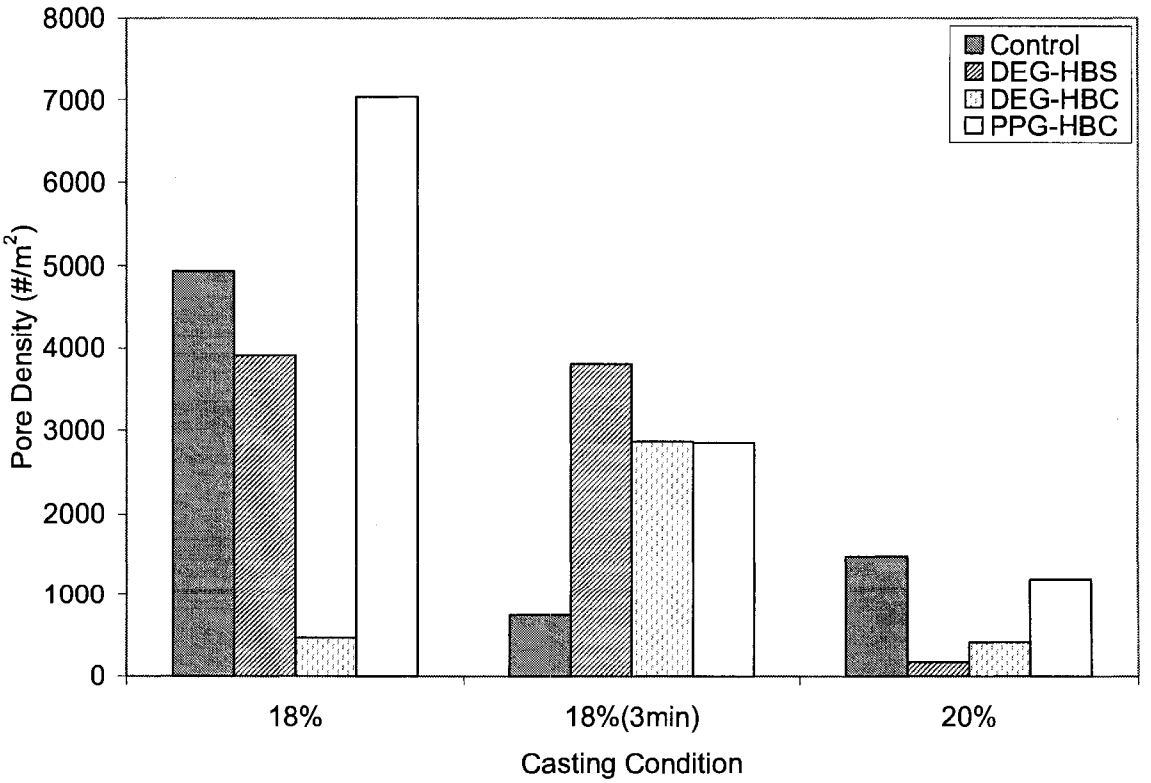

Figure C.4: Pore density of experimental membranes at different casting conditions.

APPENDIX D

Target compound calibration curves established on low temperature TOC Analyzer

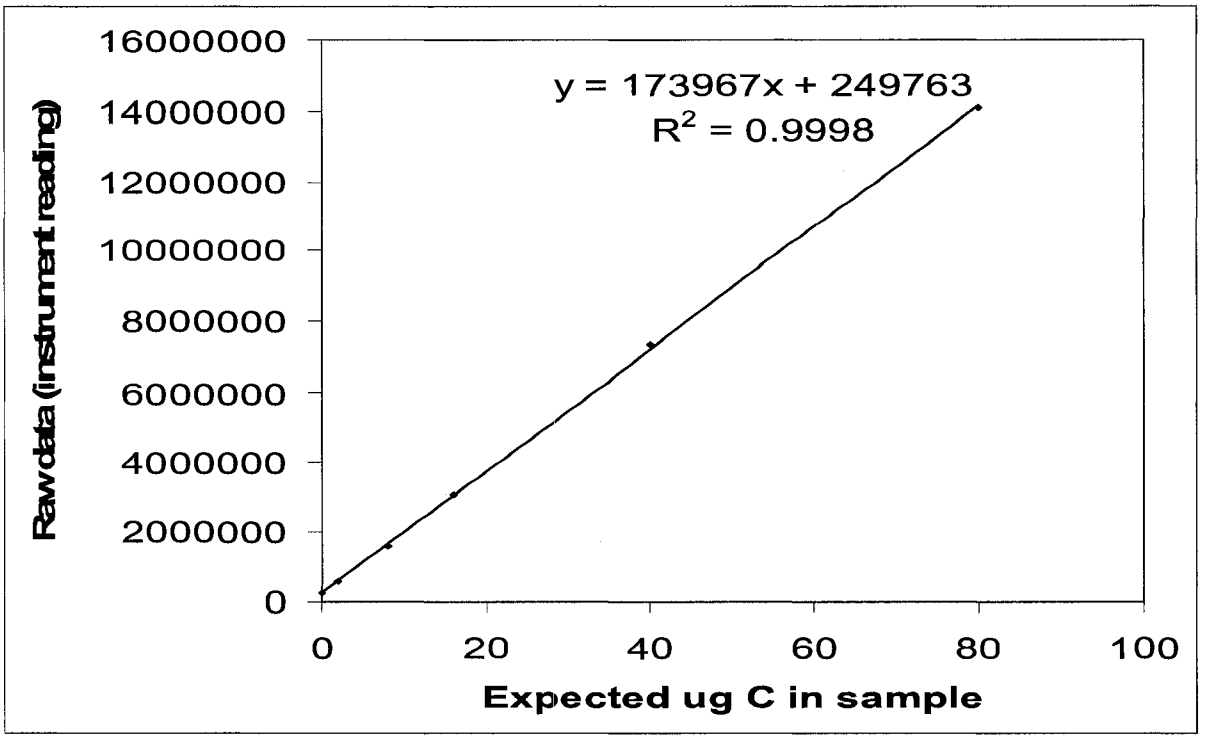

Figure D.1: Calibration curve for SMZ using low temperature TOC Analyzer

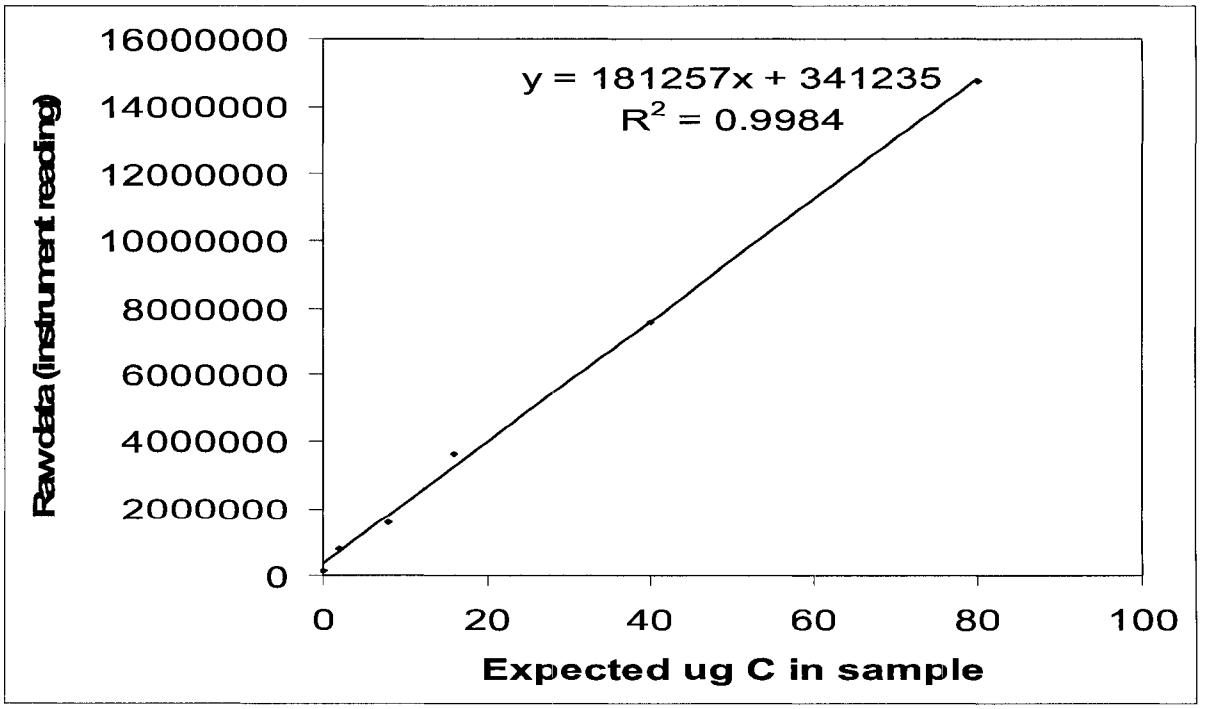

Figure D.2: Calibration curve for Carb using low temperature TOC Analyzer

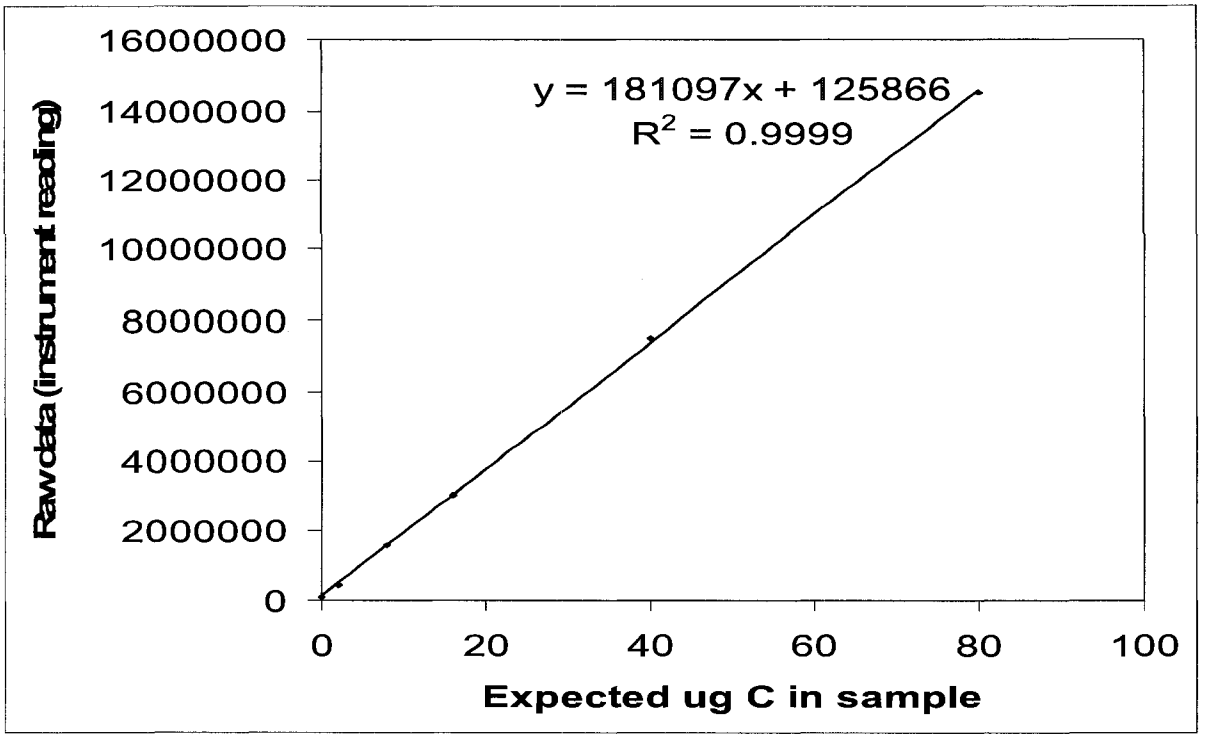

Figure D.3: Calibration curve for BPA using low temperature TOC Analyzer

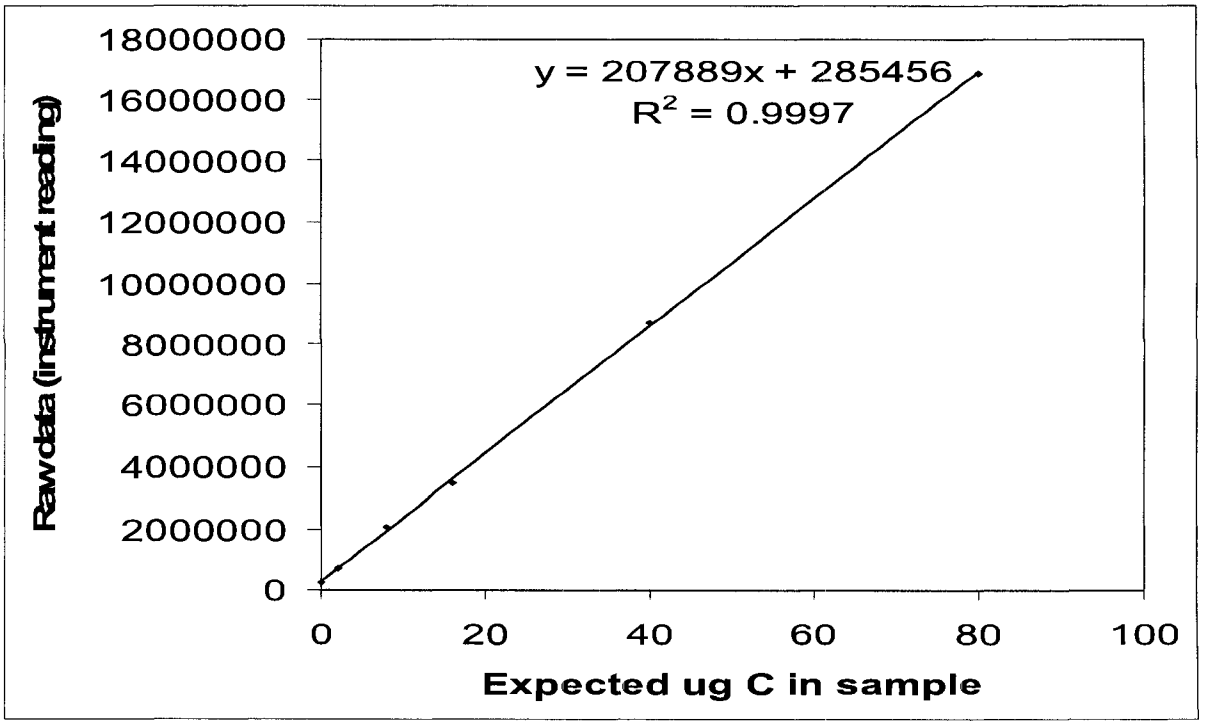

Figure D.4: Calibration curve for IB using low temperature TOC Analyzer

APPENDIX E

Temporal removal of SMZ, Carb, BPA and IB

The removal results of single solute tests conducted for the control and CSMM blended membranes using SMZ, Carb, BPA and IB were conducted over 4 hour period. Results are shown in Figures E.1-E.12. Raw data can be found in Table E.1.

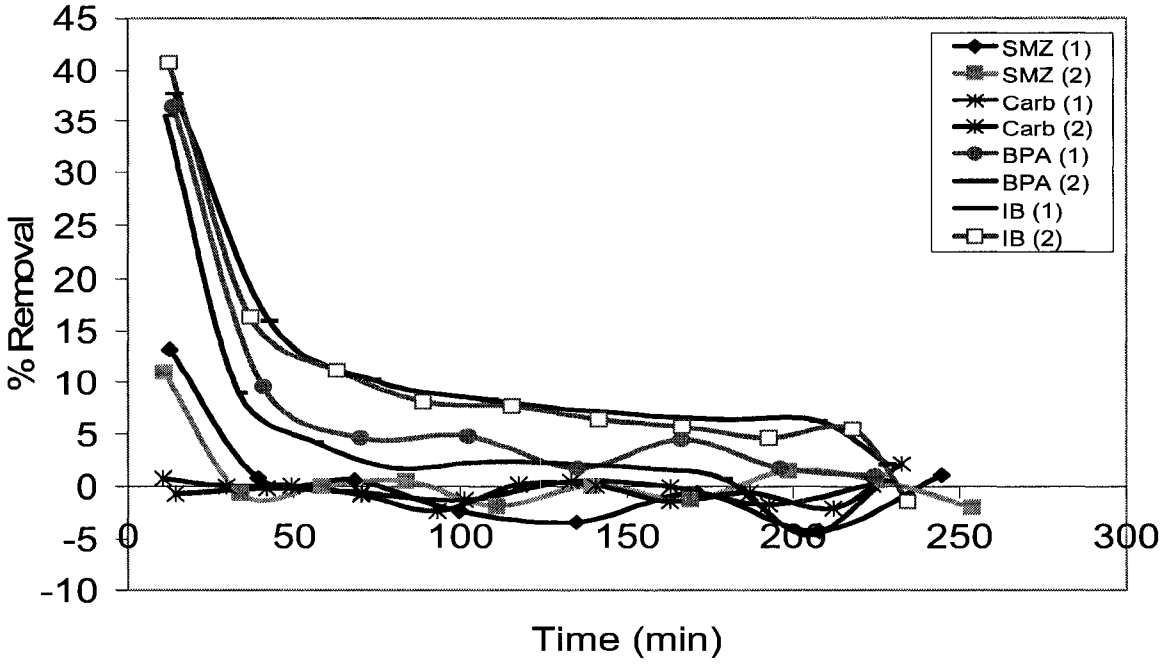

Figure E.1: Removal by 18% membrane of target compounds of control membranes

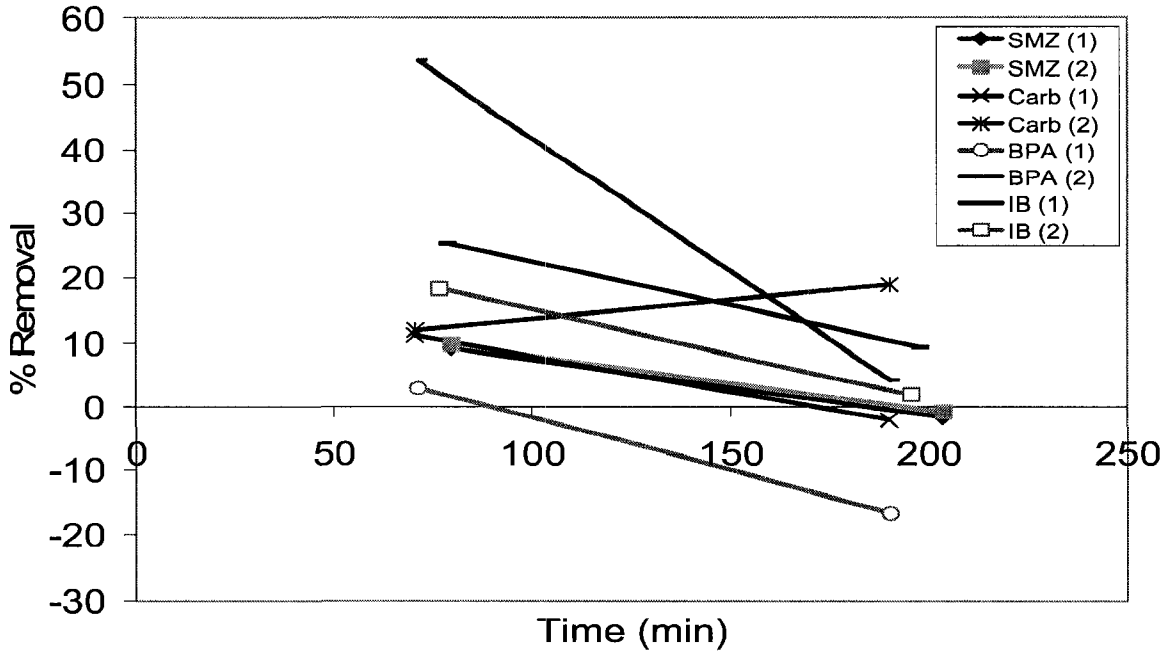

Figure E.2: Removal by 18% (3min) membrane of target compounds of control membranes

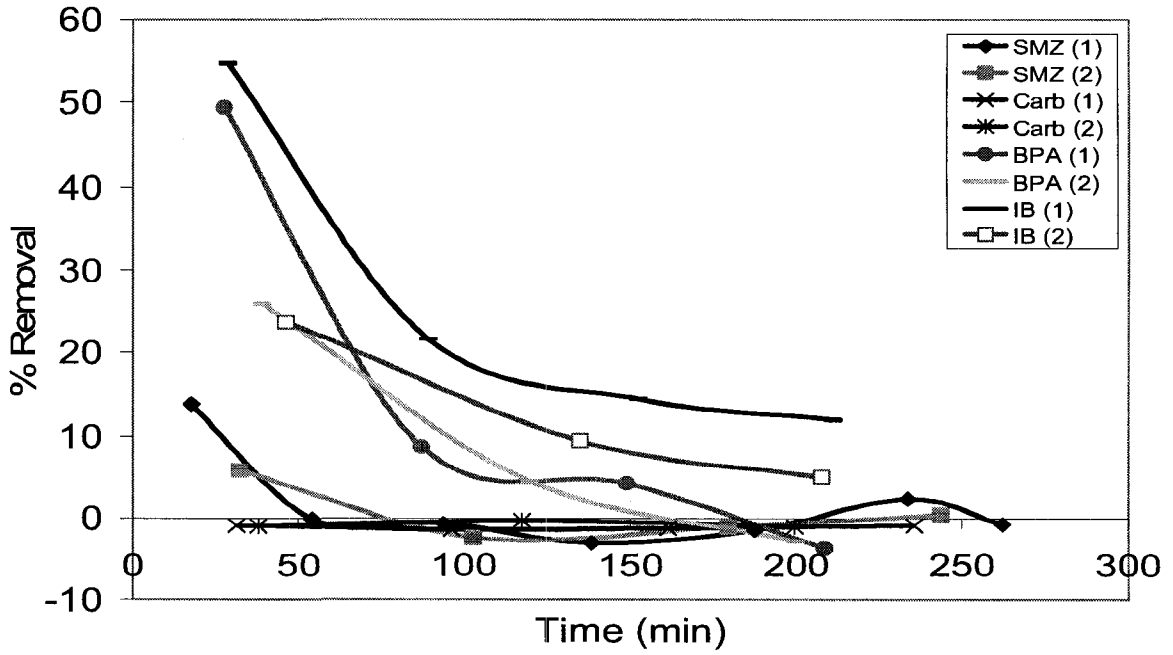

Figure E.3: Removal by 20% membrane of target compounds of control membranes

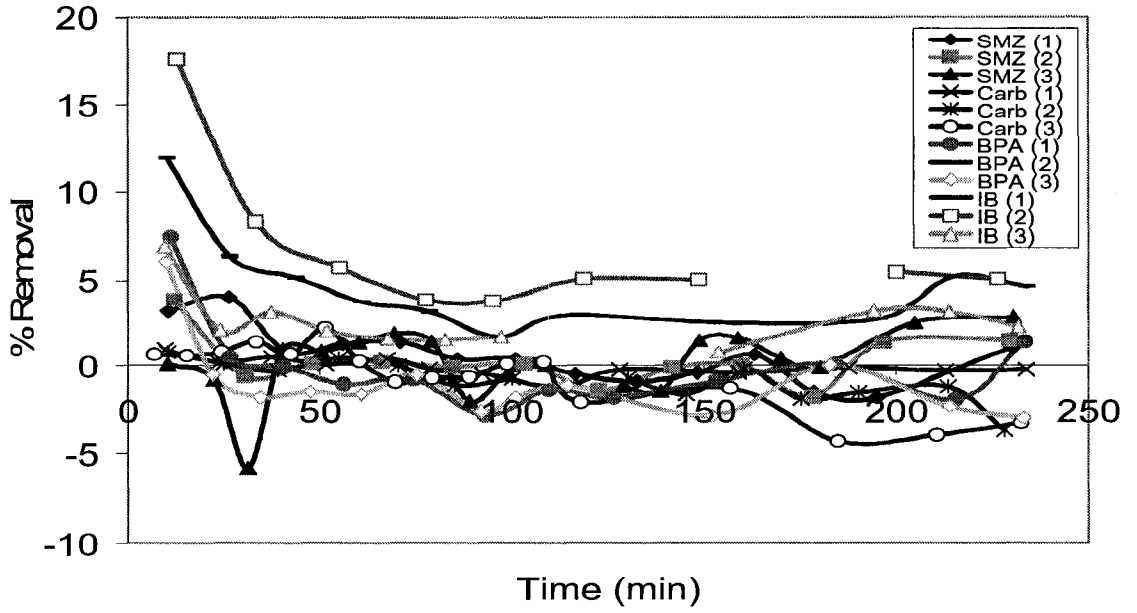

Figure E.4: Removal by 18% of target compounds of PES-DEG-HBS membranes

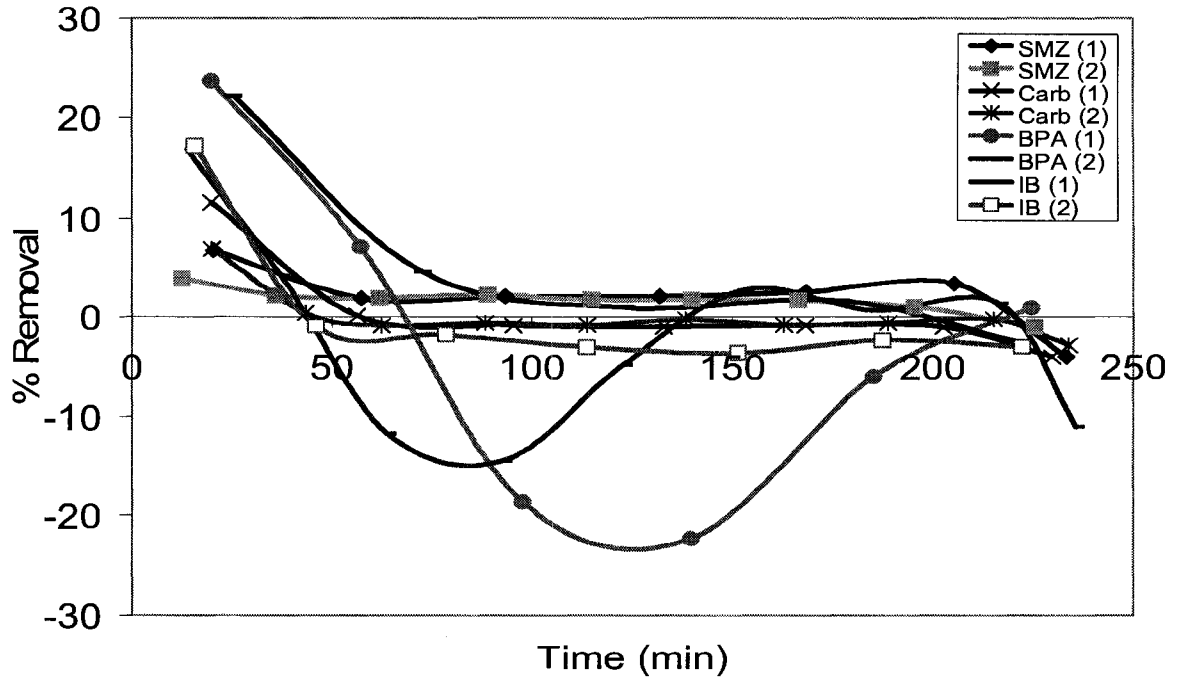

Figure E.5: Removal by 18% (3min) of target compounds of PES-DEG-HBS membranes

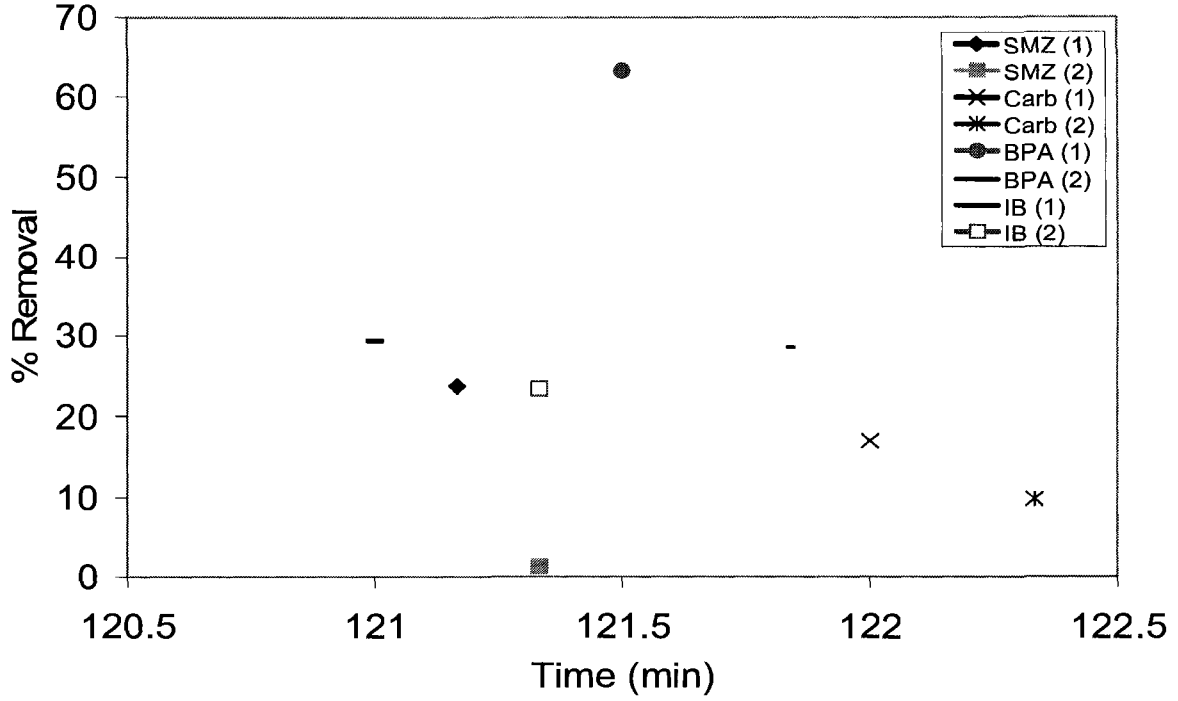

Figure E.6: Triplicate removal by 20% of target compounds of PES-DEG-HBS membranes

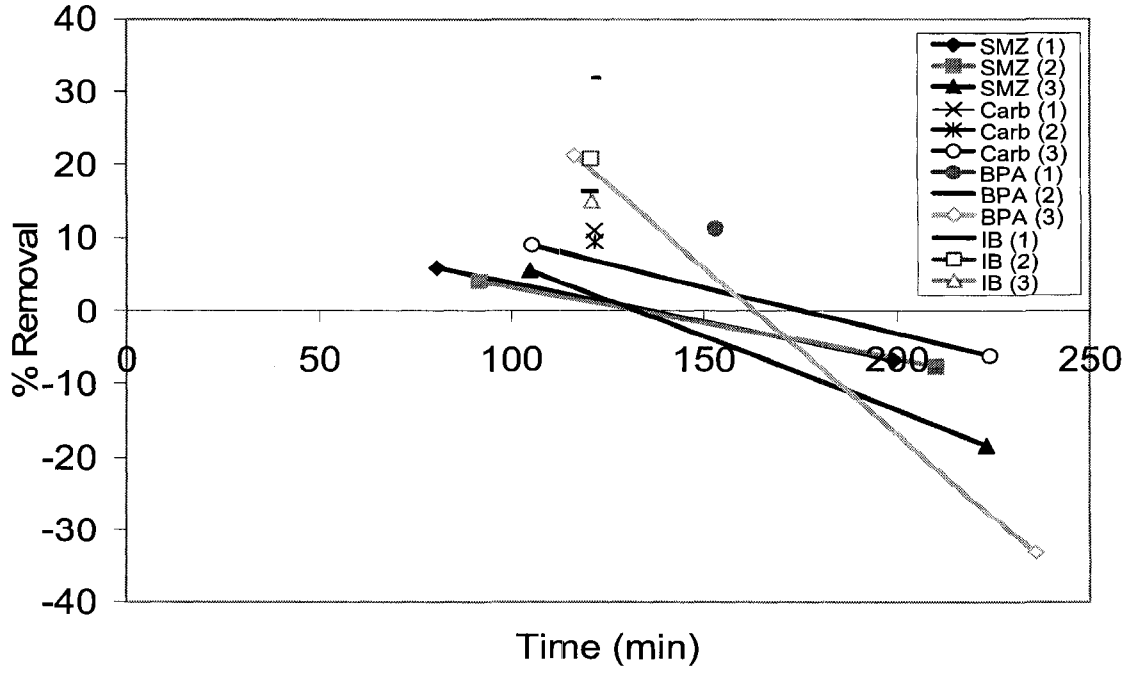

Figure E.7: Removal by 18% of target compound of PES-DEG-HBC membranes

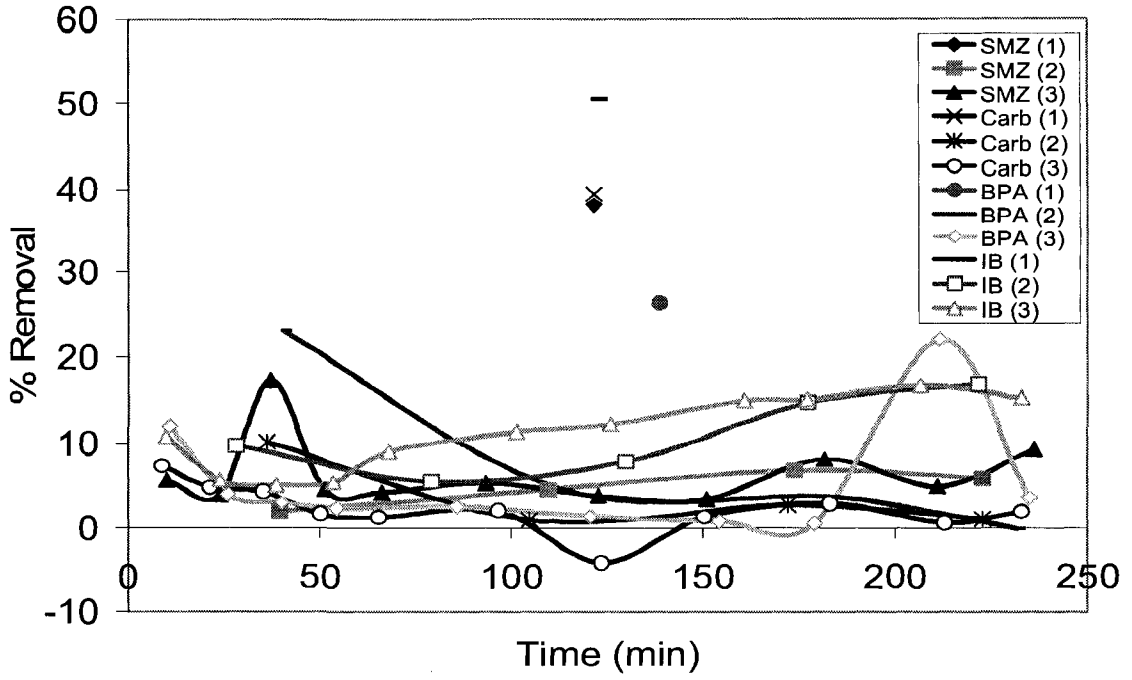

Figure E.8: Removal by 18% (3min) of target compounds of PES-DEG-HBC membranes

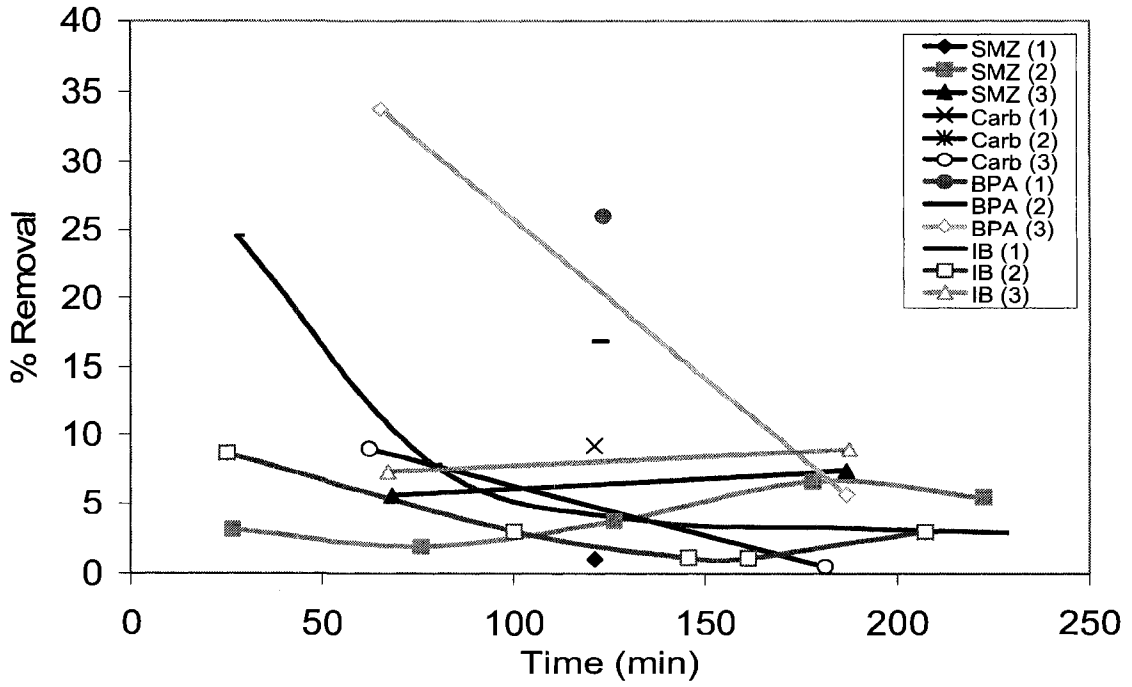

Figure E.9: Removal by 20% of target compounds of PES-DEG-HBC membranes

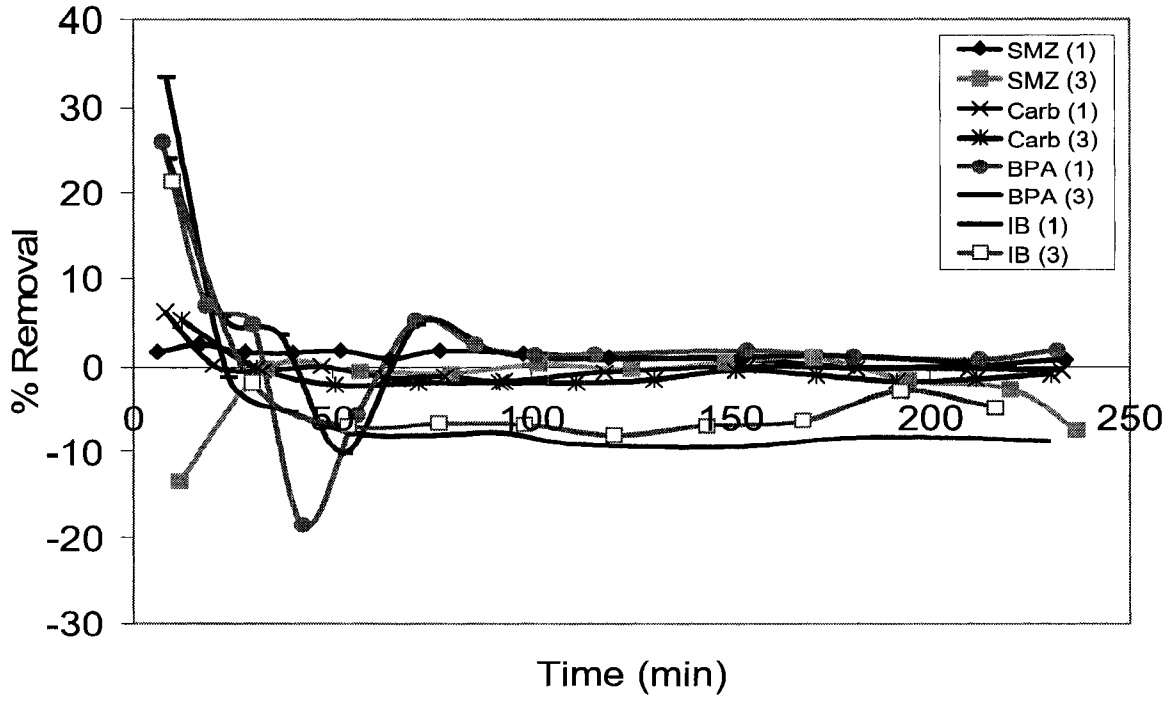

Figure E.10: Removal by 18% of target compounds of PES-PPG-HBC membranes

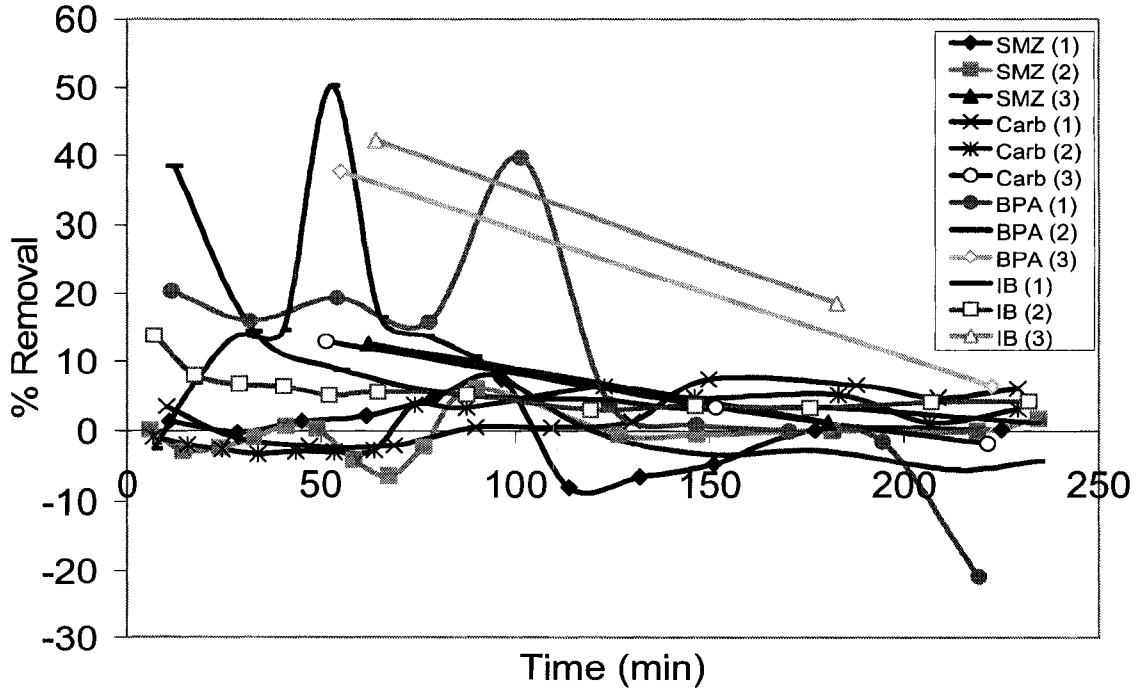

Figure E.11: Removal by 18% (3min) of target compounds of PES-PPG-HBC membranes

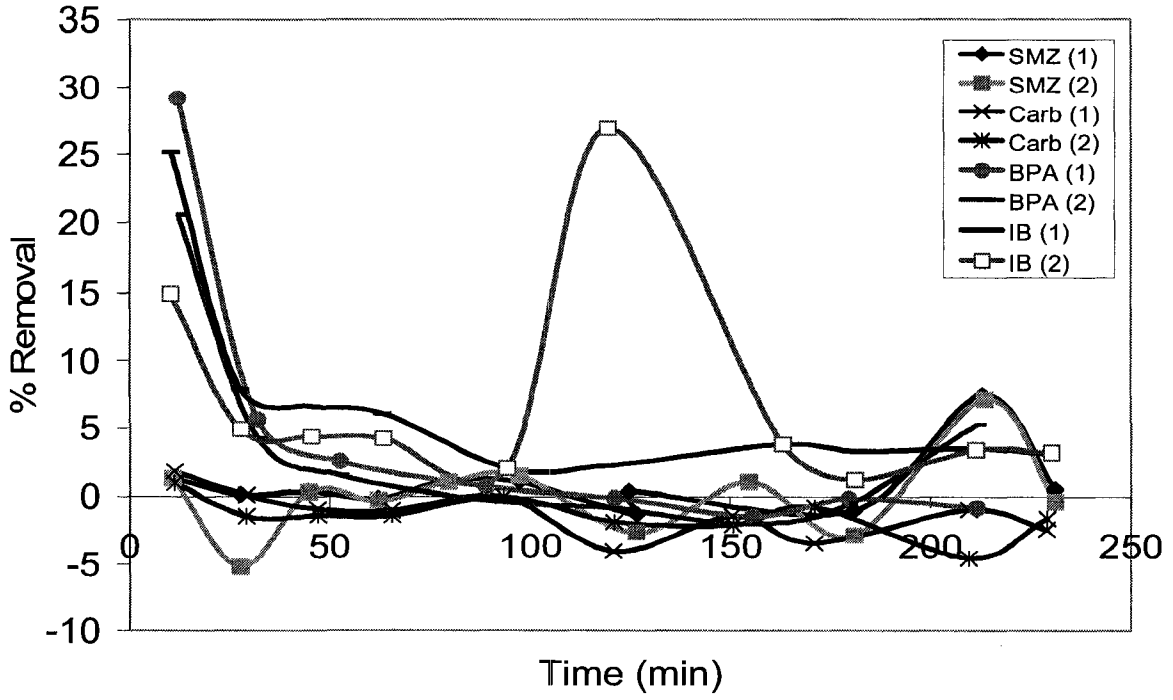

Figure E.12: Removal by 20% membrane of target compounds

Table E.1: TOC Analyzer raw data for pharmaceutical and EDC removal by experimental membranes

18% Control

Cell	ID	SMZ Conc. *ppmC*	Carb Conc. *ppmC*	BPA Conc. *ppmC*	IB Conc. *ppmC*
	Undiluted	20.169	20.2281	20.0927	20.1996
	Diluted	10.2576	10.2746	10.3456	10.0461
	Set-up	10.2024	10.2645	10.3343	10.2211
	Feed 1	9.7695	9.4491	9.4501	9.3056
	Feed 2	9.7741	9.5299	9.4316	9.2609
	Feed 3	9.7223	9.4107	9.4072	9.1841
	Feed 4	9.6862	9.4011	9.3715	9.1446
Feed	Feed 5	9.7424	9.365	9.3373	9.0175
	Feed 6	9.8055	9.3691	9.3428	9.1158
	Feed 7	9.55565	9.3776	9.3231	8.9638
	Feed 8	9.7894	9.4229	9.2987	8.9606
	Feed 9	9.7843	9.538	8.8091	8.9529
	Feed 10	9.9583	9.392	9.2577	8.977
	Feed 11	10.1798	9.4544		
	Feed 12	10.2833	2.6056		
	UF4-1	8.4851	9.1953	5.996	5.7645
	UF4-2	9.6124	9.4693	8.5116	7.6861
	UF4-3	9.752	9.3883	8.9389	8.2129
	UF4-4	9.7781	9.4273	8.8891	8.3639
UF 4	UF4-5	9.8773	9.4963	9.166	8.3302
	UF4-6	9.8476	9.4959	8.8823	8.3873
	UF4-7	10.3785	9.5431	9.1411	8.3926
	UF4-8	10.0757	9.5527	9.1669	5.0184
	UF4-9		9.4394		

Cell	ID	SMZ Conc. *ppmC*	Carb Conc. *ppmC*	BPA Conc. *ppmC*	IB Conc. *ppmC*
	UF5-1	8.6623	3.8477	5.9702	6.0969
	UF5-2	9.5411	9.2701	8.3232	7.6217
	UF5-3	9.6939	9.4063	8.7416	7.9824
	UF5-4	9.8579	9.3343	9.0883	8.1383
UF 5	UF5-5	9.7609	9.37	8.9475	8.2256
	UF5-6	9.7337	9.346	8.9629	8.2933
	UF5-7	4.4497	9.5022	9.0505	5.7644
	UF5-8		9.12925	1.6535	
	UF5-9		4.865		
	UF6-1	8.7014	9.0704	6.0794	5.4848
	UF6-2	9.7466	9.3356	8.5654	7.6853
	UF6-3	9.7398	9.3646	8.9765	8.1273
	UF6-4	9.7565	9.3664	9.1785	8.2835
	UF6-5	9.7297	9.4506	9.131	8.4166
UF 6	UF6-6	9.7821	9.5936	9.1413	8.3881
	UF6-7	9.9062	9.4087	9.1667	8.4514
	UF6-8	9.8119	9.5306	9.2362	8.5462
	UF6-9	9.9056	9.6728	9.2124	8.4618
	UF6-10	10.3745	9.4479	9.2136	4.0423
	UF6-11		9.6484		
	UF6-12		6.417		

18% (3 min) Control

Cell	ID	SMZ Conc. *ppmC*	Carb Conc. *ppmC*	BPA Conc. *ppmC*	IB Conc. *ppmC*
Feed	Undiluted	17.0714	18.1276	20.0975	20.2448
	Diluted	8.8395	9.1219	10.3583	10.0619
	Set-up	7.8492	8.3326	9.2802	9.1211
	Feed 1	7.7899	8.2027	9.3896	9.1373
	Feed 2	7.7833	8.2566	9.1466	8.9716
	Feed 3	7.7713	8.2589	9.1457	8.7169
	Feed 4	7.7812	8.2121	9.0354	8.4961
	Feed 5	7.7567	8.2053	8.9976	8.3322
	Feed 6	7.7955	8.2515	8.9737	8.3097
	Feed 7	7.9266	8.3235	8.9045	8.1115
	Feed 8	7.9162	10.4454	8.9262	7.8253
	Feed 9	7.9263	8.8389	8.9072	7.6537
UF 4	UF4-1	7.0606	7.2936	8.8239	6.3488
	UF4-2	5.3693	5.6252	6.9358	4.7242
UF 5	UF5-1	7.0197	7.2284	4.2467	6.9424
	UF5-2	5.3257	5.6144	5.6854	5.1187
UF 6	UF6-1	2.7593	2.6143	6.2046	2.9577

20% Control

Cell	ID	SMZ Conc. *ppmC*	Carb Conc. *ppmC*	BPA Conc. *ppmC*	IB Conc. *ppmC*
Feed	Undiluted	20.169	20.2281	20.0927	20.1996
	Diluted	10.2576	10.2746	10.3456	10.0461
	Set-up	10.2024	10.2645	10.3343	10.2211
	Feed 1	9.7695	9.4491	9.4501	9.3056
	Feed 2	9.7741	9.5299	9.4316	9.2609
	Feed 3	9.7223	9.4107	9.4072	9.1841
	Feed 4	9.6862	9.4011	9.3715	9.1446
	Feed 5	9.7424	9.365	9.3373	9.0175
	Feed 6	9.8055	9.3691	9.3428	9.1158
	Feed 7	9.55565	9.3776	9.3231	8.9638
	Feed 8	9.7894	9.4229	9.2987	8.9606
	Feed 9	9.7843	9.538	8.8091	8.9529
	Feed 10	9.9583	9.392	9.2577	8.977
	Feed 11	10.1798	9.4544		
	Feed 12	10.2833	2.6056		
UF 1	UF1-1	8.3761	2.7639	4.7626	4.1653
	UF1-2	9.7546	9.4505	8.5209	7.0681
	UF1-3	9.8683	9.5078	8.9284	7.6657
	UF1-4	9.8432	9.5085	9.1335	7.8763
	UF1-5	9.9286	7.6771		
	UF1-6	9.9413			
	UF1-7	3.4564			
UF 2	UF2-1	9.1215	2.0854	6.9711	6.9795
	UF2-2	9.7802	9.4553	8.919	8.114
	UF2-3	9.8865	9.4511	9.0597	5.6641
	UF2-4	6.762	9.5515		
UF 3	UF3-1	6.2087	0.2107	4.6171	2.9672
	UF3-2		9.0046		

18% DEG-HBS

Cell	ID	SMZ Conc. *ppmC*	Carb Conc. *ppmC*	BPA Conc. *ppmC*	IB Conc. *ppmC*
Feed	Undiluted	21.5477	19.8699	19.5443	19.5086
	Diluted	12.3033	9.63	9.5168	9.3973
	Set-up	10.081	8.9071	9.0437	9.1832
	Feed 1	10.1364	8.9179	9.033	9.1247
	Feed 2	9.7075	8.8835	8.9397	9.0148
	Feed 3	9.7747	8.9069	8.9123	8.9241
	Feed 4	9.6601	8.8465	8.7203	8.8882
	Feed 5	9.6555	8.8604	8.796	8.9542
	Feed 6	9.6701	8.8003	8.7627	8.9325
	Feed 7	9.5526	8.8014	8.8778	8.8625
	Feed 8	9.7542	8.8244	8.6811	8.8725
	Feed 9	9.7923	8.8471	8.6225	8.8389
UF4	UF4-1	9.8113	8.8343	8.3625	8.0389
	UF4-2	9.7297	8.8674	8.8935	8.5437
	UF4-3	9.6262	8.84	8.9428	8.5503
	UF4-4	9.6514	8.9014	9.006	8.5901
	UF4-5	9.6401	8.8719	8.9809	8.6056
	UF4-6	9.6221	8.8625	8.9679	8.7393
	UF4-7	9.6228	8.8883	8.9176	8.6881
	UF4-8	9.7018	8.9677	8.9541	8.7094
	UF4-9	9.7427	8.8809	8.8383	8.6193
	UF4-10	9.7087	8.8346	8.869	8.4091
	UF4-11	9.6103	8.8138	8.8495	8.4303
	UF4-12	9.6959	8.8499	8.5027	
	UF4-13	9.9303	8.8686		
	UF4-14	9.688642			
UF5	UF5-1	9.7452	8.8487	8.243	7.5178
	UF5-2	9.7665	8.873	8.9323	8.2693
	UF5-3	9.693	8.9099	9.0377	8.4132
	UF5-4	9.7525	8.8687	9.0939	8.5447
	UF5-5	9.7821	8.9069	9.002	8.5511
UF5 (Cont'd)	UF5-6	9.6502	8.9442	9.0073	8.5008
	UF5-7	9.7871	8.9117	8.9163	8.4817
	UF5-8	9.6831	9.0871	8.9034	0.2447
	UF5-9	9.6689	8.9229	8.9152	8.3859
	UF5-10	9.7205	8.9438	8.9582	8.3916
	UF5-11	9.6206	8.8169	8.9852	
	UF5-12		8.9661		
	UF5-13		8.9366		
	UF5-14	9.6478	8.9311		
	UF5-15		9.1723		
UF6	UF6-1	10.1275	8.8599	8.4846	8.4925
	UF6-2	9.786	8.8654	8.9862	8.827
	UF6-3	10.2722	8.8113	9.0986	8.7328
	UF6-4	9.6164	8.7598	9.0434	8.7442
	UF6-5	9.6927	8.824	9.0578	8.7864
	UF6-6	9.642	8.7103	8.9592	8.7552
	UF6-7	9.5911	8.883	8.9465	8.7401
	UF6-8	9.6353	8.9888	8.9549	0.1948
	UF6-9	9.8557	8.9073	8.8935	8.8647
	UF6-10	9.6976	8.9013	9.0118	8.5813
	UF6-11	9.6546	8.8376	8.8761	8.5935
	UF6-12		8.841	8.8831	8.6395
	UF6-13	9.770286	9.0433	8.8793	
	UF6-14	9.808883	8.9125		
	UF6-15	9.528267	9.1807		
	UF6-16	9.513078	9.1724		
	UF6-17	9.512063	9.1348		
	UF6-18	9.564329			
	UF6-19	9.509835			
	UF6-20	9.513163			

18% (3min) DEG-HBS

Cell	ID	SMZ Conc. *ppmC*	Carb Conc. *ppmC*	BPA Conc. *ppmC*	IB Conc. *ppmC*
	Undiluted	19.1507	19.504	19.0139	19.7792
	Diluted	9.6073	9.7899	9.8774	10.6616
	Set-up	8.9931	8.8772	8.9351	10.1181
	Feed 1	8.8362	8.804	8.9794	9.3731
	Feed 2	8.793	8.6766	8.7709	9.0803
	Feed 3	8.7849	8.6329	8.7871	8.9865
Feed	Feed 4	8.8283	8.6457	8.6229	9.0414
	Feed 5	8.8215	8.6365	8.627	8.9488
	Feed 6	8.8213	8.7156	8.6365	8.8805
	Feed 7	8.864	8.6532	8.6027	8.8687
	Feed 7B				8.7516
	Feed 8	8.6961	8.6644	8.5696	8.7359
	Feed 9	8.7197	8.6975	8.5617	8.5317
	UF4-1	8.7203	8.4677	7.9305	7.8712
	UF4-2	8.6041	8.6732	8.5481	9.3337
	UF4-3	8.6789	8.732	2.9891	9.5648
	UF4-4	8.7077	8.715	2.9669	9.6497
	UF4-5	8.6663	8.7227	9.1316	9.6086
	UF4-6	8.625	8.775	8.581	9.47975
	UF4-7	8.6728	8.7907	8.5167	9.5002
UF4	UF4-8	8.8066	8.7408	8.6308	9.3917
	UF4-9	8.7158	8.7012	8.61	9.305
	UF4-10	8.7389	8.762	8.5416	9.1804
	UF4-11	8.657	8.7185	8.431	9.1176
	UF4-12	8.6885	8.7572	8.3309	
	UF4-13	8.6751	7.0687	8.4267	
	UF4-14			8.4596	
	UF4-15			8.4467	

Cell	ID	SMZ Conc. *ppmC*	Carb Conc. *ppmC*	BPA Conc. *ppmC*	IB Conc. *ppmC*
	UF5-1	8.1957	7.6668	6.6941	7.0673
	UF5-2	8.6182	8.6221	8.1596	8.5762
	UF5-3	8.6411	8.7199	2.1747	8.8628
UF5	UF5-4	8.6359	8.7219	2.4028	8.7208
	UF5-5	8.639	8.7273	9.1206	8.7553
	UF5-6	8.4026	8.7552	8.4806	
	UF5-7	3.6298	6.0349		
	UF6-1	8.4905	8.0764	7.469	7.7671
	UF6-2	8.6005	8.5982	8.4046	9.0683
	UF6-3	8.6152	8.7096	3.0172	9.2037
	UF6-4	8.6265	8.6972	2.8223	9.2234
	UF6-5	8.666	8.7094	9.042	9.2061
UF6	UF6-6	8.6634	8.7386	8.3993	8.959
	UF6-7	8.7136	8.7869	8.544	8.7907
	UF6-8	8.6041	8.7083	8.4517	
	UF6-9	8.8073	8.6866	2.9253	
	UF6-10		5.1095		

20% DEG-HBS

Cell	ID	SMZ Conc. *ppmC*	Carb Conc. *ppmC*	BPA Conc. *ppmC*	IB Conc. *ppmC*
Feed	Undiluted	19.3686	20.1712	20.8076	
	Diluted	9.6938	9.8799	9.4907	10.2603
	Set-up	9.7773	9.7481	8.846	9.5049
	Feed 1	10.2998	9.4756	8.6957	9.4094
	Feed 2	9.7092	9.4299	8.6577	9.3123
	Feed 3	9.2685	9.308	8.5926	9.2825
	Feed 4	9.3639	9.312	8.5375	9.2274
	Feed 5	9.3011	9.2875	8.522	9.1793
	Feed 6	9.2513	9.2725	8.5725	9.1886
	Feed 7	9.4009	9.2187	8.5846	9.0833
	Feed 8	9.4092	9.2159	8.4636	9.1449
	Feed 9	9.3888	9.2359	8.4345	9.0003
UF4	UF4-1	2.9959	1.9278	0.7406	1.6211
UF5	UF5-1	9.2266	9.3258	7.1136	7.2163
	UF5-2	9.3461	9.4503	8.5178	8.2265
	UF5-3	9.3432	9.4393	8.5789	8.4509
	UF5-4	9.36	9.4529	8.6034	8.5265
	UF5-5	9.4607	9.4428	8.6152	8.5122
	UF5-6	9.4752	9.5057	8.6228	8.4829
	UF5-7	9.4308	9.4726	5.8707	
	UF5-8	9.4273	4.8288		
UF6	UF6-1	4.9484	5.5833	4.0636	4.6828

18% DEG-HBC

Cell	ID	SMZ Conc. *ppmC*	Carb Conc. *ppmC*	BPA Conc. *ppmC*	IB Conc. *ppmC*
Feed	Undiluted	19.3686	20.1712	20.8076	
	Diluted	9.6938	9.8799	9.4907	10.2603
	Set-up	9.7773	9.7481	8.846	9.5049
	Feed 1	10.2998	9.4756	8.6957	9.4094
	Feed 2	9.7092	9.4299	8.6577	9.3123
	Feed 3	9.2685	9.308	8.5926	9.2825
	Feed 4	9.3639	9.312	8.5375	9.2274
	Feed 5	9.3011	9.2875	8.522	9.1793
	Feed 6	9.2513	9.2725	8.5725	9.1886
	Feed 7	9.4009	9.2187	8.5846	9.0833
	Feed 8	9.4092	9.2159	8.4636	9.1449
	Feed 9	9.3888	9.2359	8.4345	9.0003
UF1	UF1-1	8.7974	8.2662	5.0704	7.6928
	UF1-2	5.0232			
UF2	UF2-1	8.973	8.4059	5.8065	7.2736
	UF2-2	3.3753			
UF3	UF3-1	8.8361	8.447	6.7177	7.8171
	UF3-2	1.7782	1.7821	0.4317	

18% (3min) DEG-HBC

Cell	ID	SMZ Conc. *ppmC*	Carb Conc. *ppmC*	BPA Conc. *ppmC*	IB Conc. *ppmC*
Feed	Undiluted	19.9934	20.1659	19.7087	20.476
	Diluted	10.0774	10.4209	10.5071	9.7061
	Set-up	9.6726	9.6362	9.8043	9.659
	Feed 1	9.6811	9.5908	9.7702	9.7753
	Feed 2	9.3166	9.5418	9.6052	9.5097
	Feed 4	9.3044	9.278	9.5202	9.4679
	Feed 5	9.3043	9.3132	9.5434	9.6091
	Feed 6	9.3312	9.3169	9.4085	9.5589
	Feed 7	9.254	9.2638	9.3359	9.9258
	Feed 8	9.5367	9.4307	9.3864	9.7929
	Feed 9	9.2228	9.3604	9.3461	9.8803
	Feed 10	9.222	9.293	9.3706	9.742
UF4	UF4-1	0.4533	0.3886	0.4606	0.2181
UF5	UF5-1	9.1424	8.5702	7.4019	8.5819
	UF5-2	8.8956	9.225	8.9848	9.0147
	UF5-3	8.8904	9.1736	9.0442	8.806
	UF5-4	5.7908	5.2712	4.6838	8.3382
	UF5-5				8.213
UF6	UF6-1	9.1418	8.8925	8.5971	8.7242
	UF6-2	8.9539	9.0888	9.2279	8.9785
	UF6-3	7.6972	9.137	9.3235	9.0314
	UF6-4	8.884	9.1315	9.3018	8.9621
	UF6-5	8.9155	9.1619	9.3061	8.6124
	UF6-6	8.8113	9.1215	9.28	8.5145
	UF6-7	8.9768	9.7086	9.2645	8.385
	UF6-8	8.9405	9.141	9.339	8.4313
	UF6-9	8.7614	9.1597	7.2893	8.3055
	UF6-10	8.7779	9.3043	9.0427	8.222
	UF6-11	4.7766	9.1134		8.2465

20% DEG-HBC

Cell	ID	SMZ **Conc.** *ppmC*	Carb **Conc.** *ppmC*	BPA **Conc.** *ppmC*	IB **Conc.** *ppmC*
Feed	Undiluted	19.9934	20.1659	19.7087	20.476
	Diluted	10.0774	10.4209	10.5071	9.7061
	Set-up	9.6726	9.6362	9.8043	9.659
	Feed 1	9.6811	9.5908	9.7702	9.7753
	Feed 2	9.3166	9.5418	9.6052	9.5097
	Feed 4	9.3044	9.278	9.5202	9.4679
	Feed 5	9.3043	9.3132	9.5434	9.6091
	Feed 6	9.3312	9.3169	9.4085	9.5589
	Feed 7	9.254	9.2638	9.3359	9.9258
	Feed 8	9.5367	9.4307	9.3864	9.7929
	Feed 9	9.2228	9.3604	9.3461	9.8803
	Feed 10	9.222	9.293	9.3706	9.742
UF1	UF1-1	3.6948	2.6062	2.3214	7.9476
UF2	UF2-1	9.0256	8.7187	7.2433	8.4809
	UF2-2	9.1274	9.0344	8.7919	8.8018
	UF2-3	8.9832	9.1606	9.0163	8.6316
	UF2-4	8.9105	9.1629	9.0839	8.3884
	UF2-5	6.2261	9.0835	9.0877	8.3375
UF3	UF3-1	8.7846	8.4481	6.3027	8.778
	UF3-2	7.0701	9.3832	8.862	8.9248

18% PPG-HBC

Cell	ID	SMZ Conc. *ppmC*	Carb Conc. *ppmC*	BPA Conc. *ppmC*	IB Conc. *ppmC*
Feed	Undiluted	19.1507	19.504	19.0139	19.7792
	Diluted	9.6073	9.7899	9.8774	10.6616
	Set-up	8.9931	8.8772	8.9351	10.1181
	Feed 1	8.8362	8.804	8.9794	9.3731
	Feed 2	8.793	8.6766	8.7709	9.0803
	Feed 3	8.7849	8.6329	8.7871	8.9865
	Feed 4	8.8283	8.6457	8.6229	9.0414
	Feed 5	8.8215	8.6365	8.627	8.9488
	Feed 6	8.8213	8.7156	8.6365	8.8805
	Feed 7	8.864	8.6532	8.6027	8.8687
	Feed 7B				8.7516
	Feed 8	8.6961	8.6644	8.5696	8.7359
	Feed 9	8.7197	8.6975	8.5617	8.5317
UF1	UF1-1	8.6799	8.2597	6.6404	6.2419
	UF1-2	8.6064	8.6537	8.1627	9.1905
	UF1-3	8.6407	8.7107	8.3489	9.5549
	UF1-4	8.6476	8.6476	2.9743	9.6967
	UF1-5	8.6159	8.7383	2.6524	9.7424
	UF1-6	8.7042	8.7434	8.322	9.7457
	UF1-7	8.6581	8.7878	8.4049	9.769
	UF1-8	8.686	8.6878	8.4986	9.7199
	UF1-9	8.7181	8.7034	8.4949	9.6104
	UF1-10	8.7354	8.6668	8.4681	9.4658
	UF1-11	8.8564	8.6838	8.4987	9.2818
	UF1-12	8.6772	8.7316	8.4912	
	UF1-13	8.6365		8.3935	
UF2	UF2-1	8.7812	7.9205	6.2953	7.9842
	UF2-2	8.7137	8.716	8.04	6.3521

Cell	ID	SMZ Conc. *ppmC*	Carb Conc. *ppmC*	BPA Conc. *ppmC*	IB Conc. *ppmC*
UF3	UF3-1	10.025	8.3363	6.817	7.3727
	UF3-2	8.6576	8.6867	8.2626	9.2439
	UF3-3	8.6616	8.8103	8.4474	9.6084
	UF3-4	8.7228	8.7976	2.7658	9.6125
	UF3-5	8.6524	8.7964	8.3599	9.6524
	UF3-6	8.7379	8.7893	8.4707	9.6697
	UF3-7	8.6912	8.8005	8.5428	9.4956
	UF3-8	8.7524	8.7494	8.5286	9.4316
	UF3-9	8.8093	8.7355	8.489	8.9937
	UF3-10	8.8987	8.7959	8.4954	9.1515
	UF3-11	3.0954	8.7827	8.5506	5.8685
	UF3-12		8.7676	4.6038	

18% (3min) PPG-HBC

Cell	ID	SMZ Conc. *ppmC*	Carb Conc. *ppmC*	BPA Conc. *ppmC*	IB Conc. *ppmC*
	Undiluted	21.9491	21.6169	21.0257	19.249
	Diluted	9.9101	10.8838	11.1689	9.5409
	Set-up	8.8327	10.1218	10.0314	8.7626
	Feed1	8.573	10.0608	9.9113	8.672
	Feed2	8.6372	10.0032	3.3548	8.694
	Feed3	8.807	10.0355	3.4579	8.611
	Feed4	9.2935	10.1628	3.2093	8.5231
Feed	Feed5	8.6904	10.2682	9.5114	8.5028
	Feed6	8.7022	10.3298	9.2113	8.417
	Feed7	8.6955	10.1588	9.1885	8.4371
	Feed8	8.7026	9.9975	9.1619	8.3874
	Feed9	8.8384	10.0718	9.1705	8.4305
	UF1-1	8.4547	9.7066	1.9722	5.3316
	UF1-2	8.6521	10.081	9.1502	7.4379
	UF1-3	8.6001	10.2334	9.0651	7.8546
	UF1-4	8.6153	10.3041	9.1237	8.0914
	UF1-5	8.6139	10.1092	2.1869	8.1139
UF 1	UF1-6	8.6018	10.1652	9.1462	8.1239
	UF1-7	2.5039	10.1235	9.1273	8.1468
	UF1-8	2.6408	9.562978	9.2007	8.1518
	UF1-9	3.6434	9.486888	9.3162	8.2133
	UF1-10	8.6866	9.520405	11.0718	5.5588
	UF1-11	8.7507	9.454967		

Cell	ID	SMZ Conc. *ppmC*	Carb Conc. *ppmC*	BPA Conc. *ppmC*	IB Conc. *ppmC*
	UF2-1	8.5603	10.1447	2.5396	7.4699
	UF2-2	8.8442	10.2295	9.6814	7.9802
	UF2-3	8.8418	10.2665	9.3791	8.1102
	UF2-4	8.7121	10.3266	9.4534	8.0978
	UF2-5	8.6626	10.3115	2.0298	8.1687
	UF2-6	8.6906	10.3309	9.3827	8.1267
	UF2-7	3.3342	10.3059	9.3528	8.0726
UF 2	UF2-8	2.6743	9.719861	9.3299	8.2443
	UF2-9	3.6973	9.822343	9.4907	8.1132
	UF2-10	8.7283	9.614877	9.5119	8.1586
	UF2-11	8.7328	9.836912	9.4448	8.0408
	UF2-12	8.7478	9.629216	9.659	8.0703
	UF2-13	8.6896	9.876065	9.5615	
	UF2-14	8.703	9.756005		
	UF2-15	8.6866			
	UF3-1	7.6977	8.7333	1.6511	4.974
UF 3	UF3-2	8.5861	9.9766	8.5769	6.8698
	UF3-3		3.7167		

20% PPG-HBC

Cell	ID	SMZ Conc. *ppmC*	Carb Conc. *ppmC*	BPA Conc. *ppmC*	IB Conc. *ppmC*
	Undiluted	20.1612	20.2603	20.369	19.7334
	Diluted	9.9062	10.1478	11.306	10.281
	Set-up	9.4621	9.4873	10.4683	9.4048
	Feed 1	9.439	9.4771	10.2992	9.3796
	Feed 3	9.4365	9.4953	10.2746	9.2013
	Feed 4	9.4114	9.4213	10.2584	9.2364
	Feed 5	9.5066		10.1188	8.8834
Feed	Feed 6	9.3543	9.3768	10.057	8.8566
	Feed 7	9.4346	9.4105	10.056	8.939
	Feed 8	9.258	9.4613	10.043	8.8915
	Feed 9	10.0841	9.4057	9.9934	8.8802
	Feed10	9.3356	9.3827	6.5109	8.9911
	UF1-1	9.5032	9.4598	8.662	7.9338
	UF1-2	9.4256	9.5838	10.0279	8.5984
	UF1-3	9.4113	9.5901	10.1903	8.5629
	UF1-4	9.5231	9.585	10.228	8.5651
	UF1-5	9.4769	9.7374	10.2473	8.4866
	UF1-6	9.474	9.7746	10.3014	8.4916
UF1	UF1-7	9.4274	9.5434	10.1578	8.4268
	UF1-8	9.3785	9.652	10.2952	8.4136
	UF1-9	9.5324	9.5944	10.4906	8.4375
	UF1-10	9.7452	9.7911	10.3361	8.5182
	UF1-11	9.4574	9.7162		8.4604
	UF1-12	9.4189			
	UF1-13	9.4065			

Cell	ID	SMZ Conc. *ppmC*	Carb Conc. *ppmC*	BPA Conc. *ppmC*	IB Conc. *ppmC*
	UF2-1	9.3165	9.3067	7.2929	7.0215
	UF2-2	9.4221	9.487	9.6946	8.4751
	UF2-3	9.4032	9.5075	9.9985	8.5904
	UF2-4	9.425	9.5166	10.048	8.6762
	UF2-5	9.4013	9.5127	10.0664	8.7034
UF2	UF2-6	9.408	9.7538	10.1979	8.66
	UF2-7	9.473	9.5409	10.0593	8.602
	UF2-8	9.318	9.782	10.0753	8.6008
	UF2-9	9.3498	9.4936	10.4119	8.5732
	UF2-10	9.3322	9.606		8.7146
	UF2-11	9.2852			
	UF3-1	9.3187	9.3848	8.1831	7.9865
	UF3-2	9.9246	9.6303	9.8378	8.7513
	UF3-3	9.4071	9.5502	10.105	8.7997
	UF3-4	9.439	9.5489	10.1443	8.847
	UF3-5	9.4094	9.523	10.1426	8.7034
UF3	UF3-6	9.3667	9.5482	10.2556	6.4768
	UF3-7	9.5974	9.6027	10.0965	8.6022
	UF3-8	9.3365	9.5325	9.467	8.7857
	UF3-9	9.5191	9.8311	10.3319	8.5831
	UF3-10	9.3677	9.5313		8.7087
	UF3-11	9.3689			

APPENDIX F

Surface charge versus compound removal

Removal of the target compounds was plotted against the membrane surface charge, for all tested membranes, shown in Figures F.1-F.4. Generally, there were no consistent trends between the charge of any one membrane and target compound removal. For BPA and IB, the compounds with the highest log K_{OW} values, the control membrane showed the strongest relationship. PES-DEG-HBC membranes however, showed only a relationship between charge and removal for SMZ and BPA. From the lack of correlation between these two parameters, it is possible to conclude they do not correlate.

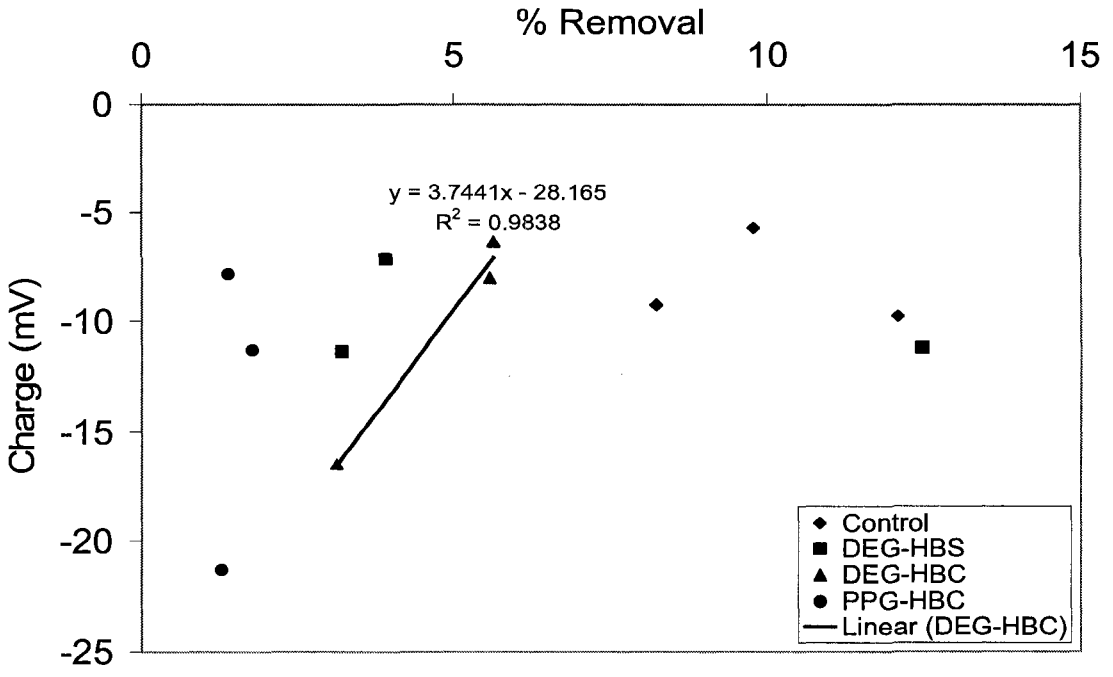

Figure F.1: Removal of SMZ compared to membrane surface charge

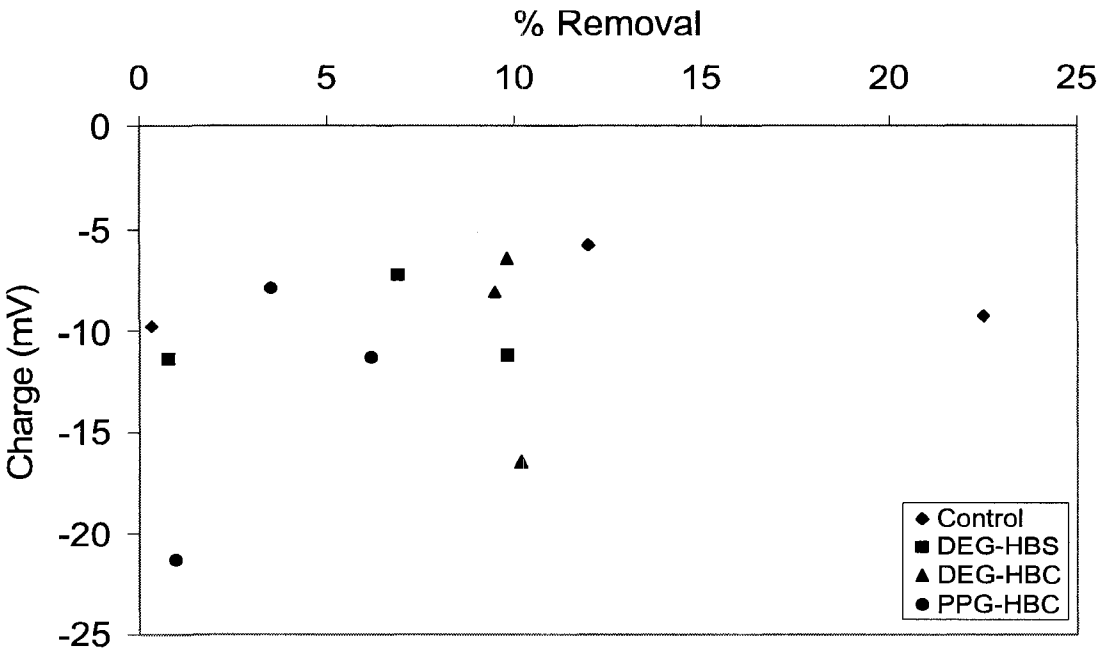

Figure F.2: Removal of Carb compared to membrane surface charge

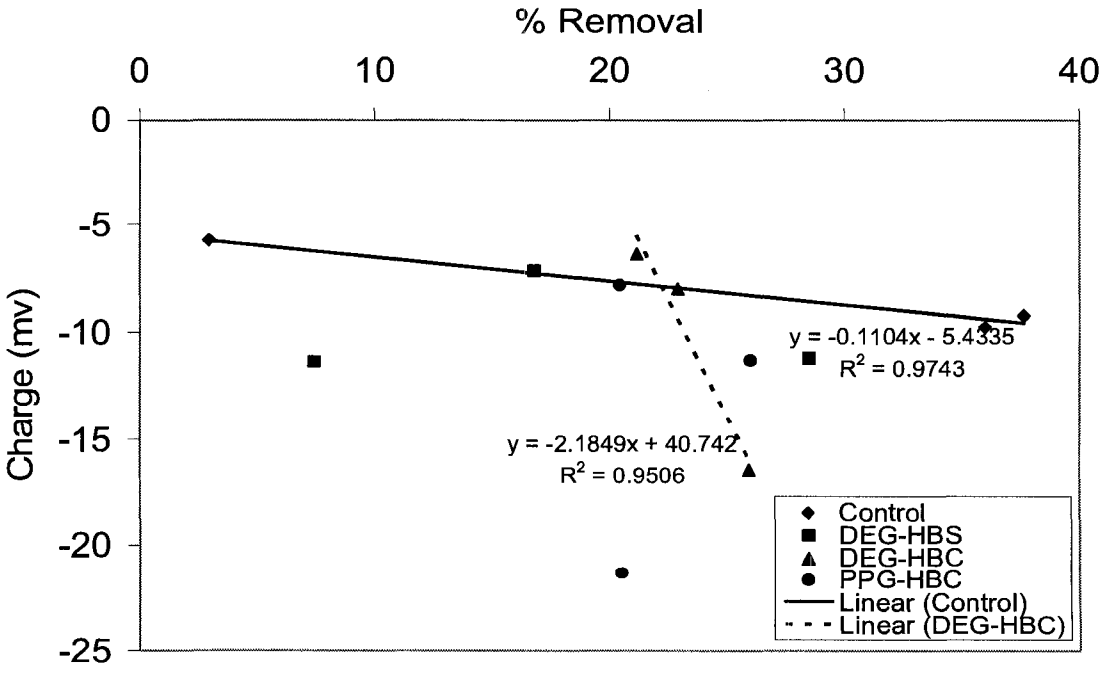

Figure F.3: Removal of BPA compared to membrane surface charge

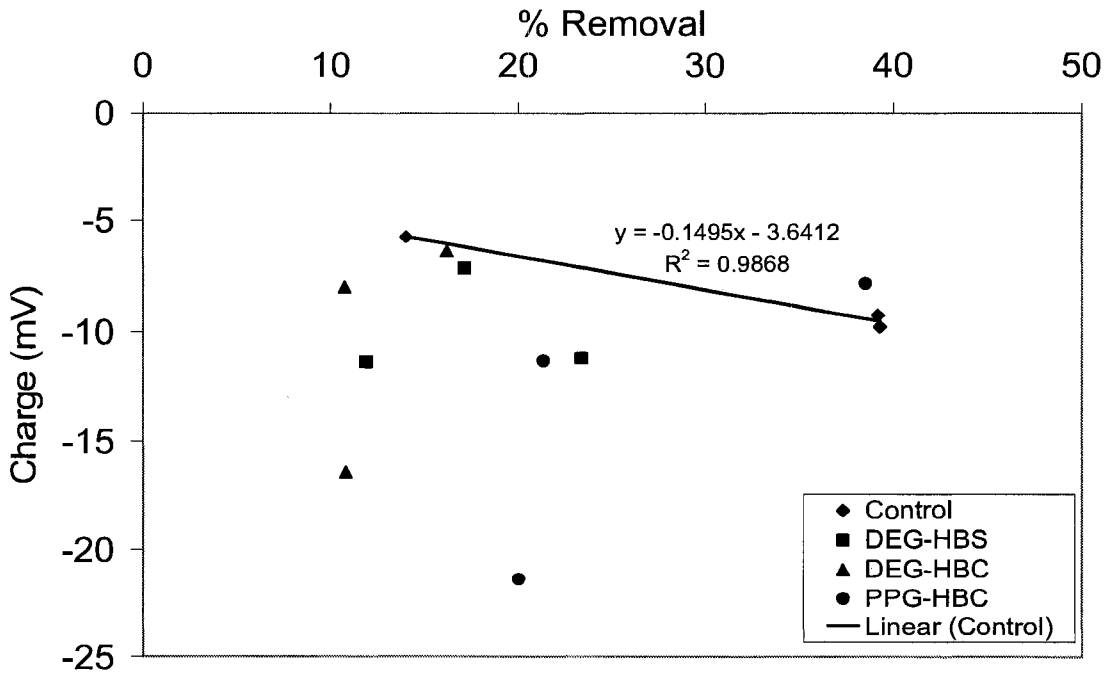

Figure F.4: Removal of IB compared to membrane surface charge

APPENDIX G

Mass adsorption calculations

In order to determine if the four target compounds were adsorbed onto the membrane, concentrations and volumes before and during the test were required. The initial volume of the stock solution was 4L. The volume of stock solution prior to dilution was 4L less the sample mass taken for the undiluted concentration to be analyzed. Subsequent diluted and set-up (at initial start-up) samples were taken. Diluted feed tank volume and total mass in the system were calculated based on equations G.1 and G.2 respectively.

$$V_{diluted} = \frac{(V_{stock} - V_{undiluted}) \times C_{undiluted}}{Average(C_{set-up}, C_{Feed1})} \quad \text{(G.1)}$$

where V_{stock} is the stock solution volume (4L), $V_{undiluted}$ is the undiluted sample volume, $C_{undiluted}$ is the undiluted sample concentration, $C_{set\text{-}up}$ is the set-up sample concentration, C_{Feed1} is the first feed sample concentration, taken at 5min ± 1min.

$$m_i = (C_{undiluted} \times V_{undiluted})/1000 \quad \text{(G.2)}$$

where m_i is the initial total mass in the feed tank (mg C), i is the iteration at time, t.

Theoretical feed concentrations were calculated in series as the samples were removed from the system. The total mass remaining in the system changes with time as does the volume remaining and the subsequent theoretical concentration. Mass and volume remaining in the system are calculated using equations G.3 and G.4.

$$m_{i,remaining} = m_{i-1,remaining} - (C_{sample} \times V_{sample})_i \quad \text{(G.3)}$$

$$V_{i,remaining} = V_{i-1,remaining} - V_{i,sample} \quad \text{(G.4)}$$

where m is the mass, C is the concentration and V is the volume.

A comparison between the theoretical and feed concentration indicates that amount of mass that has been adsorbed (based on the feed concentration) and are calculated using equations G.5 and G.6.

$$C_{Th,remaining} = m_{i,remaining} / V_{i,remaining} \quad \text{(G.5)}$$

$$m_{ads} = \left(C_{Th,remaining} - C_{sample}\right) \times V_{i,remaining} \quad \text{(G.6)}$$

The mass adsorbed with time was shown in Figures 4.19 and 4.20.