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Wengian Shan

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Ph.D. degree in **Environmental Engineering** 

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### THE ENVIRONMENTAL APPLICATIONS AND IMPLICATIONS OF NANOTECHNOLOGY IN MEMBRANE-BASED SEPARATIONS FOR WATER TREATMENT

By

Wenqian Shan

## **A DISSERTATION**

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

## **DOCTOR OF PHILOSOPHY**

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#### ABSTRACT

## THE ENVIRONMENTAL APPLICATIONS AND IMPLICATIONS OF NANOTECHNOLOGY IN MEMBRANE-BASED SEPARATIONS FOR WATER TREATMENT

By

Wenqian Shan

This dissertation presents results of three related projects focused on the applications of membrane separation technology to water treatment: 1) Experimental design and evaluation of polyelectrolyte multilayer films as regenerable membrane coatings with controllable surface properties; 2) Modeling of the interactions of nanoscale TiO<sub>2</sub> and NOM molecules in aqueous solutions of environmentally relevant compositions; 3) Experimental design and preliminary testing of a membrane-based crossflow filtration hydrocyclone process for the separation of oil-in-water dispersions.

Chapter 2 describes the design of polyelectrolyte multilayers as nanoscale membrane coatings and their application in nanofiltration of feed waters that contain suspended colloids and dissolved species. Layer-by-layer deposition of anionic and cationic polyelectrolytes was employed to prepare membrane coatings allowing for a fine control over their surface properties. This approach to membrane design also affords a possibility of regenerating coatings after they are fouled by colloids. This project demonstrated, for first time, the possibility of designing nanofiltration membranes with regenerable skin.

Chapter 3 describes a study on the mechanisms of natural organic matter (NOM) adsorption onto the surface of titania nanoparticles. Titania ( $TiO_2$ ) is often used in the

fabrication of ceramic membranes and understanding how NOM interacts with  $TiO_2$ can help to better predict ceramic membrane fouling by NOM-containing waters. The combined effect of pH and calcium on the interactions of nonozonated and ozonated NOM with nanoscale  $TiO_2$  was investigated by applying extended Derjaguin – Landau – Verwey - Overbeek (XDLVO) modeling. XDLVO surface energy analysis predicted NOM adsorption onto  $TiO_2$  in the ozone-controlled regime but not in the

calcium-controlled regime. In both regimes, short range NOM-NOM and NOM-TiO<sub>2</sub> interactions were governed by acid-base and van der Waals forces, whereas the role of electrostatic forces was found to be relatively insignificant. Ozonation increased the surface energy of NOM, contributing to the hydrophilic repulsion component of the NOM-NOM and NOM-TiO<sub>2</sub> interactions. In the calcium-controlled regime, non-XDLVO interactions such as intermolecular bridging by calcium were hypothesized to be responsible for the observed adsorption behavior.

Chapter 4 describes research on the crossflow filtration hydrocyclone separation of oil-in-water dispersions wherein a ceramic tubular membrane was used as the permeable wall of the hydrocyclone. Air sparging was applied to mitigate oil fouling. A dual membrane system consisting of an outer hydrophilic ceramic membrane and an inner hydrophobic polymeric membrane was evaluated to test the possibility of separating the dispersion into two streams: 1) oil with zero or very low concentration of water and 2) water with zero or very low concentration of oil. The performance of the dual membrane system indicated the possibility of using membranes with different chemical affinities to cost-effectively separate the oil-water dispersion into two separate phases. The incorporation of air sparging to membrane filtration was found to be effective in mitigating oil fouling with improved permeate flux.

To my father, Jinbao Shan, and my mother, Yanjiang Wang,

who have given me the best they have,

support and encourage me everyday

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# Abbreviations

AA	Atomic adsorption
ACFF	Air sparged crossflow filtration
ACFFH	Air sparged crossflow filtration hydrocyclone
CCF	Crossflow filtration
CCFH	Crossflow filtration hydrocyclone
HPI	Hydrophilic
HPO	Hydrophobic
MWCO	Molecular weight cutoff
NF	Nanofiltration
NOM	Natural organic matter
PAA	Poly(acrylic acid)
PAH	Poly(allylamine hydrochloride)
PDADMAC	Poly(diallyldimethyl ammonium chloride)
PEM	Polyelectrolyte multilayer
PSS	poly(styrene sulfonate)
PTFE	polytetrafluoroethylene
PVA	Polyvinyl alcohol
RO	Reverse Osmosis
SRNOM	Suwannee River NOM
XDLVO	Extended Derjaguin – Landau – Verwey - Overbeek

# **Chapter 1. Introduction**

#### 1.1. Nanotechnology and the environment

Drawing historical parallels with the invention of steam engines and railways in the  $19^{\text{th}}$  century and the emergence of automobiles and computers in the  $20^{\text{th}}$  century, the recent advent and the explosive growth of nanotechnologies promise to have a large impact on the scientific and economic developments in the  $21^{\text{st}}$  century [1].

Nanotechnology is a general term for the design, characterization, production and application of structures, devices and systems in which the shape and size is controlled at the nanoscale [2]. The concept of "nanotechnology" was first introduced by Richard Feynman in 1956 [3]. Nanoobjects can take different forms and shapes; examples include nanoparticles, nanorods and nanoplatelets [4].

Data show that western Europe, Japan and U.S. were all experiencing steady increases in public expenditures for the promotion of nanotechnology from 1997 to 2003 [5]. In the U.S. alone, expenditures doubled from 400 million USD in 2001 to 800 million USD in 2003. Besides the public investment, manufacturers and enterprises have invested heavily in the research, development and production of nanotechnology. As of 2004, 1 billion USD has been invested in companies that are working with nanomaterials [6]. Among that, nearly half of that money was spent in 2003 and 2004 alone. Worldwide, the total investment in nanotechnology in 2005 was in the 5 to 8 billion USD range [7]. Investments made in nanotechnology have resulted in many key interests and developments in this area. As a result, the number of the publications and patents found when searching with keywords

"nanotechnology" and "nanoparticles" in PUBMED [8] have increased enormously over the last few decades [1]. For example, less than 500 articles related to nanoparticles were published between 1995 and 1999, while over 8,000 articles focused on nanoparticles were published between January 1, 2005 and April 24, 2008 [1]. A market volume of 890 billion USD in nanotechnology is expected by 2015 based on the actual market volume in 2003 and the conservatively estimated steady rise of 8 percent per year for the next 10 years and further [9].

Nanoscale materials have been introduced into people's daily lives for the purpose of saving energy and resources, as well as for improving environmental conditions and the quality of life. The small size, high surface area and reactivity of nanomaterials make them uniquely suitable for various purposes and as a result there has been a rapid expansion in the development of nanomaterials for various industries such as textile, medicine and health, computing, transportation, aeronautics and space exploration, and environment [10]. However, these very characteristics of nanomaterials have also given rise to concerns about human exposure to these materials. People who may be exposed include not only those who are involved in nanomaterial manufacturing and handing but also consumers and end users of products. An inadvertent environmental exposure is also a possibility; there is growing evidence that under certain conditions nanomaterials can be mobile in soil, air and water [11-13]. The environmental fate and transport of the nanomaterials are indeed affected by their characteristics (e.g., size, charge, and agglomeration rate) [14].

It is important to address environmental and health related issues and uncertainties while this technology is still in early stages of development. Thus, research into applications of nanotechnology should go hand-in-hand with pro-active health and environmental implications studies.

#### 1.1.1. Nanotechnologies for a cleaner environment

Nanotechnology has had a significant impact on the development of novel environmental engineering processes and technologies. The impact has been reflected by the benefits of using nanotechnology to deal with legacy environmental pollution and to predict and prevent future environmental problems [7,15,16]. Here are some specific examples. Nutt *et al.* [17] synthesized palladium/gold nanoparticles with diameters less than 20 nm and found that such nanoparticles have a high catalytic activity in the hydrodechlorination of trichloroethylene in water, which is a common contaminant in groundwater. Mayo *et al.* [18] used magnetic properties of iron oxide nanocrystals to efficiently absorb and desorb arsenic from drinking water. Pummakarnchana *et al.* [10] developed solid state gas sensors based on nanotechnology with increased sensitivity in detecting air pollutants such as  $NO_x$ .

#### 1.1.2. Nanotechnology applications in water treatment and quality control

Water pollution has become one of the most serious environmental challenges that humans are facing. Pollution can be due to long term routine contamination and short-term catastrophic events. Produced water generated during offshore drilling operations, municipal sewage discharge and agricultural runoff are examples of long term water contamination. Oil spills, chemical spills, and flooding, despite the fact that they are short term events, may have environmental impacts that are as severe as or worse than long term routine contamination has. A 2008 report indicated that 884 million people lacked access to safe water supplies, which is approximately one in eight people worldwide [19]. One of the urgent challenges of the environmental engineering profession is to develop new technology to improve the quality of drinking water to minimize the likelihood of water-related disease outbreaks. The fact that water scarcity and related sanitary problems will become only more severe over time makes it imperative for our society to seek solutions for improved water treatment processes and for remediating wastewater to meet water quality standards. We also need to achieve these objectives with high efficiency and at lowest possible cost [20].

There are established wastewater treatment processes that can be and are used to treat and reclaim polluted water [21]. The limited energy efficiency of existing methods and, in some cases, concerns with respect to the quality of the treated water bring questions of the sustainability of these traditional technologies. For example, while chlorination is known to be effective in deactivating most pathogenic water-born microorganisms, it was determined that chlorination byproducts are toxic and some are carcinogenic. To give another example, some of the conventional water treatment processes are not effective at removing emerging contaminants (e.g., pharmaceuticals, surfactants) from municipal and industrial wastewater [22-24].

A range of accepted water treatment technologies (e.g., adsorption, ion exchange, redox processes, membrane filtration, and disinfection processes) have benefited from nanotechnology-enabled discoveries [25]. Nanotechnology has been used to improve the effectiveness and efficiency of water treatment, remediate contaminated water and to increase the sensitivity of detection of various water toxic contaminants. Some specific examples of the use of nanomaterials to improve water quality are: microbial disinfection with silver nanometallic particles [26], photocatalytical destruction of biological toxins in wastewater using TiO<sub>2</sub> nanoparticles [27], adsorption of heavy metals from water using self-assembled functional ligands that form a nano-coating

[28], removal of toxic dissolvable metal (copper, uranium) by dendritic polymers [29], removal of radioactive cesium with nanocomposite film containing carbon nanotubes [30], application of metal and oxide nanoparticles in the removal of pesticides [31], and remediation of groundwater contaminated by chlorinated solvents and heavy metals using reactive zero-valent iron nanoparticles [32].

The application of nanotechnology for water treatment and quality control is expected to become a major industry over the next 10-15 years [20].

#### 1.1.3. Potential environmental risks of nanotechnology

As briefly outlined above, there are a growing number of nanotechnology-based solutions to environmental protection and remediation of environmental pollution. At the same time, there are also concerns that nanomaterials may pose environmental challenges of their own. As noted by Breggin and Pendergrass [33], certain classes of nanomaterials may, in the future, be considered hazardous waste due to their as-of-yet unknown toxicological properties, creating potential legal liabilities for manufacturers, investors, and insurers. So far there is insufficient evidence to support the broad claim that nanoparticles with undesirable effects (toxicity, and radioactivity, for example) constitute a new class of non-biodegradable pollutants [34]. However, it has been determined that if removal of nanomaterials from the environment (soil, water and air) is necessary, it would be difficult to accomplish due to the extremely small size and, in some cases, high mobility of nanomaterials.

It is clear that a better understanding of nanoparticles' interactions in the environment is necessary. Studies have been published focusing on the interactions of nanomaterials with microorganisms, which are an integral component of environmental media such as soils and surface waters. There is already some evidence showing that nanoparticles may have an adverse effect on microorganisms depending on the physicochemical factors (size, charge, morphology) and material properties of the nanoparticles. For example, in the study of antibacterial activity of aqueous  $nC_{60}$ suspension with bacterium *Bacillus subtilis*, larger  $nC_{60}$  particles (> 100 nm in diameter) appeared to be 100 times less toxic than smaller (< 100 nm) particles [35]. Another study showed that cationic fullerene derivatives were bacteriostatic while anionic derivatives were not, and that the surface coating on quantum dots of CdS and CdSe is relevant in determining their toxicity [36]. Another ecotoxicity study has already found that nanoparticles may affect marine organisms by contaminating their food web; it has been demonstrated that gold nanorods can easily be transferred from the water column to the estuarine food web [37]. Further, it has been shown that nano-silver can disrupt key soil microbial communities [38].

In summary, given the uncertainty with respect to the balance between useful applications and adverse impacts of nanotechnology, the environmental effects of engineered nanomaterials and nanomaterial-based technologies should be proactively assessed prior to their mass introduction to the markets.

#### **1.2. Membranes nanotechnologies**

Nanotechnology has great potential in the development of novel membrane materials (with improved permeability and selectivity, with additional functionalities, etc) and for the development of novel approaches to the mitigation of membrane fouling, which is the most egregious problem precluding wider applications of membranes in water treatment.

#### 1.2.1. Nanoparticle-enabled membranes

The incorporation of nanoparticles into reverse osmosis [39], nanofiltration [40] and ultrafiltration membranes [41,42] has already been shown to be effective in improving membrane properties. Nanoparticle-enabled membranes combine traditional membrane materials and preparation methods with novel nanomaterials and methods. Two typical methods used to incorporate nanoparticles into the membrane matrix are: decoration of the membrane surface with nanoparticles [43,44] and incorporation of nanoparticles within the membrane matrix during membrane preparation [45]. For example, membranes self-assembled with TiO<sub>2</sub> nanoparticles have been used to modify both ultrafiltration [44] and reverse osmosis [43] membranes by self-assembly technology; such membranes have been used as photocatalytic membranes to oxidize organic contaminants and to reduce membrane fouling by these organics. As another example, membranes modified with aligned carbon nanotubes were used to remove 25 nm sized polio viruses from water as well as larger pathogens such as E. coli and Staphylococcus aureus bacteria [46]. Nanoscale silver particles have been incorporated into ultrafiltration membranes to inhibit membrane biofilm growth [42]. Titanium dioxide ( $TiO_2$ ) nanoparticles have also been embedded with polyamide membranes to decrease biofouling [43].

Generally speaking, nanoparticle-enabled membranes can be designed to be multifunctional with enhanced features such as functional/catalytic properties with respect to certain reactions, increased resistance to fouling potential and improved chemical, mechanical or thermal stability [20].

# 1.2.2. Novel nanoscale membrane coating – polyelectrolyte multilayer filmsPolyelectrolyte multilayer films (PEMs) are prepared by a layer-by-layer adsorption

of polycations and polyanions. These films have been applied on different types of substrates including membranes. These nanoscale surface films have a controllable molecular architecture [47,48] and are typically in the nanoscale thickness range. The resultant ultrathin membrane skin allows a high permeation rate [49] and can be used to alter the surface chemistry of the membrane.

The control over surface chemistry (e.g., roughness, charge, hydrophobicity) of the membrane is important from the fouling standpoint. For example, the major foulant of nanofiltration membranes – natural organic matter (NOM) – fouls hydrophilic membranes less than hydrophobic membranes [50]. Similar effects of membrane hydrophilicity have also been observed in protein filtration experiments [51]. Flux reduction during the removal of colloids [52,53] and toxic chemicals [54] has been correlated to membrane roughness. Surface charge of membranes is an important factor in controlling salt rejection by membranes [55,56].

The development of PEM films is an example of the application of nanotechnology to control membrane surface properties. The interactions of PEM films with proteins [57-66], mammalian cells [62,63,67-71], and bacteria [64,68,72,73] have been studied. The attributes of the PEM surface do affect the interaction with these substances. For example, it was found that a PEM surface with higher roughness results in lower adhesion of human gingival fibroblast cells [74], while another study found that a PEM film with lower stiffness results in lower cell adhesion [70].

In addition, PEM films have also been used to promote self assembly of proteins [75], dyes [75], nanoparticles (e.g., quantum dots [75], polystyrene [76-78], ferritin [79], SiO<sub>2</sub> [80], latex particles [81-83]), and microsized particles (e.g., 0.5-1  $\mu$ m SiO<sub>2</sub> [84]). Depending on the combination of absorbent and PEM films, self assembly processes can be dominated by short-range hydrophilic interaction [75], surface

roughness [76,77], or surface charge [76,77]. When using a polyelectrolyte coating to prepare a surface for the self assembly of nanoparticles, the aggregation state of nanoparticles will be different depending on the preparation methods of the PEM coatings, and water chemistries of nanoparticle suspensions and polyelectrolyte solutions. Such dependence can be reflected by the fact that the same type of polyelectrolyte film surface (e.g., PEM film with poly(diallyldimethyl ammonium chloride) as the top layer) will result in either monolayers of nanoparticles [80] or aggregation of the nanoparticles [85]. The resulting form of self-assembly is chemical dependent [84] and is also affected by the experimental washing and drying processes [79]. A review paper has summarized the experiments and theory of the irreversible adsorption of particles (such as latex particles, globular proteins) on heterogeneous surfaces such as PEM-modified surfaces [86].

Membranes coated with PEMs have been designed to provide a selective barrier to aqueous ionic species [87]. A  $Cl^{-}/SO_4^{2^-}$  selectivity of 30 has been achieved with 4.5 bilayers PSS/PAH (poly(styrene sulfonate)/ poly(allylamine hydrochloride)) films [88]. When changing the PEM compositions to PAA/PAH (poly(acrylic acid)/PSS), the selectivity could be increased to 80 by sacrificing half of the solution flux [88]. These results indicate that it is easy and feasible to control membrane properties by changing the compositions of the PEM film. High separation performance of mono-, di-, and multivalent cations and anions [88-95] or neutral molecules [96-99] has achieved with PEM modification on a surface [88,90,91,94,95] or within the inner pore structure [100] of a porous membrane support. Besides having a controllable surface chemistry, the PEM films have another attractive feature that they are sensitive to chemical conditions [101], which allows the film dissociate from the support under certain chemical conditions and a new film can be reapplied to the same

support.

# 1.3. Nanoparticle interactions in aqueous media as a key to elucidating environmental impacts of nanomaterials

Interactions of nanoparticles in the natural water matrix determine nanoparticle transport, fate, and ecotoxicity in aqueous environments. The likelihood of nanomaterials entry into the environment is increasing with the growth of the nanotechnology industry. The natural bodies receive runoff and effluent from wastewater treatment facilities, and nanomaterials may be present in each of these sources. In addition, nanomaterials are increasingly used in environmental remediation and can enter the environment via this route [102]. At this point the understanding of the transport and fate of nanomaterials in aquatic environments is lacking [103].

Aggregation and deposition are the two main processes that control the transport and fate of nanomaterials in aqueous conditions [104]. The major principles of colloid science (e.g., Smoluchovsky's equations and DLVO theory [105-107]) may still be applicable for engineered nanoparticles [108], except that the BrØnsted concept needs to be applied for nanoparticles that are smaller than 10 nm [108].

The processes of aggregation and deposition of nanomaterials are governed by their physicochemical properties, such as particle size, particle charge, morphology, and hydrophobicity [109]. These physicochemical properties of nanoparticles suspended in water can be a function of the chemical makeup of the water (i.e., ionic strength, pH) and can affect the stability of nanoparticles [110-112]. In a recent review, Wiesner *et al.* pointed out that it is not always true that the small size of nanoparticles will yield a high mobility in porous media (e.g., groundwater aquifer) [103]. Their

relatively large diffusivity, a direct consequence of their small size, would also enhance their chance to attach/deposit on the surfaces of porous media and thus lose their mobility. Lecoanet *et al.* studied the mobility of fullerene-based materials in porous media and showed that single-walled nanotubes and fullerol particles can pass through the porous medium more rapidly than  $nC_{60}$  nanoparticles [113]. The relatively slow transport of  $nC_{60}$  was attributed to its hydrophobic interactions with porous media.

The aggregation and deposition of nanomaterials in aqueous media would also affect their bioavailability and ecotoxicity. Farre's review paper on ecotoxicity of nanomaterials [102] summarized the studies on ecotoxicity of nanomaterials such as silver nanoparticles [114,115], fullerene [116,117], and single-walled carbon nanotubes [118-120]. These materials elicited toxic response in species such as zebrafish, *Daphnia magna*.

# Chapter 2. Polyelectrolyte multilayer films used as renewable membrane coatings with tunable surface properties

This work has been recently published in the Journal of Membrane Science [121].

### 2.1. Introduction

Polyelectrolyte multilayer (PEM) films are prepared by alternately adsorbing oppositely charged polyelectrolytes onto supports using a layer-by-layer technique [122-124] and can serve as regenerable surface coatings with controllable physicochemical properties (e.g. charge, hydrophilicity, swellability, stiffness) that regulate adhesion to the surface [65,125,126]. The resistance to adsorption of different substances (e.g., proteins, mammalian cells or bacteria) and the selectivity to aqueous ionic species of PEM films were discussed in section 1.2.2.

When assembled on a surface [88,90,91,94,95] or within the inner pore structure [100] of a porous membrane support, PEMs can function as nanofiltration [88,90,91,94,95] or reverse osmosis [93] membranes to separate mono-, di-, and multivalent cations and anions [88-95] or neutral molecules [96-99]. For example, membranes composed of five bilayers of poly(styrene sulfonate)/poly(allylamine hydrochloride) (PSS/PAH) on porous supports allow a high flux at regular nanofiltration pressures and exhibit 95% rejection of MgCl<sub>2</sub> along with a Na<sup>+</sup>/Mg<sup>2+</sup> selectivity of 22 [127]. As another example, 4.5-bilayer PSS/PDADMAC (poly

(diallyldimethylammonium chloride)) films on porous supports show  $Cl^{/}F$  and  $Br^{/}F$  selectivities larger than 3 along with solution fluxes that are 3-fold higher than those of commercial membranes [128].

The PEM approach to membrane design is highly versatile in that separation and antiadhesive properties of PEMs can be adjusted through the choice of the constituent polyelectrolytes, the number and sequence of polyelectrolyte layers in the film, and the deposition conditions (solution pH and ionic strength, e.g., [91]). A unique advantage of some PEM membranes is that when appropriately constructed, the film can be removed from the porous support via exposure to solutions with high pH values (10-12) or ionic strengths [129-131]. The film can then be regenerated through the layer-by-layer process. Thus, a PEM film assembled on a UF support can combine separation and antiadhesive properties with the ability to renew the surface (Fig. 2.1).





Nearly all studies on the separation properties of PEMs employed synthetic feed solutions with only one or two compounds in solution. The performance of PEM

membranes challenged by suspensions of colloids (other than proteins) and regeneration of fouled PEMs have not been investigated. Very little is known about the effects of operational variables on PEM separation properties. In the only published study on the topic, Tieke and coworkers examined rejection with a very dense 60-bilayer poly(vinylamine)/ poly(vinylsufate) PEM membrane as a function of transmembrane pressure [93]. They observed pronounced concentration polarization effects, but a rigorous analysis was not possible because the study was conducted in a dead-end geometry. Importantly, while PEMs have been effective in simultaneously increasing protein retention and reducing protein adhesion [58], there have been no reports on the design of PEM membranes that combine resistance to colloidal fouling with desirable *ion* separation properties. This study aims at filling some of these knowledge gaps. Specific objectives of this work are:

1) to evaluate water and solute permeabilities of a diverse set of PEM membranes to understand the dependence of rejections on pressure and solute concentration;

2) to determine how the permeability and rejection of PEM membranes are affected by concentration polarization and colloidal fouling;

3) to assess PEM regeneration alternatives, including backflushing, for as-prepared PEMs and PEMs fouled by colloids.

### 2.2. Background and approach

#### 2.2.1. Colloidal fouling

Although source waters usually undergo pretreatment that is designed to remove the colloidal fraction, in practice both dissolved and residual suspended phases are present in nanofiltration (NF) or reverse osmosis filtration (RO) feed waters [132,133]. The colloids that persist through the pretreatment stage can form membrane deposits with a high hydraulic resistance on membrane surfaces, contributing to the permeate flux decline. The size of a colloid has a significant effect on its diffusivity and thus fouling potential. It was experimentally determined [134] and mathematically calculated [135] that the minimum in particle back-transport diffusivity is occurred with colloids with a diameter of approximately 100 nm, and thus particles of this size have the highest membrane fouling potential (see Figure 2.2). Therefore, a colloid of this size yields a minimum in back-transport diffusivity and thus a maximum in deposition propensity [136]. In addition, colloids deposited on a nanofiltration membrane surface tend to inhibit back-diffusion of dissolved species, resulting in precipitation of sparingly soluble salts in the pores of the deposited layer, and also causing cake-enhanced osmotic pressure [137]. Colloids cause fouling either externally, on the membrane surface (a build-up of a cake/gel-like layer on the upstream face of a membrane) or internally, inside of the pores of a membrane [138]. When the colloids get into the internal pores of the membrane, they are hard to remove and this condition is considered as permanent/irreversible fouling.



Figure 2.2. Particle diffusivity as a function of radius for conditions typical of hollow fiber UF membranes [136]

2.2.2. Approach

Nanofiltration properties of PEM-coated membranes were compared with the corresponding properties of a commercial membrane, NF270. Firstly, permeability to deionized water and MgSO<sub>4</sub> rejection were measured for all membranes in crossflow filtration experiments. Solute transport to the membrane surface and transport across the membrane were modeled using a thin film model and Kedem-Katchalsky equations, respectively. Measured values of the permeate flux and the concentration of solute in the permeate were used to determine the MgSO<sub>4</sub> permeability coefficients of the membranes, which is an important criterion for nanofiltration membranes. By performing the crossflow experiments over a range of transmembrane pressure differentials, a range of concentration polarization conditions were tested, and the MgSO<sub>4</sub> permeability coefficients as a function of salt concentration were recorded for each membrane.

Secondly, the performance of membranes under conditions of colloidal fouling was evaluated with experiments on the crossflow filtration of  $SiO_2$  colloids suspended in an electrolyte solution. Based on i) the measured values of permeate flux and Mg<sup>2+</sup> concentration in the permeate and ii) the previously determined MgSO<sub>4</sub> permeability coefficient as a function of concentration, the resistance to the permeate flow due to the deposited layer of colloids was computed for each membrane and used as a measure of the extent of colloidal fouling.

#### Determination of intrinsic rejection

To characterize the selectivity of membranes in the colloidal fouling study, MgSO<sub>4</sub> rejection was measured. The mass transfer coefficient, k, for MgSO<sub>4</sub> in the

membrane cell channel was estimated from the Sherwood correlation ([139]):

$$Sh = \frac{kd_h}{D} = \left(3.66^3 + 1.61^3 Re \cdot Sc \cdot \frac{d_h}{L}\right)^{\frac{1}{3}}$$
(2.1)

where Sh is the Sherwood number, L is the channel length, D is the diffusion coefficient of MgSO<sub>4</sub> in water ( $8.5 \cdot 10^{-10} \text{ m}^2/\text{s}$  [140]), Re is the Reynolds number, Sc is the Schmidt number, and  $d_h$  is the hydraulic diameter of the channel. For the membrane cell used in this study,  $d_h \approx 2h$ , where h is the channel height. The value of  $\left(Re \cdot Sc \cdot \frac{d_h}{L}\right)$  is a criterion in using the Sherwood correlation of eq. 2.1, and

the value is computed as follows:

$$\left(Re \cdot Sc \cdot \frac{d_h}{L}\right) = \frac{\rho v d_h}{\eta} \cdot \frac{\eta}{\rho D} \cdot \frac{d_h}{L} = \frac{v d_h^2}{DL}$$
(2.2)

where v is the crossflow velocity. The value of  $\left(Re \cdot Sc \cdot \frac{d_h}{L}\right)$  was in the (9,020 to

10,300) range, which was close to the upper bound of the applicability range

$$\left(0.1 < \left(Re \cdot Sc \cdot \frac{d_h}{L}\right) < 10,000\right) \text{ of eq. 2.1.}$$

The thin film model was used to estimate the concentration of MgSO<sub>4</sub> at the membrane surface,  $C_m$  [141]:

$$\frac{C_m - C_p}{C_f - C_p} = \exp\left(\frac{J}{k}\right)$$
(2.3)

and to determine the intrinsic rejection,  $R_{in}$ , as a function of the permeate flux, J,

for all permeate sampling times:

$$R_{in} = 1 - \frac{C_p}{C_m} = 1 - \frac{C_p}{C_p + (C_f - C_p) \cdot \exp\left(\frac{J}{k}\right)}$$
(2.4)

where  $C_p$ ,  $C_f$ , and  $C_m$  are the concentrations of MgSO<sub>4</sub> in the permeate, in the bulk feed, and in the portion of the feed directly adjacent to the membrane, respectively. In this study, permeate flux and salt rejection were measured at different transmembrane pressure differentials,  $\Delta P$ , and values of  $R_{in}$  were determined as a function of J using eq. 2.4. These experiments were conducted using colloid-free MgSO<sub>4</sub> electrolyte as the feed.

#### Determination of solute permeability coefficient

The coupled transport of solute and solvent in a membrane is described by the Kedem-Katchalsky equations [142]:

$$J = L_p(\Delta P - \sigma \Delta \pi) \tag{2.5}$$

$$J_s = \omega \Delta \pi + (1 - \sigma) J \overline{C} \tag{2.6}$$

where J and  $J_s$  are volume and solute fluxes across the membrane, respectively,  $L_p$  is the hydraulic permeability of the membrane,  $\sigma$  is the reflection coefficient, and  $\omega$  is the solute permeability. Volume flux is given by  $J = J_w \tilde{V}_w + J_s \tilde{V}_s$ , where  $\tilde{V}_w$  and  $\tilde{V}_s$  are molar volumes of water and solute, respectively and  $J_w$  is the permeate water flux across the membrane. In eq. 2.6,  $\overline{C}$  is the logarithmic mean of the average concentration of solute within the membrane:

$$\overline{C} = (C_m - C_p) \cdot \ln^{-1} \left( C_m / C_p \right)$$
(2.7)

For large volume flows and high concentration gradients across the membrane, the changing concentration profile inside the membrane can be taken into the account by recording eq. 2.6 in the differential form. Noting that

$$J_s = JC_p \tag{2.8}$$

and substituting the expression for the local osmotic pressure differential

$$\Delta \pi = n\varphi RT[C(x) - C(x + \Delta x)]$$
(2.9)

into eq. 2.6, one obtains the Kedem-Katchalsky expression for the volume flux across a differential element of the membrane:

$$JC_p = -\overline{P}\frac{dC}{dx} + (1-\sigma)J\overline{C}$$
(2.10)

where  $\overline{P} = n\phi RT\omega\Delta x$  is the *local* solute permeability coefficient, *n* is the total number of constituent ions in the salt (n = 2 for MgSO<sub>4</sub>),  $\overline{C}$  now has the meaning of the logarithmic mean of the average concentration of solute within the differential element, and  $\phi$  is the osmotic coefficient, which is generally a function of the solute concentration [143] and can be calculated using the Pitzer equation [144].

Note that the physical meaning of  $\sigma$  can be deduced from the Spiegler-Kedem relationship [145] that is obtained by integrating the differential form (eq. 2.10) of the Kedem-Katchalsky expression (eq. 2.6) across the membrane in the presumption of concentration-independent phenomenological coefficients  $\sigma$  and  $\overline{P}$ :

$$R_{in} = \frac{\sigma(1-F)}{1-\sigma F} \tag{2.11}$$

$$F = \exp\left(-\frac{J(1-\sigma)}{P_s}\right)$$
(2.12)

where  $P_s$  is the solute permeability coefficient  $(P_s = n\phi RT\omega = \frac{\overline{P}}{\Delta x})$ . It follows from eq. 2.11 and 2.12 that the reflection coefficient,  $\sigma$ , represents the limiting value of the intrinsic rejection achieved at  $J \rightarrow \infty$ .

Experimental evidence indicates that  $P_s$  is generally concentration-dependent (e.g., [146-149]). Accordingly, in this study we used the Kedem-Kachalsky model (eq. 2.6) to determine the MgSO<sub>4</sub> permeability coefficient as a function of concentration,  $P_s = P_s(C)$ . To compute  $P_s = P_s(C)$ , eq. 2.6 was used in its modified form:

$$J_s = P_s(C_m - C_p) + (1 - \sigma)J\overline{C}$$
(2.13)

In deriving eq. 2.13 the following expressions for the solute permeability and osmotic pressure differential were used:  $\omega = \frac{P_s}{n\varphi RT}$  and  $\Delta \pi = n\varphi RT(C_m - C_p)$ . By

incorporating eq. 2.7 and 2.8, eq. 2.13 can be rewritten as:

$$JC_{p} = P_{s}(C_{m} - C_{p}) + (1 - \sigma)J\frac{C_{m} - C_{p}}{\ln(C_{m} / C_{p})}$$
(2.14)

The reflection coefficient  $\sigma$  was presumed to be concentration independent and its value was approximated by the maximum value of intrinsic rejection,  $R_{in}^{\max}$ . More specifically, the value of  $\sigma$  was obtained by measuring rejection at the highest

experimental permeate flux in each conditioning experiment and calculating  $R_{in}^{\max}$ from eq. 2.4. With  $\sigma$  available, the only unknown in eq. 2.14 is  $P_s$ . By measuring J and  $C_p$  in an experiment on the filtration of colloid-free electrolyte (i.e. membrane conditioning stage of experiments; see stage 3 in section 2.3.5) and computing  $C_m$  using eq. 2.3 and the Sherwood correlation (eq. 2.1), we applied eq. 2.14 to determine  $P_s$  for the given  $C_m$ . By performing the above procedure at a series of different transmembrane pressure differentials  $\Delta P$  (and, correspondingly, different permeate fluxes, J), the dependence  $P_s = P_s(C)$  was determined for a wide concentration range for each membrane.

To evaluate the error introduced into the computation of  $P_s = P_s(C)$  by presuming the reflection coefficient to be concentration independent and equal to the value of intrinsic rejection at the maximum permeate flux, we evaluated the ratio, G, of the two terms on the right hand side of eq. 2.13 (note that this ratio is a measure of the importance of the coupling between solvent and solute transport).

$$G = \frac{(1-\sigma)J\overline{C}}{P_s(C_m - C_p)}$$
(2.15)

By determining this ratio, we can have the idea of the possible error introduced into the computation of  $P_s = P_s(C)$  by presuming the reflection coefficient to be concentration independent.

Quantifying concentration polarization and resistance of colloidal cake in colloidal fouling experiments

Under conditions of colloidal fouling, concentration polarization is enhanced due to
the formation of a colloidal cake that hinders back-diffusion of rejected salt [137,150]. This process is called cake enhanced concentration polarization and typically occurs for salt rejecting membranes. The accumulation of particles forms a barrier to the backtransport of salt species and as a result, a higher osmotic pressure will be created due to the increased difference in salt concentration on the upstream face of a membrane and the salt concentration in the permeate. With mass transfer correlations such as eq. 2.1 available only for well-defined geometries and with the value of the hindered diffusion coefficient in the cake not known, thin film theory (eq. 2.3) can no longer be used to determine  $C_m$ . To overcome this difficulty, we fitted the experimental  $P_s(C_m)$  data obtained in experiments on the filtration of colloid-free electrolyte solution (see Fig. 2.7) to determine an analytical  $P_s(C_m)$  expression for different PEM membranes as well as the NF270 membrane. Then, eq. 2.14 was used to determine the value of  $C_m$  for each sampling time in experiments on colloidal fouling ( $\sigma$  was assumed to be  $R_{in}^{\max}$  as mentioned above). Dividing  $C_m$  by the concentration of MgSO<sub>4</sub> in the feed,  $C_f$ , gives the concentration polarization factor,  $C_m/C_f$ , which can be determined at different times during the colloidal filtration experiment.

The hydraulic resistance exerted by the colloidal deposit,  $R_d$ , was computed using the following equation for the permeate flux:

$$J = \frac{\Delta P - \sigma \Delta \pi_m}{\mu (R_m + R_d)} \tag{2.16}$$

where  $\Delta P = P_b - P_p$  is the pressure differential between the bulk feed and the

permeate,  $\Delta \pi_m = \pi_m - \pi_p$  is the transmembrane osmotic pressure differential,  $R_m$  is the hydraulic resistance of the membrane, and  $\mu$  is the water viscosity.

# 2.3. Experimental

#### 2.3.1. Materials

All reagents were of ACS analytical grade or higher purity and were used without further purification. Ultrapure water was supplied by a commercial RO/DI system (LabFive, USFilter Corp., Hazel Park, MI) equipped with a terminal 0.2  $\mu$ m capsule microfilter (PolyCap, Whatman Plc., Sanford, ME). The resistivity of the water was greater than 16 M $\Omega$  cm.

Silica colloids (SnowTex-ZL, Nissan Chemical America Corp., Houston, TX) were received in the form of a concentrated suspension. Dynamic light scattering (BI-MAS particle sizing module, ZetaPALS, Brookhaven Instrument Corp., Holtsville, NY) was used to measure the particle size distribution in SiO<sub>2</sub> suspensions. Samples were diluted with 0.1 mM MgSO<sub>4</sub> to reach the recommended count rate. The  $\zeta$ -potential of particles was measured by a zeta potential analyzer (ZetaPALS). The pH of the SiO<sub>2</sub> suspension in 0.1 mM MgSO<sub>4</sub> was in the 6.1-6.6 range. SiO<sub>2</sub> colloids were (140 ± 1) nm in diameter with a  $\zeta$ -potential of (-30 ± 5) mV.

Magnesium sulfate salt was used to evaluate the salt rejection in the presence of colloids filtering with different membranes.  $Mg^{2+}$  concentrations were determined using flame atomic absorption (AA) spectroscopy (Perkin-Elmer 1100, Waltham, MA). A stock solution of lanthanum chloride (Fisher Scientific) was added to all samples and standards to achieve a LaCl<sub>3</sub> concentration of 0.1% by weight. The

calibration range for Mg<sup>2+</sup> concentration was (0.1 to 0.6) mg/L.

## 2.3.2. Preparation of PEM membranes

A polyethersulfone (PES) membrane (Pall Corp., East Hills, NY) with a MWCO of 50 kDa served as the support for PEM films. The permeability of this UF membrane is considerably higher than that of the PEMs, but its surface porosity is sufficiently low to allow complete coverage of the support (i.e. complete bridging of the support's surface pores by the polyelectrolyte molecules) by PEMs with only a few adsorbed bilayers [94,151]. Prior to the PEM deposition, the support membranes were soaked first in 0.1 M NaOH for 3 h and then in deionized water for 24 h at 4 <sup>o</sup>C with water exchanged after the first 12 h of storage, as recommended by the manufacturer. Anionic and cationic polymers were alternately adsorbed on the UF substrate by immersing the substrate in the corresponding polyelectrolyte solutions with a 1 min water rinse after the deposition of each layer. Table 2.1 specifies the conditions for deposition of each layer for all of the polyelectrolyte membranes in this study.

PDADMAC ( $M_w = (100,000 \text{ to } 200,000)$ ), PAH ( $M_w = 70,000$ ), and PSS ( $M_w$ 

=70,000) were purchased from Aldrich, and PAA ( $M_w = 90,000, 25\%$  aqueous solution) was obtained from Polysciences. Figure 2.3 shows the structure of the polyelectrolytes used in the study.

IDESCRIMINATION PSS/0.5/2.1 PAH/0.5/3.5 PAA/2.5/4.5	(2 min) (5 min) (5 min)
PSS/2.5/2.1 (2 min)	PSS/2.5/2.1 (2 min) PAA/2.5/4.5 (5 min)
	[PSS/PAH]2+[PAA]      PSS/0.5/2.1      PAH/0.5/3.5      PAA/2.5/4.5        (2 min)      (5 min)      (5 min)      (5 min)

Table 2.1. Ionic strength (I<sub>c</sub>) and pH of the PEM solutions used to prepare PEM membranes. The adsorption time for each layer is listed in parentheses.

 a The subscript of 4.5 means that one single layer of PSS was deposited on top of the four [PSS/PAH] bilayers.

b

The pH of the PAH solution used in depositing the [PAA/PAH]<sub>1.5</sub> was 3.5. The subscript of 1.5 means that one additional layer of PAA was deposited on top of one bilayer of [PAA/PAH].

- <sup>c</sup> The ionic strength of the solution used for depositing the first PAA layer in [PAA/PAH]<sub>1.5</sub> was 0.5 mol/L.
- d The pH was that of the as-prepared PEM solution and was not adjusted.
- e The ionic strength of the solution during the deposition of the terminating layer was increased to 2.5 mol/L [88,127] except when PDADMAC was the terminating layer, because PDADMAC films dissociate at high ionic strength [131].
- f For strong polyelectrolytes, 3 min (for PDADMAC) or 2 min (for PSS) adsorption time was sufficient, while for weak polyelectrolytes such as PAH and PAA, a 5 min adsorption time was used.



Figure 2.3. Structure of polymers used in PEM films (a) PDADMAC, (b) PAA, (c) PSS, (d) PAH.

The polyelectrolyte solutions were prepared at a repeat unit concentration of 0.02 mol/L, and the pH and ionic strength of polyelectrolyte solutions were adjusted using

1M HCl, 1M NaOH and 1M NaCl solutions. The ionic strength of the solution during the deposition of the terminating layer was increased to 2.5 mol/L [88,127] except when PDADMAC was the terminating layer, because PDADMAC films dissociate at high ionic strength [131]. The deposition was always initiated with PSS to ensure the attachment of the multilayer membrane to the PES support due to hydrophobic interactions between PSS and PES [94]. The additional PAA-containing layers of [PSS/PAH]<sub>2</sub>+[PAA] and [PSS/PAH]<sub>2</sub>+[PAA/PAH]<sub>1.5</sub> were added to increase the hydrophilicity of these membranes.

In order to compare the performance of PEM films to commercially available nanofiltration membranes with similar water permeability during colloidal fouling, coupons of commercial polyamide thin-film composite NF270 membrane (FilmTec, Dow Chemical Company, Midland, MI) were cut from the as-received membrane sheet and soaked in ultrapure water for 24 h at room temperature prior to being characterized and used for filtration.

#### 2.3.3. Membrane characterization

The streaming potentials of membranes were measured using an electrokinetic analyzer (BI-EKA, Brookhaven Instrument Corp., Holtsville, NY). Before the test, membranes were soaked in deionized water for 24 h. The KCl (pH 4) electrolyte solution used in these measurements had an ionic strength of 0.4 mM, which was the same as that of the 0.1 mM MgSO<sub>4</sub> solution used in the filtration experiments.

To examine the hydrophilicity of the membranes, water contact angles were measured using a FTÅ 200 contact angle analyzer (First Ten Angstroms, Portsmouth, VA). A 5  $\mu$ L drop of ultrapure water was formed on the tip of a stainless steel syringe needle and placed onto the membrane surface by raising the membrane until contact was made. An image of the drop was taken two seconds after the drop formed on the surface, and the left and the right contact angles were determined. To measure surface energy of different PEM membranes, contact angle measurements were also carried out with the other two different probe liquids – glycerol (Columbus Chemical Industries, Inc., Columbus WI) and diiodomethane (Spectrum Quality Products Inc., Gardena, CA). At least three membrane coupons were tested with five images taken for each membrane.

Scanning electron microscope images were recorded using a Hitachi S-4700II field emission SEM operated in ultrahigh resolution mode. Samples were mounted on aluminum SEM specimen stubs and made conductive by sputtering pure osmium (NEOC-AN, Meiwa Shoji Co. Ltd, Japan) on the samples for 30 s at a current of 10 mA.

## 2.3.4. Bench-scale crossflow filtration system

The schematic of the crossflow filtration system is shown in Fig. 2.4 The high pressure membrane filtration cell (Sepa CF II, GE Osmonics, Minnetonka, MN) in a medium/high fouling configuration was pressurized using an external hand pump (P19-1000, SPX powerteam, Rockford, IL). A positive displacement pump (Hydra-cell M-03, Wanner Engineering, Minneapolis, MN) equipped with a flow rate control unit (model MM231001C, Minarik Drive, South Beloit, IL) was used to deliver the feed water to the filtration cell, and a pulsation dampener (Hydra-cell 110-065, Wanner Engineering, Minneapolis, MN) was installed immediately downstream from the pump outlet. A back pressure regulator (BP-3, Circle Seal Controls Inc., Corona, CA) was used to maintain the transmembrane pressure differential at a constant value in the range of  $(10 \pm 5)$  psi ((0.07 ± 0.04) MPa) to (250

 $\pm$  5) psi ((1.72  $\pm$  0.04) MPa). A pressure gauge (111.11, Wika Instruments Ltd., Oakville, ON, Canada) was installed in the retentate line. Two in-line digital flowmeters (101-7, McMillan Co., Georgetown, TX and L-100ccm-D, Alicat Scientific Inc., Tucson, AZ) were used to record the retentate and permeate fluxes every 30 s, respectively.



Figure 2.4. The schematic of the crossflow filtration system

Both permeate and retentate flows were directed back into the feed tank, and small (ca. 10 ml) samples of the feed suspension and the permeate were periodically collected to determine the value of salt rejection. In all colloidal fouling experiments, the retentate flow rate was maintained at  $(1.04 \pm 0.07)$  L/min, which corresponds to a crossflow velocity of ca. 0.1 m/s and a Reynolds number of ca.  $353\pm 24$ . The data from the flowmeters were logged to the computer via a data acquisition module (PCI-6221/SC-2345, National Instruments Corp., Austin, TX). The temperature of the water in the 28.4 L (7.5 US gal) high density polyethylene feed tank (Nalgene

Labware, Rochester, NY) was maintained at  $(20.0 \pm 0.5)$  <sup>o</sup>C using a programmable circulating chiller (model 9512, PolyScience, Niles, IL) with an external temperature probe. The chiller circulated a 1:1 (vol: vol) mixture of distilled water and ethylene glycol through a custom-made stainless steel chilling element immersed in the feed tank. The temperature of the feed suspension was recorded, and the measured values of permeate flux were adjusted based on eq. 2.17 to account for the change in viscosity due to the oscillations of temperature in the (19.5 to 20.5) <sup>o</sup>C range. After each filtration experiment, the retentate and permeate lines of the crossflow system were flushed with detergent solution once and then with deionized (DI) water four times. Equation 2.17 showed the correlation between temperature and permeate flux that we used in the computation.

$$J = J' \cdot \frac{1.777 - 0.052 \cdot (T - 273.15) + 0.000625 \cdot (T - 273.15)^2}{0.987}$$
(2.17)

where J' is measured flux, J is the normalized flux and T is the absolute temperature in the permeate [152].

## 2.3.5. Experimental protocol for crossflow filtration

To make sure that the different PEM membranes and the commercial nanofiltration membrane undergo the same filtration procedures for comparison purposes, each crossflow filtration experiment was carried out in the following stages:

#### Stage 1. Membrane compaction

Ultrapure water was filtered through the membrane for 24 h to ensure that irreversible compaction would not contribute to the flux decline observed in the colloidal fouling experiment. The transmembrane pressure differentials during compaction of membranes were set to exceed the pressures used in the fouling tests (Table 2.2). The impact of the compaction of the UF support on the separation properties of the overlying PEM layer was evaluated in experiments with [PSS/PAH]<sub>4.5</sub> as a representative PEM. It was found that the water permeability and salt rejection were similar for both PEM membranes deposited on compacted and non-compacted PES supports. In view of this result, the PEM membranes used in all the colloidal experiments in this study were prepared by depositing the polyelectrolytes onto uncompacted UF membranes.

Membrane	Transmembrane pressure, $\Delta P$ (psi)	Transmembrane pressure, $\Delta P$ (psi)	Initial permeate flux, J $\cdot 10^{-5}$ (m/s)	Initial specific permeate flux, $J / \Delta P \cdot 10^{-11}$ (m/s/Pa)
	during compaction	during colloidal fouling tests		
[PSS/PDADMAC]4	40	11	2.8	36.3
[PSS/PAH]4	250	215	2.7	1.9
[PSS/PAH]4.5	200	110	3.0	4.0
[PSS/PAH] <sub>2</sub> +[PAA]	120	52	3.1	8.8
[PSS/PAH]2+[PAA/PAH]1.5	200	110	2.8	3.7
NF 270	220	122	2.8	3.3

Table 2.2. Transmembrane pressures and resulting permeate fluxes during SiO<sub>2</sub> filtration by PEM membranes. Also indicated are transmembrane pressures used to compact membranes prior to filtration tests

## Stage 2. Measurement of membrane hydraulic resistance

After compaction, pure water permeate flux was recorded at several transmembrane pressure differentials: 80 psi (0.55 MPa), 120 psi (0.83 MPa), 160 psi (1.10 MPa) and 200 psi (1.38 MPa) for all membranes except [PSS/PDADMAC]<sub>4</sub>. For [PSS/PDADMAC]<sub>4</sub>, a sequence of lower pressures was used: 10 psi (0.07 MPa), 20 psi (0.14 MPa), 30 psi (0.21 MPa) and 40 psi (0.28 MPa). The hydraulic resistance,

 $R_{m0}$ , of the clean membrane to water was determined using linear least squares fitting of  $J(\Delta P)$  from equation 2.18:

$$J = \frac{\Delta P}{\mu R_{m0}} \tag{2.18}$$

## Stage 3. Membrane conditioning and characterization

5 mL of 0.4 M MgSO<sub>4</sub> was added to 20 L of ultrapure water in the feed tank to adjust the magnesium concentration to  $0.1 \cdot 10^{-3}$  M. The pH of the feed water was in the (6.1-6.6) range. Membranes were conditioned by filtering the electrolyte at the same pressure used in the 24 h water compaction stage (stage 1) until the permeate flux stabilized (ca. 20 h). When the permeate flux became stable after approximately 20 h of conditioning, the transmembrane pressure was changed in increments to achieve different permeate fluxes, J. During this process, permeate and feed water samples were periodically collected to determine values of the MgSO<sub>4</sub> rejection for a series of different values of J. At the end of conditioning, the transmembrane pressure differential needed to achieve a permeate flux of  $(2.8\pm0.2)\cdot10^{-5}$  m/s was determined for subsequent use in the colloidal fouling experiment. Setting the initial permeate flux to the same value in all colloidal fouling tests ensured the same initial colloid deposition conditions in experiments covering membranes with different values of water permeability,  $L_p$ .

# Stage 4. Membrane fouling experiments

15 g of SiO<sub>2</sub> ST-ZL stock solution was added into the 20 L of feed electrolyte to

achieve a colloid loading of 300 mg/L. Crossflow filtration of the colloid-containing solution was then carried out for 20 h at the pressure determined in stage 3 to give an initial flux of  $(2.8\pm0.2)\cdot10^{-5}$  m/s. Small amounts of permeate and feed water were collected periodically to determine observed MgSO<sub>4</sub> rejection,  $R_{obs}$ . Each filtration experiment was conducted twice, and the flux profiles for the two membranes were reproducible with a maximum deviation of 11%.

## Stage 5. PEM regeneration and backflushing test

PEM removal and regeneration tests were performed with [PSS/PAH]<sub>4</sub> and [PSS/PAH]<sub>4.5</sub> membranes only. To remove the PEMs from the UF support, the PEM-coated support was immersed for 10 min in a pH 10 buffer solution containing 0.060 M Na<sub>2</sub>CO<sub>3</sub> and 0.596 M NaHCO<sub>3</sub>. To evaluate the influence of colloidal deposition on the efficiency of PEM regeneration, both as-prepared and fouled PEM membranes were immersed in the buffer solution. Backflushing step was added prior to chemical treatment step to assist the regeneration of a new PEM film on a fouled PEM membrane. The experimental procedure was described as follows: i) membranes were placed upside down in the membrane cell and backflushed with water for 1 h at an applied pressure differential that was 30 psi higher than that used in the preceding fouling experiments; ii) membranes were then soaked in the buffer solution and rinsed with water; and iii) finally a new PEM was applied to the surface of the cleaned membrane using the same layer-by-layer procedure as before. After each step of the modified regeneration procedure, the hydraulic resistance and MgSO<sub>4</sub> rejection were measured.

# 2.4. Results and discussion

2.4.1. Charge, hydrophilicity, and water permeability of PEM membranes

As discussed in section 1.1.2, PEM technology provides a simple way to vary the membrane surface chemistry in terms of surface charge, hydrophobicity and swellability. Meanwhile, this alternation also allows membranes to have different filtration properties such as salt rejection and water permeability.

Table 2.3 summarizes properties of the five PEM membranes and the commercial nanofiltration membrane (NF270) employed in this study. Both, the hydrophilicity and the surface charge of PEM membranes were primarily determined by the choice of the terminating polyelectrolyte and the ionic strength of the polyelectrolyte deposition solution (Table 2.1). As expected, terminating the polyelectrolyte film with a polycation (PAH or PDADMAC) produced a PEM with a positive surface charge, while terminating the film with a polyanion (PSS or PAA) resulted in a negative surface charge. To maximize the magnitude of the surface charge of the PEMs, the terminating layer was deposited from a solution with a high ionic strength (2.5 mol/L) for all membrane types except [PSS/PDADMAC]<sub>4</sub>. The reason we don't use high ionic strength for [PSS/PDADMAC]<sub>4</sub> film is that the film gets dissociable at ionic strength that is higher than 0.6 mol/L [131].

Additionally, Table 2.3 shows variations in the water contact angle among both positively and negatively charged PEM films. Notably, one PEM membrane, [PSS/PAH]<sub>2</sub>+[PAA/PAH]<sub>1.5</sub>, was more hydrophilic and more negatively charged than the commercial NF270 membrane.

Membrane	a Contact angle , θ (°)	Streaming potential, $\zeta_m$ (mV)	b Hydraulic resistance , $R_{m0}$ , $\cdot 10^{13}$ (m <sup>-1</sup> )
[PSS/PDADMAC]4	76 ± 6	21.4 ± 0.9	0.27 ± 0.09
[PSS/PAH]4	34 ± 3	$13.4 \pm 0.3$	4.3 ± 0.7
[PSS/PAH]4.5	36 ± 2	$-10.8 \pm 0.7$	$2.9 \pm 0.4$
[PSS/PAH]2+[PAA]	27 ± 4	$-0.9 \pm 0.6$	$0.84 \pm 0.32$
[PSS/PAH]2+[PAA/PAH]1.5	20 ± 3	-7.7 ± 0.3	3.6 ± 1.1
NF 270	$29 \pm 3$	-6.1 ± 0.5	$2.5 \pm 0.2$

Table 2.3. Surface and transport properties of the membranes

a Contact angle for a water droplet on the membrane surface.

<sup>b</sup> The hydraulic resistance of the 50 kDa ultrafiltration membrane used as the support for PEM membranes was ca.  $R_{m0} = 0.1 \times 10^{13} \text{ m}^{-1}$  after compaction.

Varying the composition of PEMs also modifies the water permeabilities of these films. For example, PDADMAC-terminated coatings are known for their propensity to swell [127,153], so [PSS/PDADMAC]<sub>4</sub> films show the highest permeability to water (Table 2.3) of all PEMs studied. The number of deposited layers also affects flux as shown by a comparison of [PSS/PAH]<sub>2</sub>+[PAA/PAH]<sub>1.5</sub> and [PSS/PAH]<sub>2</sub>+[PAA] films (Table 2.3).

We also evaluated the surface energy components (Table 2.4) of different membranes based on the contact angle experiments with three different probing liquids. The high contact angle correlates to the high hydrophobicity of the [PSS/PDADMAC]<sub>4</sub> film. The investigation of surface energy components for different membranes showed that [PSS/PDADMAC]<sub>4</sub> has a low value of the electron donor component of free energy ( $\gamma^-$ ), which is due to the high hydrophobicity of

# PDADMAC polymer.

	Surface energy, mJ/m <sup>2</sup>				
	γ <sup>LW</sup>	γ+	γ <sup>-</sup>	γ <sup>AB</sup>	$\gamma^{TOT}$
Probe liquid	L	L	L	L	
Ultrapure water	21.8	25.5	25.5	51.0	72.8
Glycerol	34.0	3.9	57.4	30.0	64.0
Diiodomethane	50.8	0.0	0.0	0.0	50.8
Membranes	L		L	L	- <b>-</b>
NF270	43.52	0.25	50.43	7.03	50.56
[PSS/PDADMAC]4	46.12	0.01	8.94	0.64	46.76
[PSS/PAH] <sub>4</sub>	48.30	0.40	41.68	8.13	56.43
[PSS/PAH] <sub>4.5</sub>	48.71	1.08	33.12	11.95	60.66
[PSS/PAH] <sub>2</sub> +[PAA]	48.22	0.04	51.55	2.74	50.97
[PSS/PAH] <sub>2</sub> +[PAA/PAH] <sub>1.5</sub>	49.54	0.00	55.75	0.07	49.61

Table 2.4. Surface energy of probe liquids and different membranes

## 2.4.2. Determining the salt permeability coefficient of PEM membranes

PEM membranes are used as nanofiltration membranes, therefore, the salt permeability of such membranes is important from the point of desalination applications. Here we use the Sherwood correlation and thin film model to compute the intrinsic rejection as a function of transmembrane pressure.

Expectedly, the *intrinsic* rejection,  $R_{in}$ , increased with an increase in the

transmembrane pressure and the corresponding increase in the permeate flux (Fig. 2.5 (a)), although the observed rejection,  $R_{obs}$ , decreased with an increase in the permeate flux for NF270 and all the PEM membranes (Fig. 2.5 (b)). This indicates that a higher  $R_{obs}$  can be achieved under a lower concentration polarization condition by lowering the permeate flux [127], or adding a spacer onto the membrane to create turbulent flow and thus reduce concentration polarization [132]. The increase of  $R_{in}$  with higher flux is due to an increase in the amount of water, relative to the amount of salt, transported across the membrane at higher transmembrane pressures. When considering observed rejection, its decrease with an increase in the transmembrane pressure was due to the overcompensation of the better intrinsic rejection at higher permeate fluxes by the higher concentration polarization that led to a higher salt concentration gradient across the membrane and, consequently, higher salt flux.



Figure 2.5. Intrinsic (a) and observed (b) rejection of MgSO<sub>4</sub> by NF270 and five PEM membranes as a function of permeate flux during filtration of colloid-free MgSO<sub>4</sub> electrolyte.

The MgSO<sub>4</sub> permeability coefficient,  $P_s$ , of all membranes decreased with an

increase in the MgSO<sub>4</sub> concentration near the membrane surface,  $C_m$  (Fig. 2.6).

This decrease in  $P_s$  somewhat mitigated decreases in the observed rejection due to the concentration polarization. The concentration dependence of the MgSO<sub>4</sub> permeability coefficient for NF270 was reported earlier by Al-Zoubi et al. [148]; in that paper  $P_s$  was reported to increase with increasing MgSO<sub>4</sub> concentration, which is opposite to what we observed in our experiments. In our work,  $0.19 < \tau < 0.83$  for all membranes, including NF270, for which  $\tau \approx 0.42$ .



Figure 2.6. Dependence of the MgSO<sub>4</sub> permeability coefficient on MgSO<sub>4</sub> concentration at the membrane surface for NF270 and five PEM membranes.

For all membranes, the values of  $R_{in}$  determined for successively higher transmembrane pressure differentials,  $\Delta P$ , asymptotically converged to a value close to 1 (Fig. 2.5), indicating that the reflection coefficient,  $\sigma$ , was close to 1. Although the permeability of PEM membranes with respect to MgSO<sub>4</sub> was higher than that of the NF270 membrane (Fig. 2.6), PEM membranes were highly selective  $(\sigma \approx 1)$  so that nearly complete MgSO<sub>4</sub> rejection by the membranes could in principle be achieved at sufficiently high fluxes if concentration polarization could be minimized.

Fig. 2.7 shows experimentally determined and fitted concentration dependence  $(C_m)$  of the salt permeability coefficient  $(P_s)$  and G ratio for each membrane. The grey areas indicate the range of  $C_m$  where  $P_s(C_m)$  correlations were applied in computing  $C_m$  in corresponding colloidal fouling stage. Under the concentration polarization conditions observed in our colloidal fouling experiments, G ratio (eq. 2.15) is relatively low:  $G \le 0.1$  for all membranes except [PSS/PAH]<sub>4</sub> and  $[PSS/PAH]_2 + [PAA/PAH]_{1.5}$ , for which  $G \le 0.2$ . Because  $R_{in}^{max}$  provides the lower bound for  $\sigma$ , the above values are *upper* bounds for G values for different membranes; the true G values are even smaller. Therefore, the second term in eq. 2.14 is small in comparison with the first term and the error introduced into the computed salt permeability coefficient  $P_s = P_s(C)$  dependence is at most 17%. The maximum error would occur if  $\sigma$  is in reality 1 for the highest values of G. It should be noted that by approximating  $(1-\sigma)J\overline{C}$  as  $(1-R_{in}^{\max})J\overline{C}$  we over-estimated this term and, therefore, under-estimated  $P_s$  (see Fig. 2.6).





Figure 2.7. Experimentally determined (symbols) and fitted (lines) concentration

# dependence $(C_m)$ of the salt permeability coefficient $(P_s)$ and G ratio (see equation 2.15) for each membrane.

2.4.3. Rejection and permeate flux in colloidal fouling experiments: overall comparative assessment of NF270 and PEM membranes

Figure 2.8 summarizes values of specific permeate flux, MgSO<sub>4</sub> rejection, and concentration polarization factor for all membranes before and after they were fouled by SiO<sub>2</sub> colloids. Several general observations can be made regarding the flux and rejection performance of NF270 and PEM membranes during the filtrations of a simple salt solution followed by a complicated aqueous mixture of salt and colloids:

1) Initially, NF270 membranes exhibited the highest rejection (Fig. 2.8 (b)) because of the low MgSO<sub>4</sub> permeability of NF270 (Fig. 2.6,) and the relatively low value of the initial permeate flux (ca. 100  $L/m^2/h$ ) set for all membranes (Fig. 2.6). As discussed above, at higher fluxes, rejection of PEM membranes greatly increases.

2) [PSS/PDADMAC]<sub>4</sub> stood out as a membrane with the highest specific permeate flux (Fig. 2.8 (a)), which was due in part to the high hydraulic permeability of this membrane (Table 2.3) and in part due to its high permeability to MgSO<sub>4</sub> (Fig. 2.6) and the resulting low osmotic pressure.

3) Although there were significant differences between different membranes in the salt rejection initially (Fig. 2.8 (b)), it is evident that these differences evened out after 20 h of colloidal fouling.

4) Remarkably, the observed salt rejection of all PEM membranes (except for [PSS/PAH]<sub>4</sub>) fouled by colloids was higher than that of the same membrane before colloidal fouling occurred (Fig. 2.8 (b)). This improvement in rejection was

accompanied by a decrease in concentration polarization for those membranes (see Fig. 2.8 (c)). The most attractive PEM film is the [PSS/PDADMAC]<sub>4</sub> membrane. With respect to NF270, the [PSS/PDADMAC]<sub>4</sub> membrane's combination of comparable rejection and superior specific permeate flux clearly indicates that a membrane with highly beneficial properties is formed as a result of deposition of negatively charged colloids onto the surface of the [PSS/PDADMAC]<sub>4</sub> film (Fig.







Figure 2.8. Steady state values of the specific permeate flux (a), observed MgSO<sub>4</sub> rejection (b), and concentration polarization factor (c) for membranes before fouling (ca.  $J=2.8 \times 10^{-5}$  m/s) and after fouling with SiO<sub>2</sub> colloids.

Note that the initial rejection values are given for the initial permeate flux that varied only very slightly (27 m/s to 31 m/s) from one membrane to another (Table 2.2). The permeate flux after fouling (i.e. t = 20 h) was approximately the same (ca. 40% of the initial permeate flux) for all membranes expect for [PSS/PDADMAC]<sub>4</sub> and [PSS/PAH]<sub>2</sub>+[PAA]. For the latter two membranes, the flux after colloidal fouling was ca. 20% of the initial value. This has to be taken into account when comparing observed rejections of different membranes at 20 h.

2.4.4. Membrane performance in colloidal fouling experiments: Transient behavior of permeate flux, MgSO<sub>4</sub> rejection, and cake resistance

The effect of membrane fouling on different PEM membranes was evaluated together with the fouling effect on a commercial nanofiltration membrane under the same feed water and hydraulic conditions.

Figure 2.9 illustrates the transient behavior of normalized permeate flux, J, observed salt rejection,  $R_{obs}$ , and colloidal cake resistance,  $R_d$ , in colloidal fouling

experiments. (The non-normalized values of the initial and final permeate flux are given in Fig 2.8a.) Permeate flux and rejection data were recorded experimentally, while the  $R_d$  values were calculated after the contribution of the cake-enhanced osmotic pressure to the overall flux decline was accounted for.





Figure 2.9. Transient behavior of the normalized permeate flux (a), observed MgSO<sub>4</sub> rejection (b) and colloidal cake resistance (c) in experiments on the filtration of SiO<sub>2</sub> colloids.

There are two considerations that need to be taken into account when analyzing the data presented in Fig. 2.9.

i) Because a higher rejection results in higher osmotic pressures, the temporal evolution of the permeate flux should be interpreted together with the rejection data. In turn, the observed rejection is a function of the salt concentration at the membrane surface, which depends on the amount of deposited colloids brought to the membrane. At the same time, the rate of colloidal deposition depends on the permeate flux. Thus, the dynamics of all three variables - J,  $R_{obs}$ , and  $R_d$  - are interdependent and should be analyzed together.

ii) Only at the very early stages of the fouling experiments is the unfouled membrane surface exposed to the permeate flow. With the formation of a layer of colloidal particles on the membrane, the properties of the surface (charge and hydrophilicity) with which depositing colloids interact will be the properties of the already deposited colloids, and not properties of the as-prepared membranes.

(c)

Generally speaking, the membranes fell into two categories: (i) membranes with anticipated MgSO<sub>4</sub> rejection behavior wherein the rejection decreased with the growth of the colloidal cake (NF270, [PSS/PAH]<sub>4</sub>) and (ii) membranes with Mg rejection that increased with filtration time ([PSS/PDADMAC]<sub>4</sub>, [PSS/PAH]<sub>4.5</sub>, [PSS/PAH]<sub>2</sub>+[PAA], and [PSS/PAH]<sub>2</sub>+[PAA/PAH]<sub>1.5</sub>).

# Performance of NF270, [PSS/PAH]4\_

For NF270 and [PSS/PAH]<sub>4</sub> membranes, MgSO<sub>4</sub> rejection decreased with filtration time as expected (Fig. 2.9 (b)). This decrease in observed rejection was due to (i) the decrease in the permeate flux (Fig. 2.9 (a)) and (ii) cake-enhanced concentration polarization (Fig. 2.10 (a)). The concentration polarization factor,  $\frac{C_m}{C_f}$ , was

calculated as described in section 2.2.  $\frac{C_m}{C_f}$  for these two membranes increased

significantly at first and then gradually declined to partially offset the initial increase (Fig. 2.10 (a)); the corresponding trend in observed rejection (Fig. 2.9 (b)) is consistent with the behavior reported earlier for LFC-1 [132,150,151] and BW30 [132,150,151] reverse osmosis membranes fouled by  $SiO_2$  colloids. In experiments with  $SiO_2$  colloids, the concentration polarization factor for NF270 was ca. 15 times higher than that for the [PSS/PAH]<sub>4</sub> membranes after 20 h of colloidal filtration.



Figure 2.10. Evolution of the concentration polarization factor during filtration of SiO<sub>2</sub> suspensions by different membranes.

In experiments with  $SiO_2$  colloids, the observed salt rejection of NF270 was significantly higher than that of [PSS/PAH]<sub>4</sub> during the initial stages of filtration (Fig. 2.9 (b)), which explains the more than 15-fold higher polarization factor for NF270 during the early stages of the experiment (Fig. 2.10 (a), t < 5 h). During the filtration stage that followed, however, the rejection of all membranes was similar and yet the polarization factor of NF270 was still up to 15 times higher than that of the [PSS/PAH]<sub>4</sub> membrane (Fig 2.10). Considering that the resistance of the cake formed on the membrane surface is higher for [PSS/PAH]<sub>4</sub> than that for NF270 (Fig. 2.9 (c)), the large difference in the polarization factor can not be explained solely in terms of colloid and MgSO<sub>4</sub> transport. We hypothesize that the deposition of colloids alters the structure of the PEM film so that the extra resistance to the permeate flux due to the deposited colloids translates into a smaller increase in concentration polarization than for the more crosslinked commercial membranes such as NF270. It is possible that such changes in the membrane structure entail changes in the salt permeability coefficient  $P_s = P_s(C)$  dependence (Fig. 2.5), in which case the results on the concentration polarization factor (Figures. 2.8 c and 2.10) and resistance of colloidal deposit (Fig. 2.9 (c)) for PEM membranes would need to be interpreted with caution.

In evaluating flux and observed rejection data (Fig, 2.9 (a), (b)), one can see that, at steady state, the performance of the [PSS/PAH]<sub>4</sub> membrane under conditions of fouling by SiO<sub>2</sub> colloids is very similar to that of the NF270 membrane. Given the possible regeneration of PEM membranes, the [PSS/PAH]<sub>4</sub> films might provide an nanotechnology assisted alternate for controlling fouling by negatively charged colloids.

# Performance of [PSS/PAH]<sub>2</sub>+[PAA], [PSS/PAH]<sub>2</sub>+[PAA/PAH]<sub>1.5</sub>, and

## [PSS/PDADMAC]<sub>4</sub>, [PSS/PAH]<sub>4.5</sub> membranes

The second category of membranes consists of the positively charged [PSS/PDADMAC]<sub>4</sub>, neutral [PSS/PAH]<sub>2</sub>+[PAA], charged and negatively [PSS/PAH]<sub>4.5</sub> and [PSS/PAH]<sub>2</sub>+[PAA/PAH]<sub>1.5</sub> membranes. The rejections of these four PEM membranes unexpectedly increased with filtration time. Furthermore, for these membranes the calculated concentration polarization factor decreased with the filtration time. For [PSS/PDADMAC]<sub>4</sub> (and, at the very end of filtration, for [PSS/PAH]<sub>2</sub>+[PAA/PAH]<sub>1.5</sub>) the concentration polarization factor, computed assuming a constant  $P_s(C_m)$  dependence, was found to decline over the time of filtration to below 1, which is in the domain of unphysical values (Fig. 2.10 (b)). We attribute this phenomenon to the possible decrease of the salt permeability coefficient Ps with the deposition of significant amount of SiO<sub>2</sub> colloids onto the PEM surface or even inside the PEM film. The  $P_s(C_m)$  correlation was examined with [PSS/PDADMAC]<sub>4</sub> membrane that is covered by only a submonolayer of SiO<sub>2</sub> colloids. In this case, there was no evidence showing significant changes in  $P_s(C_m)$ on the same type of PEM film after it was covered with SiO<sub>2</sub> deposition purely by adsorption.

Generally, for a net depositional system such as a membrane filter, prior to the attainment of steady state flux, the trend of increasing rejection with time can not be explained without invoking changes in the membrane properties. A modification of the salt-rejecting properties of these membranes due to changes in the PEM structure upon colloidal deposition is a likely explanation of such a trend. Thus, the above results bring into question the model's basic assumption that the membrane transport coefficients remain unchanged with time.

We hypothesize that a PEM-colloid nanocomposite is formed on the UF support surface during colloidal filtration. This hypothesis is based on the anomalous behavior of rejection and concentration polarization factors as well as on the observations that PEM films can swell. PDADMAC-capped [PSS/PDADMAC]<sub>4</sub> films in water have a swollen thickness of ca. 100 nm [153], which is comparable to the diameter of SiO<sub>2</sub> particles and could allow the particles to be embedded inside the PEMs. In this regard, it is interesting to note that during colloidal filtration [PSS/PDADMAC]<sub>4</sub> exhibited the most rapid flux decline among the six membranes, but the increase in cake resistance was not as rapid as it was for the other membranes, resulting in the lowest steady state  $R_d$  value among all membranes. One possible reason for the improved rejection by such PEM-colloid nanocomposite films is that the colloids create a charged layer that contributes to rejection.

# 2.4.5. Regeneration of [PSS/PAH]<sub>4</sub> and [PSS/PAH]<sub>4.5</sub> films

PAH becomes weakly charged at high pH and thus dissociation of multilayers composed of [PSS/PAH] (and, thereby, removal of the PEM from the UF support [153,154]) can be achieved by increasing the pH of the external solution [126,131,155]. PEMs can potentially then be re-deposited (i.e. *regenerated* at the support surface) from low pH solutions. The removal of 1) as-deposited and 2) colloid-fouled [PSS/PAH]<sub>4</sub> or [PSS/PAH]<sub>4.5</sub> PEM films from the UF support was monitored by recording changes in hydraulic resistance,  $R_m = (\mu \cdot L_p)^{-1}$ , and observed salt rejection,  $R_{obs}$ , of the membrane at different steps of the regeneration

# procedure (Fig. 2.11).



Figure 2.11. Hydraulic resistance (R<sub>m</sub>) and observed salt rejection (R<sub>obs</sub>) values of a UF 50 kDa support before (1) and after the following sequential steps: (2) modification by a PEM; (3) fouling by SiO<sub>2</sub> colloids for 20 h; (4) backflushing with water for 1 h; (5) soaking in pH 10 buffer for 10 min; (6) redeposition of a PEM layer. (In cases where no data are visible, corresponding steps were omitted.) PEM membranes employed included (a) as prepared [PSS/PAH]<sub>4.5</sub>; (b) a [PSS/PAH]<sub>4.5</sub> film with SiO<sub>2</sub> filtration and backflushing prior to soaking in pH 10 buffer.

After soaking as-prepared PEM membranes (Fig. 2.11 (a);  $[PSS/PAH]_{4.5}$  membrane) in the pH 10 buffer solution (step 5 in Fig. 2.11 (a)), the values of  $R_m$  and  $R_{obs}$  both decreased to the level typical of the UF membrane (step 1 in Fig. 2.11 (a)), suggesting removal of the polyelectrolyte film. (Note that the relatively low

values of observed rejection by the PEM membranes are due to concentration polarization.) Reapplication of the PEM (step 6) returned  $R_m$  and  $R_{obs}$  to nearly the levels characteristic of an as-prepared PEM-coated membrane. The same procedure was followed with [PSS/PAH]<sub>4.5</sub> and [PSS/PAH]<sub>4</sub> membranes fouled by SiO<sub>2</sub>, it seems that the fouling did inhibit the regeneration of PEMs by the low values of  $R_m$  and  $R_{obs}$  after step 6 (data not shown). Therefore, the simple soaking of the fouled membrane in the buffer solution apparently is not sufficient to completely remove the PEMs and the foulants. SEM images taken for this membrane after step 6 (Fig. 2.12) confirm the presence of residual SiO<sub>2</sub> colloids on the membrane surface and offer further evidence that regeneration by soaking alone was not succesful for [PSS/PAH]<sub>4.5</sub> and [PSS/PAH]<sub>4</sub> fouled by SiO<sub>2</sub>.



Figure 2.12. SEM images of membranes at the different steps described in section 2.3.5: (a) UF 50 kDa support (step 1); (b) after the UF support was modified by [PSS/PAH]<sub>4.5</sub> (step 2); (c) after the membrane was fouled by SiO<sub>2</sub> for 20 h (step 3); (d) after the SiO<sub>2</sub>-fouled [PSS/PAH]<sub>4.5</sub> membrane was soaked in pH 10 buffer and regenerated with a new PEM.

The backflushing step greatly improved the efficiency of PEM regeneration (Fig. 2.11 (b), step 6). The membranes were backflushed with ultrapure water (step 4 in Fig. 2.11 (b); [PSS/PAH]<sub>4.5</sub> membrane) to remove [PSS/PAH]<sub>4.5</sub> films from membranes severely fouled by SiO<sub>2</sub> colloids (300 mg (SiO<sub>2</sub>)/L, 20 h filtration). After backflushing-assisted PEM removal and PEM regeneration, the value of  $R_m$  returned to the level characteristic of an as-prepared PEM membrane. The value of  $R_{obs}$  increased as well although only to about 50% of the rejecting capability of an

as-prepared PEM membrane. While the composition of the soaking solution and backflushing duration need to be optimized to improve the efficiency of regeneration, the demonstrated feasibility of backflushing points to the possibility of using PEM films as regenerable nanofiltration coatings with controllable charge, hydrophilicity, and permeability.

# 2.5. Conclusions

By choosing constituent polyelectrolytes and by adjusting the conditions of their deposition, supported PEM membranes with controllable surface charge, hydrophilicity and permeability to water and salt were designed and characterized in terms of their ion transport properties and resistance to colloidal fouling. It was found that:

- 1. Highly hydrophilic and charged PEMs can be designed.
- 2. The designed nanoscale PEM membranes were highly selective and could achieve nearly complete intrinsic rejection of MgSO<sub>4</sub> at sufficiently high fluxes, which is also indicated by the fact that reflection coefficient of PEM membranes were estimated to be close to 1.
- 3. Salt permeability coefficients of NF270 and all PEM membranes exhibited power law dependence on concentration:  $P_s = C_m^{-\tau}$ ,  $0.19 < \tau < 0.83$ .
- Under the highly fouling conditions employed in this study, certain PEMs
  ([PSS/PAH]<sub>4</sub>) had steady-state performance similar to that of the commercial
  NF270 membranes, especially in the longer term (> 5 h)
- 5. The separation properties of certain PEMs improved dramatically with the deposition of colloids onto their surface. For these membranes, the

concentration polarization decreased and MgSO<sub>4</sub> rejection increased with an increase in the amount of deposited colloids. We hypothesize that a PEM-colloid nanocomposite was formed on the UF support surface as a result of colloidal fouling of the PEM film.

6. The feasibility of regenerating the PEM coating with "snake skin effect" has been demonstrated. Although regeneration of highly fouled membranes by soaking alone was inhibited by the incomplete removal of deposited colloids, an additional backflushing step resulted in an almost complete removal of the fouled PEMs and enabled reassembly of a PEM film with permeabilities similar to those of the initial PEM membrane but with 50% lower rejection capacity.

In summary, ultrathin PEM membranes prepared using the layer-by-layer deposition method showed high salt selectivity, high water flux and could be regenerated under appropriate conditions. Such membranes can potentially be designed to use in many different membrane applications where the characteristics of high ion selectivity, anti-adhesive surface properties and regenerability of the separation layer are desirable.
# Chapter 3. Interactions of aqueous NOM with nanoscale TiO<sub>2</sub>: Implications for ceramic membrane filtration-ozonation hybrid process

This work was done in collaboration with Dr. Jeonghuan Kim *et al.*, and has been published in the Environmental Science and Technology journal [156].

## 3.1. Introduction

 $TiO_2$  is one of the most abundant, man-made, and commercially available nanoparticles. It has been applied to pharmaceutical products, personal care products and auto parts. Nanoscale  $TiO_2$  particles have also been used to fabricate nanocomposite membranes [43,157-159] and used as catalysts in advanced oxidation processes [160-166]. In previous work, Kim *et al.* used  $TiO_2$  ceramic membranes that are resistant to oxidation by ozone to act as a catalyst for the decomposition of ozone into highly reactive OH-radicals that can react with deposited NOM and thus mitigate fouling [166].

The reason why it is important to control NOM fouling is that NOM has been identified as a major foulant especially in nanofiltration of drinking water treatment [167-171]. NOM is of great concern in water treatment systems because it is ubiquitous in the environment and is known to react with chlorine, the most commonly used disinfectant in the U.S., to form carcinogenic chlorinated compounds [172]. It has been suggested that ultrafiltration and nanofiltration can be effective in removing NOM; however, in most cases, extensive NOM fouling limits membrane performance significantly. To understand how to prevent or mitigate NOM fouling of membranes, a better understanding of the NOM fouling mechanisms is needed; therefore, studies of NOM-membrane interaction are of significant practical relevance to membrane filtration. A number of previous studies describe NOM fouling of polymeric membranes in terms of the surface charge and molecular conformation of the NOM which is controlled largely by solution properties, such as pH and ionic strength [173,174]. The strong dependence on the water environment was also observed in the TiO<sub>2</sub>-NOM adsorption and TiO<sub>2</sub> ceramic membrane filtration in this study [156].

On the other hand, the investigation into such interactions is very important from the perspective of environmental implications of nanotechnology; this is so because 1)  $TiO_2$  nanoparticles find increasingly wide usage in various technologies and therefore, are very likely to enter natural water systems; 2) NOM is a common component in natural water; 3) NOM is known to easily adsorb at solid surfaces in water and consequently this adsorption modifies the surface with a different charge and hydrophilicity [175-178]; and 4) one type of NOM – humic acid was reported to be effective in stabilizing aqueous nanoparticle suspensions [179,180]. Therefore, by understanding the interaction between NOM molecules and TiO<sub>2</sub> nanoparticles, we will be able to understand the resultant structure, surface properties, stability, and fate/transport of TiO<sub>2</sub> in natural water.

To summarize, the specific objectives of this work were: 1) experimentally characterize  $TiO_2$  nanoparticles and (ozonated and non-ozonated) NOM with respect

to hydrophobicity and size distribution; 2) analyze NOM-TiO<sub>2</sub> interactions under different water chemistries using XDLVO modeling. With the modeling study of the interaction, we would understand the mechanism in improved filtration performance with hybrid ozonation TiO<sub>2</sub> catalytic ceramic membrane filtration. It should also give us clues to understanding the behavior of TiO<sub>2</sub> nanoparticles when they enter natural water and interact with NOM under different chemical conditions.

## 3.2. Approach

The extended DLVO (XDLVO) theory predicts the energy of particle-particle and particle-surface interaction [106,181,182]. The XDLVO model has been applied to describe how aqueous colloids interact with surfaces of polymeric membranes [183-185]. When a particle is suspended at a close affinity to another particle or interface, besides gravity and hydrodynamic forces acting on that particle, particles also experience non-covalent forces that include van der Waals forces ( $F_{LW}$ ), electrostatic double layer forces ( $F_{EL}$ ), and Lewis acid-base forces ( $F_{AB}$ ) exerted by the other particle or interface. XDLVO is an extended DLVO model wherein acid-base (polar) interactions are also taken into consideration. Incorporation of the polar interactions has been shown to result in a significant change in the predicted energies of *short range* (< 5 nm) particle-particle and particle-surface interactions.

In this work we determine the interaction energy (free energy of adhesion) per unit area between two planar surfaces with surface tension parameters and charges of NOM and  $TiO_2$ . Although the model does not take into the account the size distribution of NOM molecules and the likely differences in hydrophilicity and charge between various size fractions of NOM, this approach should adequately describe effects, averaged NOM sizes, of ozonation-, pH-, and calcium induced changes in NOM chemistry on the NOM-TiO<sub>2</sub> interactions.

The free energy of adhesion between two materials (NOM, N and  $TiO_2$ , T) immersed in a liquid (water, W) due to van der Waals forces is calculated as follows [186]:

$$\Delta G_{y_0}^{LW} = 2 \left( \sqrt{\gamma_w^{LW}} - \sqrt{\gamma_T^{LW}} \right) \cdot \left( \sqrt{\gamma_N^{LW}} - \sqrt{\gamma_w^{LW}} \right)$$
(3.1)

where  $\gamma_w^{LW}$ ,  $\gamma_T^{LW}$ , and  $\gamma_N^{LW}$  are LW components of the surface tension for water, the TiO<sub>2</sub> nanoparticles, and NOM molecules respectively. Here,  $\Delta G_{y_0}^{LW}$  is the LW

free energy of adhesion between a TiO<sub>2</sub> nanoparticle and an NOM molecule that are at a distance of  $y_0$ , which is the minimum equilibrium cut-off distance and is usually assigned a value of 0.157 nm [186].

The free energy of adhesion between a  $TiO_2$  particle and NOM molecules due to EL (electrostatic) interaction can be estimated using the following expression [187]:

$$\Delta G_{y_0}^{EL} = \varepsilon_0 \varepsilon \cdot \zeta_N \zeta_T / \lambda_{EL}$$
(3.2)

where  $\lambda_{EL} = (3.28 \times 10^9 \sqrt{C_{el}})^{-1}$ ,  $\varepsilon_r \varepsilon_0$  is the dielectric permittivity of the bulk fluid;  $\zeta_N$  and  $\zeta_T$  are surface potentials of NOM molecules and TiO<sub>2</sub> nanoparticles,

respectively;  $C_{el}$  is the concentration of the background electrolyte in mol/L;  $\lambda_{EL}$  is

the characteristic decay length for EL interactions in water.

The free energy of adhesion per unit area between two different materials immersed in the same liquid due to acid-base (AB) interaction is given by:

$$\Delta G_{h_0}^{AB} = 2\sqrt{\gamma_w^+} \left(\sqrt{\gamma_T^-} + \sqrt{\gamma_N^-} - \sqrt{\gamma_w^-}\right) + 2\sqrt{\gamma_w^-} \left(\sqrt{\gamma_T^+} + \sqrt{\gamma_N^+} - \sqrt{\gamma_w^+}\right) -2\left(\sqrt{\gamma_T^+\gamma_N^-} + \sqrt{\gamma_T^-\gamma_N^+}\right)$$
(3.3)

where  $\gamma^+$  is the electron acceptor component and  $\gamma^-$  is the electron donor component of the free energy. The surface tension parameters of NOM molecules  $\gamma_N^+$ ,  $\gamma_N^-$ ,  $\gamma_N^{AB}$ ,  $\gamma_N^{LW}$ ,  $\gamma_N^{TOT}$ ) and TiO<sub>2</sub> nanoparticles ( $\gamma_T^+$ ,  $\gamma_T^-$ ,  $\gamma_T^{AB}$ ,

 $\gamma_T^{LW}$ ,  $\gamma_T^{TOT}$ ) can be determined from the extended Young equation after measuring contact angle data for three probe liquids with known surface tension parameters ( $\gamma_l^{LW}$ ,  $\gamma_l^+$ ,  $\gamma_l^-$ )

$$(1+\cos\theta)\gamma_l^{TOT} = 2\left(\sqrt{\gamma_s^{LW}\gamma_l^{LW}} + \sqrt{\gamma_s^+\gamma_l^-} + \sqrt{\gamma_s^-\gamma_l^+}\right)$$
(3.4)

$$\gamma^{AB} = 2\sqrt{\gamma^+ \gamma^-} \tag{3.5}$$

$$\gamma^{TOT} = \gamma^{AB} + \gamma^{LW} \tag{3.6}$$

where  $\theta$  is the contact angle for a given probe liquid. The subscripts s and l correspond to the solid surface and the liquid, respectively.

## 3.3. Material and methods

#### 3.3.1. Materials

TiO<sub>2</sub> particles (TiO<sub>2</sub> nanopowder, <100 nm (BET), mixture of rutile and anatase, 99.9% metals basis, Aldrich) were used as received. Suwannee River NOM (SRNOM), isolated by reverse osmosis, was purchased from International Humic Substances Society (Denver, CO). A 20 mg/L colloidal suspension of SRNOM was prepared by dispersing the SRNOM in deionized (DI) water. The total organic carbon (TOC) content of the SRNOM feed solution was  $10 \pm 0.5$  mg C/L. The pH of the solution was adjusted by adding either HCl or NaOH and a borate (0.0625 mmol/L) buffer solution. The borate buffer was prepared by mixing aqueous solutions of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O (100 mL, 0.025 M) and HCl (41 mL of 0.1 M). Prior to each filtration experiment, the total ionic strength of the solution was adjusted to 7.5·10<sup>-3</sup> M using 10<sup>-2</sup> M NaCl.

#### 3.3.2. Characterization of NOM molecules and TiO<sub>2</sub> nanoparticles

Contact angle measurements were conducted to determine the hydrophobicity of nonozonated SRNOM molecules, ozonated SRNOM molecules and TiO<sub>2</sub> nanoparticles, The TiO<sub>2</sub>, non-ozonated SRNOM and ozonated NOM suspensions were filtered through 1 kDa polyethersulfone UF membranes (Pall Corp., East Hills, NY) using a stainless steel filtration cell (HP4750, Sterlitech Corp., Kent, WA) without stirring. Prior to the filtration, membranes were soaked in DI water for at least 10 h at room temperature and 200 ml of DI water was filtered through each membrane to remove trace chemicals, as recommended by manufacturer. The ionic strength, pH, and Ca<sup>2+</sup> concentration of all the suspensions (Table 3.1) were adjusted prior to filtration. The SEM micrographs (Fig 3.1) show that the material deposited on the membrane surface formed a cake layer is approximately 0.2  $\mu$ m thick. For the ozonated SRNOM solutions with and without Ca<sup>2+</sup>, the first 600 mL were filtered twice to improve NOM recovery. The membranes with deposits were dried in a

desiccator before the contact angles were measured. The contact angles for three materials (TiO<sub>2</sub>, ozonated SRNOM, and non-ozonated SRNOM) were determined at three different pH values (3, 5, and 8) and two concentrations of  $Ca^{2+}$  (0 mM, 1 mM). Thus, contact angles were measured for a total of 18 different material/solution chemistry combinations.





(d)



Figure 3.1. SEM micrographs of the cross-section of (a) the bare membrane and membranes with the layer of filtered (b) NOM, (c) ozonated NOM, and (d) ozonated NOM in the presence of Ca<sup>2+</sup>. The fouled membranes are representative of samples used in contact angle measurements. Arrows point to the NOM cake.

		Surface energy parameters (mJ/m <sup>2</sup> )					Contact angle $\begin{pmatrix} 0 \\ \end{pmatrix}$			
			γ <sup>LW</sup>	γ+	γ <sup>-</sup>	$\gamma^{AB}$	γ <sup>TOT</sup>			
Probe	liquid	a					<u> </u>			
Ultrapure water			21.8	25.5	25.5	51.0	72.8			
Glycerol			34.0	3.9	57.4	30.0	64.0			
Diiodomethane			50.8	0.0	0.0	0.0	50.8			
mate rial	р Н	[Ca 2+ ], mM					1	H <sub>2</sub> O	Glycerol	Diiod omet hane
TiO <sub>2</sub>	3	0	50.8 ±	1.05 ± 0.12	46.3 ± 0.77	13.9 ± 0.8	64.7 ± 0.8	0	16 ± 1.8	0
(250 ml, 0.5 g/L)	5	0	50.8 ±	1.05 ± 0.18	46.3 ± 1.17	13.9 ± 1.2	64.7 ± 1.2	0	16 ± 2.7	0
	8	0	50.8 ±	1.00 ± 0.15	46.6±	13.7 ± 1.0	64.5 ± 1.0	0	17 ± 2.2	0
TiO <sub>2</sub>	3	1	50.8 ±	0.96 ± 0.07	46.9± 0.52	13.4 ± 0.5	64.2 ± 0.5	0	18 ± 1.1	0
(250 ml, 0.5 g/L)	5	1	50.8 ±	1.08 ± 0.22	46.1 ± 1.41	14.1 ± 1.4	64.9 ± 1.4	0	16 ± 3.4	0
	8	1	50.8 ±	1.18 ± 1.14	45.4 ± 0.86	14.6 ± 0.9	65.4 ± 0.9	0	14 ± 2.4	0
NOM (300	3	0	48.6 ± 1.4	0.02 ± 0.07	40.0 ± 4.51	1.7 ± 3.3	50.3 ± 3.6	38 ± 2.5	46 ± 3.0	17 ± 3.9
ml, 20	5	0	48.5 ± 0.9	1.0E-4 ±0.003	40.9 ± 4.98	0.1 ± 1.9	48.6 ± 2.2	39 ± 3.5	48 ± 1.3	18 ± 2.4

Table 3.1. Contact angles measured and surface energy parameters calculated for SRNOM, ozonated SRNOM, and TiO<sub>2</sub> at different pH and concentrations of Ca<sup>2+</sup>.

mg/L	Table 3.1 (cont'd)									
)			47.3 ±	0.004	34.1 ±	0.7 ±	48.1	46 ±		21 ±
	8	U	1.3	± 0.03	4.00	2.6	± 2.9	2.3	$51 \pm 2.2$	2.8
NOM	3	1	48.6 ±	0.02 ±	41.8 ±	2.0±	50.6	36 ±	45 + 1 7	17 ±
(300	5		0.7	0.06	4.27	2.4	± 2.5	2.9	45 ± 1.7	1.8
ml	5	1	48.3 ±	0.12 ±	40.0 ±	4.4 ±	52.8	35 ±	42 + 1.8	18 ±
20	5	•	0.6	0.10	3.01	1.9	± 2.0	2.0	42 ± 1.0	1.6
mg/L	Q	1	48.6 ±	3.3E-5	39.0 ±	0.1 ±	48.7	40 ±	40 + 1.6	17 ±
)	0	1	0.6	0.002	4.18	2.0	± 2.0	2.8	47 1.0	1.5
02			47.5 ±	1.3E-4	54.8 ±	0.2 ±	47.7	24 ±		21 ±
NOM	3	0	1.2	± 0.01	4.89	3.4	± 3.6	3.6	44 ± 2.7	2.8
(1600			46.9 ±	1.6E-5	51.8 ±	0.1 ±	46.9	29 ±		23 ±
ml.	5	0	1.4	±	5.72	3.8	± 4.1	3.8	46 ± 3.0	3.0
20				0.002						
mg/L	8	0	48.3 ±	0.01 ±	35.2 ±	1.4 ±	49.7	43 ±	40 + 3 5	18 ±
)	U	Ŭ	1.2	0.07	4.20	3.7	± 3.9	1.6	49 - 9.5	3.0
03	2	1	47.5 ±	0.07 ±	47.1 ±	3.7 ±	51.2	29 ±	42 1 2 4	21 ±
NOM		1	1.5	0.15	5.7	3.9	± 4.2	3.9	42 ± 3.4	3.5
(1000	5	1	46.9 ±	1E-4 ±	42.3 ±	0.1 ±	47.0	39 ±	40 + 2 0	23 ±
(1000 ml.	5	1	1.5	0.01	5.81	3.7	± 3.9	3.5	4) 4 2.9	3.1
20						<b>.</b>				
mg/I	8	1	48.6 ±	0.53 ±	39.6 ±	9.2 ±	57.8	30 ±	34 ± 2.3	17 ±
ιιι <u>κ</u> γι.			0.9	0.25	4.3	2.2	± 2.4	3.6		2.5
,										

A FTÅ 200 analyzer (First Ten Angstroms) was used to measure contact angles. Measurements were carried out with three different probe liquids – DI water, glycerol and diiodomethane. The ionic strength, pH and calcium concentration of the DI water were adjusted to match the water chemistry in the droplet to that of the suspensions from which the  $TiO_2$  and SRNOM deposits on membrane filters were formed. Measurements were made by forming, at the rate of 0.5 µL/s, a 5 µL drop of liquid on the tip of a stainless steel syringe needle and then placing the drop onto the membrane surface by raising the membrane until contact was made. An image of the drop was taken and the left and the right contact angles were measured. For each probe liquid-sample combination at least two membrane coupons were analyzed with five images recorded for each membrane coupon.

To evaluate the size distribution of NOM molecules in aqueous suspensions with different ionic strength, pH and Ca<sup>2+</sup> concentrations (Table 3.1), we fractionated SRNOM using a series of ultrafiltration membranes with different molecular weight cut off (MWCO). Basically, the procedure of size fractioning of NOM molecules is described in Mellema's Master thesis [188]. In our study, a 40 mg/L colloidal aqueous suspension of SRNOM was prepared. The pH, ionic strength and Ca<sup>2+</sup> concentration of the suspension were adjusted in the same way as described in Table 3.1. Five types of ultrafiltration membranes with different MWCO were used in sequence from large MWCO to small MWCO. YM30, YM10, YM3, YM1 and YCO5 have a MWCO of 30, 10, 3, 1, and 0.5 kDa, respectively. Filtration was conducted with Amicon 8200 ultrafiltration stirred cells pressurized with nitrogen gas at 60 psi. To clean the cellulose acetate membranes (YC05, YM1, YM3, YM10, YM30, Amicon) prior to filtration, YC membranes were soaked in 1 M NaCl for 30 min while YM membranes were soaked in 0.1 M NaOH for 30 min. In order to remove the TOC interference from these membranes, the membranes were pre-filtered with ca. 200 ml deionized water. The filtration started with 4 L of SRNOM solution (40 mg/L) through a YM30

membrane. During each filtration, 500 mL of permeate was collected, and the rest of the permeate solution was filtered with the membrane of smaller MWCO. The filtration took place under stirring conditions to prevent concentration polarization as much as possible. Then we measured the TOC content in the permeate samples that were collected from each filtration using a TOC analyzer (OI Analytical Model 1010 Analyzer, College Station, TX).

## 3.4. Results and Discussion

#### 3.4.1. Fractionation of Suwannee River NOM (SRNOM)

We have plotted the fractioning results in two different ways. Fig 3.2 shows the original data of TOC that were collected and measured from different permeate samples. The bars in each plot stand for the concentration of TOC which belongs to the SRNOM molecules that are smaller than the MW of the corresponding membrane. Fig 3.3 is another way to present the TOC results. Each bar stands for the TOC concentration of the SRNOM molecules in the MW range that are indicated in the X-axis. The fractioning results (Fig. 3.3) tell us that ozonation did break the large NOM molecules (10-30 kDa) into smaller sized NOM and made the suspension more polydispersed. By adding only Ca<sup>2+</sup>, not much difference was observed in the size charts (Fig. 3.3 (a) and (c)). For ozonated NOM, the presence of Ca<sup>2+</sup> helped make a suspension with even a smaller size distribution.





Figure 3.2. TOC fraction of (a) NOM, (b) O<sub>3</sub>-NOM, (c) NOM(Ca<sup>2+</sup>) and (d) O<sub>3</sub>-NOM(Ca<sup>2+</sup>) that has a smaller molecular weight than the number indicated on the x-axis. The error bars represent 90% confidence interval.



Figure 3.3. TOC fraction of (a) NOM, (b) O<sub>3</sub>-NOM, (c) NOM(Ca<sup>2+</sup>) and (d) O<sub>3</sub>-NOM(Ca<sup>2+</sup>) that has molecules in the size range indicated on the x-axis. The TOC content in each MW class was computed as the difference between the TOC contents of the filtrates from the two membranes used in the isolation of the corresponding size fraction.



Figure 3.4. Combined effect of pH, Ca<sup>2+</sup> and pre-ozonation on hydrophilicity of SRNOM. The error bars correspond to 90% confidence intervals.

#### 3.4.2. Hydrophilicity of SRNOM

Figure 3.4 illustrates the dependence of the water contact angle of the ozonated and non-ozonated SRNOM on pH and calcium content. The measured contact angles for SRNOM were in the range of  $35^{\circ}$  to  $46^{\circ}$  indicating that SRNOM is less hydrophobic than Aldrich NOM ( $\theta = 74^{\circ}$ , [177]). Both the addition of calcium and ozonation resulted in a decrease in the contact angle of SRNOM in water; the effect of calcium was more pronounced at higher pH values, while the effect of ozonation was greater at lower pH values. The same effect of ozonation on the hydrophilicity of NOM was reported by Reckhow and co-workers [189]. The result is consistent with the fact that the ozonation of the SRNOM produces lower molecular weight, polar, oxygen-rich compounds with a higher content of hydroxyl, carbonylic, and carboxylic groups [190]. It is not clear, however, why the addition of calcium rendered SRNOM more

hydrophilic and why the same trend was not observed when calcium was added to the ozonated SRNOM solution.

The reaction of ozone with the NOM is pH dependent and the predominant reaction mechanisms of ozonation depend upon pH (i.e., reactions involving molecular O<sub>3</sub> predominate at lower pH and those involving OH-radicals and other secondary oxidants predominate at higher pH) [191]. The chemical nature of the ozonated NOM will depend upon reaction pH (see Fig. 3.4). As a result, the interpretation of the contact angle data for ozonated SRNOM is difficult. For example, SRNOM oxidation by molecular ozone should generate more hydrophilic NOM species than those produced during the oxidation of NOM by OH. This difference, however, is countered by the protonation of hydrophilic functional groups at lower pH.

## 3.4.3. Free energy of SRNOM-SRNOM cohesion and SRNOM-TiO<sub>2</sub> adhesion

The hydrophilicity of the SRNOM determines the magnitude of the forces of hydrophilic repulsion or hydrophobic attraction (i.e., acid-base forces) that, together with electrostatic and van der Waals forces, define SRNOM interactions with other SRNOM colloids and with the  $TiO_2$  nanoparticles. To quantitatively evaluate acid-base interactions, contact angle measurements with two more probe liquids with known surface tension parameters were conducted. Based on measured contact angles and estimated surface tension parameters (Table 3.2), free energies of adhesion (Eqs. 3.1, 3.2, 3.3) corresponding to van der Waals, electrostatic, and acid-base forces were calculated for the cases of adhesion of 1) ozonated and 2) non-ozonated SRNOM to the surface of a  $TiO_2$  nanoparticle at different pH values (Table 3.2, Fig. 3.5 and Fig. 3.6). The negative free energy represents a thermodynamically unstable state

(attractive to each other), while the positive free energy means a thermodynamically stable state (repulsive to each other).

	Solution		Surface energy, mJ/m <sup>2</sup>						
Sample	chemistry								
	pН	[Ca <sup>2+</sup> ],	$\Delta G_{y_0}^{LW}$	$\Delta G_{y_0}^{AB}$	$\Delta G_{y_0}^{EL}$	$\Delta G_{y_0}^{TOT}$			
		mM							
NOM- TiO <sub>2</sub> interaction (adhesion)									
SRNOM	3	0	$-11.3 \pm 0.5$	27.5 ± 3.7	$-0.16 \pm 0.01$	$16.0 \pm 3.7$			
SRNOM	5	0	$-11.3 \pm 0.3$	28.5 ± 3.7	-0.01 ± 0.01	17.2 ± 3.7			
SRNOM	8	0	$-10.9 \pm 0.5$	24.1 ± 3.5	0.45 ± 0.03	13.7 ± 3.5			
SRNOM	3	1	$-11.3 \pm 0.2$	29.1 ± 3.2	-0.12 ± 0.01	17.7 ± 3.2			
SRNOM	5	1	$-11.2 \pm 0.2$	26.6 ± 2.6	$-0.02 \pm 0.003$	$15.3 \pm 2.6$			
SRNOM	8	1	$-11.3 \pm 0.2$	26.5 ± 3.2	0.04 ± 0.004	$15.3 \pm 3.2$			
O3-SRNOM	3	0	-10.9 ± 0.4	36.6 ± 3.4	-0.21 ± 0.01	25.4 ± 3.4			
O3-SRNOM	5	0	-10.7 ± 0.5	35.0 ± 4.1	-0.01 ± 0.01	24.3 ± 4.1			
O3-SRNOM	8	0	-11.2 ± 0.4	24.7 ± 4.0	0.46 ± 0.01	13.9 ± 4.0			
O3-SRNOM	3	1	-10.9 ± 0.6	31.9 ± 4.2	-0.10 ± 0.01	20.9 ± 4.2			
O3-SRNOM	5	1	-10.7 ± 0.5	29.2 ± 4.6	-0.02±0.002	18.5 ± 4.6			
O3-SRNOM	8	1	-11.3 ± 0.3	24.4 ± 3.2	0.03 ± 0.01	13.1 ± 3.2			
NOM-NOM interaction (cohesion)									
SRNOM	3	0	-10.6 ± 0.9	25.1 ± 8.1	0.10 ± 0.02	14.7 ± 8.2			
SRNOM	5	0	$-10.5 \pm 0.6$	27.1 ± 8.5	$0.20 \pm 0.02$	16.8 ± 8.5			
SRNOM	8	0	-9.8 ± 0.8	15.7 ± 7.4	$0.42 \pm 0.06$	6.4 ± 7.4			
SRNOM	3	1	$-10.6 \pm 0.4$	27.7 ± 7.3	0.05 ± 0.01	17.2 ± 7.3			
SRNOM	5	1	$-10.4 \pm 0.4$	23.9 ± 5.1	0.04 ± 0.01	13.5 ± 5.1			

Table 3.2. Free energy of adhesion of SRNOM on the surface of  $TiO_2$  nanoparticles and SRNOM-SRNOM cohesion

Table 3.2 (cont'd)							
SRNOM	8 1		$-10.6 \pm 0.4$	24.1 ± 7.4	0.03 ± 0.004	13.6 ± 7.4	
O3-SRNOM	3	0	-9.9 ± 0.8	47.4 ± 8.5	0.17 ± 0.01	37.7 ± 8.5	
O3-SRNOM	5	0	-9.5 ± 0.9	43.4 ± 9.9	0.28 ± 0.01	34.2 ± 9.9	
O3-SRNOM	8	0	$-10.4 \pm 0.8$	17.4 ± 8.0	0.44 ± 0.01	7.4 ± 8.0	
O3-SRNOM	3	1	-9.9 ± 1.0	34.7 ± 9.6	0.03 ± 0.01	24.8 ± 9.7	
O3-SRNOM	5	1	-9.5 ± 0.9	29.3 ± 10.3	0.02 ± 0.004	19.8±10.4	
O3-SRNOM	8	1	$-10.6 \pm 0.6$	21.4 ± 6.5	0.01 ± 0.004	10.8 ± 6.5	



**(b)** 





(c)











(f)

Figure 3.5. LW, AB, EL and Total energy of SRNOM-TiO<sub>2</sub> interactions for non-ozonated SRNOM (a, c, e) and ozonated SRNOM (b, d, f) at pH 3 (a, b) pH 5 (c, d), and pH 8 (e, f)

(b)



(c)







(d)

(e)

(f)



Figure 3.6. LW, AB, EL and Total energy of SRNOM-SRNOM interactions for non-ozonated SRNOM (a, c, e) and ozonated SRNOM (b, d, f) at pH 3 (a, b) pH 5 (c, d), and pH 8 (e, f)

Short range NOM-NOM and NOM-TiO2 interactions were governed by polar (acid-base) and van der Waals forces, while the contribution of electrostatic interaction ( $\Delta G_{y_0}^{EL}$ ) to the overall free energy of adhesion was found to be minor (Figures 3.5 & 3.6). The most salient trend in the interaction energy was the effect of ozonation at pH 3 and pH 5, which, in the absence of calcium, increased the relative contribution of hydrophilic repulsion between SRNOM molecules and between SRNOM and TiO<sub>2</sub>. Basically, at low pH, ozonation made the SRNOM-SRNOM and SRNOM-TiO2 interactions less favorable. Dramatic changes were observed in the electron donor and electron acceptor components of free energy of the SRNOM interactions (Table 3.2). Ozonation led to an increase in the value of the electron donor component of free energy ( $\gamma^-$ ), resulting in more positive values of the acid-base interaction energy ( $\Delta G_{y_0}^{AB}$ ). This increase, reflected by the increase in hydrophilicity determined in contact angle measurements, was more pronounced at lower pH.

Combined surface energies due to the three non-covalent interfacial energies (LW, AB, EL) were presented in Fig 3.7 The addition of calcium decreased differences in interaction energies for both ozonated and nonozonated SRNOM. In view of the observed strong effect of calcium on adsorption and permeate flux [156], this observation indicates that non-XDLVO forces (e.g., steric effects, bridging by calcium) play an important role in SRNOM-SRNOM and SRNOM-TiO<sub>2</sub> interactions.

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Figure 3.7. Combined effect of pH, Ca<sup>2+</sup> and pre-ozonation on the XDLVO energy of interaction between (a) SRNOM molecules, and (b) SRNOM molecule and TiO<sub>2</sub> surface. The error bars correspond to 90% confidence intervals.

The trends observed for the free energy of the SRNOM-TiO<sub>2</sub> adhesion as a

(a)

(b)

function of ozonation, pH and calcium content (Table 3.2, upper half) were qualitatively the same as those for the energy of cohesive interaction of a pair SRNOM molecules implying that the SRNOM-TiO<sub>2</sub> interaction energy is determined by the properties of the SRNOM molecules and not properties of the TiO<sub>2</sub> surface. It follows that the SRNOM sorption onto TiO<sub>2</sub> is insensitive to the amount of SRNOM already absorbed on the TiO<sub>2</sub> surface. This indicates that when TiO<sub>2</sub> nanoparticles enter natural water, as long as the interaction between NOM molecules and interaction between NOM and TiO<sub>2</sub> are favored, TiO<sub>2</sub> nanoparticles will be covered by multilayers of NOM molecules.

## 3.5. Conclusions

The surface energy analysis described in this study provides a reasonable interpretation of the effect of ozonation in reducing NOM fouling of TiO<sub>2</sub> ceramic membranes. When natural water is being ozonated, the average size of NOM molecules become smaller, and their surface becomes more hydrophilic. Given this change in surface chemistry, the interaction between TiO<sub>2</sub> and NOM becomes less favorable mainly due to hydrophilic repulsive forces between the NOM and TiO<sub>2</sub>. This ozonation effect is also observed in the adsorption study where adsorption of ozonated SRNOM on TiO<sub>2</sub> nanoparticles was significantly less compared to the adsorption of SRNOM on the same particles, with all the other water conditions being the same (e.g., ionic strength, pH and presence of calcium). It is also true that the adsorption of the ozonated SRNOM onto the membrane is improved when TiO<sub>2</sub> has

positive charge (at low pH). This finding indicates that when  $TiO_2$  particles enter into natural water, NOM will have lesser tendency to adsorb on  $TiO_2$  if the water has been oxidized to some extent. Therefore, it is likely that  $TiO_2$  particles will keep their natural surface chemistry and exists as isolated particles without much adsorption of NOM in such pre-ozonated natural water.

There is no obvious and general trend for the pH effect on changing surface energies between NOM/NOM and NOM/TiO<sub>2</sub> when there is no calcium present, although the surface charge of NOM and TiO<sub>2</sub> particles do show a strong correlation to the pH of the suspensions. However, the adsorption data does show that the amount of sorbed SRNOM decreases with pH in the absence of calcium. This phenomenon is attributed to the fact that SRNOM adopts a more compact conformation at lower pH, which is partly proved by the fractioning results. Thus at lower pH, SRNOM can pack more densely at the TiO<sub>2</sub> surface.

In view that the strong observed effect of calcium on adsorption and permeate flux is not consistent with the analyzed calcium effect by XDLVO modeling, this inconsistency indicates that non-XDLVO forces (e.g., steric effects, bridging by calcium) may play an important role in SRNOM-SRNOM and SRNOM-TiO<sub>2</sub> interactions. Calcium ions are considered to serve as bridges between NOM-TiO<sub>2</sub> and NOM-NOM and allow for a multi-layer adsorption to occur.

# Chapter 4. Hybrid dual media membrane crossflow filtration hydrocyclone system for produced water treatment

## 4.1. Introduction

Produced water is the water that comes to the surface with oil and gas during offshore drilling operations [192]. The chemical makeup of produced water depends on water composition in the location of drilling and on the chemical additives used at the offshore platform; dissolved salts and organics, inorganic particles, and, of course oil and grease, are main constituents. The typical range of oil concentration in produced water is in the (100 to 5000) mg/L range [193]. Produced water is generated in extremely large quantities. For example, more than 1.6 billion m<sup>3</sup> of produced water were generated in 2002 in the U.S. alone [194,195]. This is equivalent to a volume of 1.15 billion gallons per day. A recent report on produced water management estimated the total volume of produced water generated in 2007 to be about 21 billion barrels, which equals to 3.2 billion  $m^3$  per year [196]. Nearly 1 million wells that actively produce oil and gas were present in the U.S. by the time the report was published [196]. This high rate of increase in generating produced water (1.6 billion m<sup>3</sup> in 2002 and 3.2 billion m<sup>3</sup> in 2007) was caused by both the increasing demand for oil and by the decreasing production rate of developed oil wells with time as the water-to-hydrocarbon ratio increases over the life of the well. A typical oil-producing platform produces large quantity of produced water from daily operations (0.66 m<sup>3</sup>/s [197]). Besides the U.S., other countries also produce extremely large amounts of produced water every day. It has been reported that more than 2,000 million tons of oily wastewater were produced by oil refineries in the European Union countries [198]. Based on the allowable oil concentration in discharged water (15 to 40 mg/L [199-202]), these waters cannot be directly discharged back to the water system due to their high oil content. The high oil concentration as well as the large quantity of produced water from daily operations (0.66 m<sup>3</sup>/s [197]) makes cost-effective treatment necessary. The need for cost-efficient technologies for oil-water separation has become more urgent in light of the recent oil spill events in the Gulf of Mexico.

Oil with droplet sizes smaller than 20  $\mu$ m is recognized as *emulsified oil* while the other two categories of oil droplets are *dispersed oil* (20  $\mu$ m to 150  $\mu$ m) and *free oil* (>150  $\mu$ m) [203]. Membrane separation has been studied as an approach to oily wastewater treatment [204]. While there are other conventional ways to achieve oil water separation, such as centrifugation [205], dissolved air flotation [206,207] and hydrocyclone separation [208], their efficiency decreases dramatically as the size of the oil droplets drops below approximately 20  $\mu$ m [209,210]. Given that a substantial fraction of oil in produced water may exist as emulsified oil (droplet size less than 20  $\mu$ m), a multi-step treatment is often required to reduce oil concentration to comply with environmental regulations. For example, coagulation is employed as a pretreatment step to destabilize the emulsified oil [205-207].

One of the benefits of using membrane filtration is that small oil droplets (< 20 um) can be removed from the oil-water dispersion [211]. However, fouling of the membranes by oil prevents the acceptance of membranes as a standard means of

de-oiling water [212].

Membrane-based separation techniques have been used to separate oil-water dispersions generated in a range of industrial processes. For example, dehydration of oil emulsion by pervaporation utilizes hydrophilic cellulose ultrafiltration membrane with oil retained in the feed [213]. Hydrophobic polypropylene microfiltration membranes were applied in membrane distillation process to extract water vapor from a feed dispersion with low oil concentration [214]. Flocculation was applied together with microfiltration to attain higher sustainable water permeate flux [215,216]. There have been studies that used a one-step membrane treatment to separate oil-water dispersions [217-220]. In these studies, the choice of membranes and operating conditions is varied because of two main reasons. Firstly, characteristics of the oil-water dispersion in terms of droplet size, concentration, stability and chemical composition vary considerably due to large differences in the preparation procedures, the oil/water formulation, and the chemical conditions used in preparing the oil-water dispersion [221]. Secondly, membranes are often modified or hybridized by other technologies to enhance their performance.

The inclusion of centrifugal separation into membrane filters was implemented by placing a helical insert inside a cylindrical metallic membrane [197]. With the insert there was sustainable water flux at a constant transmembrane pressure, while the membrane without the helical insert required a large increase in pressure to maintain a similar permeate flux. This improvement was attributed to the creation of a forced swirl/vortex that helps to separate oil from water and thereby mitigating oil fouling [197].

Adding air sparging into membrane filtration is known to be effective in reducing concentration polarization and fouling in various membrane applications (e.g., wastewater treatment [222,223] and surface water treatment [224]) In Li's study [225], the injection of air into a tubular polymeric membrane rapidly increased the permeate flux and decreased the permeation of protein. These phenomena were attributed to the enhanced local mixing near the membrane surface or the secondary flow generated by the air bubbles. An air sparging system was incorporated into the hydrocyclonic separator and it was demonstrated to be effective in solid-liquid separation [226].

The specific objectives of this work were: 1) to evaluate the oil water separation performance of  $TiO_2$  ceramic membranes with different pore sizes for dispersions that may contain a surfactant; 2) to design a hybrid filtration/separation system that incorporates membranes with opposite affinities; 3) to evaluate the efficiency of air sparging and the effect of hydrocyclone characteristics on the membrane filtration performance.

## 4.2. Basics of hydroclone and oil water separation

The proposed hybrid crossflow filtration system has some of the operating characteristics of a centrifugal separation device such as a hydrocyclone.

#### 4.2.1. The separation principle of hydrocyclones

The hydrocyclone was invented as a water purification device in 1891 by Eugene Bretney [227]. The initial idea was to separate water or other liquids from impurities by employing the centrifugal force, caused by the swirling motion of the dispersion introduced under pressure into the apparatus. In the 20<sup>th</sup> century, hydrocyclone designs have been suggested for liquid-liquid separation [228] with reverse flow [229] and forward flow configurations (Fig. 4.1). The separation is based on the specific gravity difference between phases in liquid-liquid emulsions. The separation principle can be described as follows: the emulsion enters the chamber in a tangential direction through an inlet tube connected to the sidewall of the cylindrical portion of the cyclone and creates a primary vortex flow. The liquid with the higher density is driven by centrifugal force to the outer layer of the liquid with lower density; therefore, the heavier liquid flowing next to the interior surface of the sides of the cyclone is forced to flow toward the apex of the cone by the pressure exerted from the air cushion that forms above the water level. This heavier liquid exits the bottom of the cyclone through the underflow orifice. The lighter liquid migrates to the centerline of the cyclone and exits from the overflow orifice. The equation that describes the relative radial velocity of a droplet of the dispersed phase in the continuous secondary phase is given by:

$$\left[u_{d,r} - u_{c,r}\right] = \frac{(\rho_d - \rho_c)d^2}{18\mu_c} \cdot \frac{u_{d,t}^2}{r}$$
(4.1)

where x is the droplet diameter,  $\rho_d$  is the density of dispersed phase,  $\rho_c$  is the density of continuous phase, and r is the radial position of the drop within the hydrocyclone,  $u_{d,r}$  and  $u_{c,r}$  is the radial velocity of the dispersed phase and the continuous phase respectively, and  $u_{d,t}$  is the tangential velocity of the dispersed phase.



Figure 4.1. Diagram of a reverse flow (a) and a forward flow hydrocyclones (b) [230]

The hydrocyclone's shape of an inverted cone increases the angular velocity of the fluid as the diameter is reduced (for the angular momentum to be conserved). This increase in angular velocity results in an improved separation efficiency of the dispersed and continuous phases.

### 4.2.2. Critical pressure

The Young-Laplace equation [231] was applied to compute the critical pressure. The critical pressure sets the upper limit of the transmembrane pressure that can be applied to the membrane where the liquid can be eliminated to break into membrane pores.

$$P_{crit} = -\frac{2\sigma\cos\theta}{r_{pore}} \tag{2}$$

where  $\sigma$  is the interfacial tension between the two liquids,  $\theta$  is the contact angle of membrane with that liquid and  $r_{pore}$  is the pore radius of the membrane.

When the droplet size was taken into account, the equation of critical pressure is calculated as [210,232]:

$$P_{crit} = \frac{2\sigma\cos\theta'}{r_{pore}} \cdot \left[ 1 - \left( \frac{2 + 3\cos\theta' - \cos^3\theta'}{4\left(\frac{r_{drop}}{r_{pore}}\right)^3\cos^3\theta' - \left(2 - 3\sin\theta' + \sin^3\theta'\right)} \right)^{\frac{1}{3}} \right]$$
(3)

where  $r_{drop}$  is the droplet radius and  $\theta' = 180 - \theta$ .

## 4.3. Material and methods

#### 4.3.1. Materials

Kerosene was chosen as the model oil in this study. The oil concentration was determined through the measurement of copper concentration via Atomic Absorption spectrometer (AA, see section 4.3.2). The copper was exchanged from a water phase to an oil phase with a reagent called Accorga (5050, Cytec Industries Inc, New Jersey). To prepare the oil stock solution, 100 g of kerosene was gently stirred with 20.5 g of Accorga solution for 5 min. Then a solution of copper sulphate was prepared by dissolving 5.6 g of CuSO<sub>4</sub>·5H<sub>2</sub>O in 50 g of deionized water. From this solution 35 g were added to the oil/Accorga mixture and this was gently stirred for another 30 min. The color of the oil phase turned from yellowish to brown, which indicated that the

copper was being transferred to the oil phase. Stirring was then stopped, the phases rapidly separated, and the aqueous phase was removed from the oil phase using a separating funnel. This stock kerosene solution is ready to be added into water for an oil-water dispersion at different concentrations. In a subset of experiments, polyvinyl alcohol (PVA, MW=25,000, 88% hydrolysis, Polyscience Inc, Warrington, PA) was used to stabilize the oil-water dispersion [210,233]. For dispersions with PVA present, the stock oil was mixed with a solution of PVA in water. The PVA-water solution was prepared by dissolving PVA crystals in approximately 60 °C DI water at the concentration of 0.2 g/L.

The tubular ceramic membranes made from titania with different pore sizes were manufactured by TAMI Industry (Filtanium, TAMI North America, St. Laurent, Quebec). The polytetrafluoroethylene (PTFE,  $1.1 \text{ g/cm}^3$ , Teflon) hollow fiber membranes were generously provided by Markel Corporation (Plymouth Meeting, PA).

#### 4.3.2. Characterization of oil-water dispersions and membranes

Light scattering system (Malvern Mastersizer, Westborough, MA) was used to determine oil (refractive index = 1.45) droplet sizes in the retentate water. The sample was mixed with 1000 mg/L piperazine (Aldrich) to "freeze" the oil droplets before the measurements.

Flame atomic absorption (AA) spectroscopy (Perkin-Elmer 1100) was used to determine oil concentration via the measurement of copper concentration. In order to measure the concentration of copper in the oil phase, the copper was stripped back into an aqueous solution using sulphuric acid with pH of 0.5. The copper concentration in the aqueous solution was analyzed at the wavelength of 324.7 nm. To

ensure that all copper was transferred to the aqueous solution, samples were sonicated in the sonication bath for 5 min before the measurements. A calibration curve (Fig. was obtained by plotting the absorption versus the concentrations of the diluted copper standards (SC194-500, Fisher Scientific, Pittsburgh, PA).



Figure 4.2. Calibration curve for copper

Scanning electron microscope images were recorded using a Hitachi S-4700II field emission SEM operated in ultrahigh resolution mode. Both the cross section and the skin surface were sputter coated with 5 nm of gold (Pelco SC-7 auto sputter coater) before imaging.

#### 4.3.3. Hybrid crossflow filtration system

The scheme of our hybrid crossflow filtration setup is shown in Fig. 4.3. The feed oil-water dispersion was prepared in a 5 gallon stainless steel reservoir (Alloy products corp., Waukesha, WI). The stock oil solution was diluted with deionized water in ratios of 1:808 (vol: vol). The resultant oil concentration was close to that used in studies of oil/water hydrocyclone separation [234,235]. The 8 L dispersion was stirred with an electric powered stirrer and continuously mixed by circulating the

dispersion using a diaphragm pump (Hydra-cell M-03) in order to obtain a dispersion with desirable oil droplet size distribution. The diaphragm pump continued pumping the dispersion during the entire filtration. The temperature of the feed water was maintained at 20  $\pm$  2°C.

The feed water was sent to the membrane with a low shear Moyno pump (33201, Springfield, OH). Three tubular ceramic  $TiO_2$  microfiltration membranes with pore sizes of 0.14 µm, 1.4 µm and 3.5 µm were selected in the study. All membranes had inner diameter of 6 mm, length of 25 cm and surface area of 47 cm<sup>2</sup>. The membranes were housed in a stainless steel filter holder (TAMI). In the dual membrane filtration experiments, a hydrophobic PTFE hollow fiber was installed inside and along the centerline of the ceramic membrane.

To sweep the oil off from the inner wall of the hollow fiber, air was applied continuously and injected into the lumen of the hollow fiber at the rate of approximately 500 ml/min. (Fig. 4.4). A back pressure regulator (BP-3, Circle Seal Controls Inc., Corona, CA) was used to maintain the transmembrane pressure differential at a constant value during the experiments. A pressure gauge was installed in the retentate line to measure the pressure at that location. One flow meter was installed in the permeate line, and one flow meter and one pressure sensor were installed in the retentate line. Thus, two flow rates and the transmembrane pressure could be recorded automatically to the computer, which has a Labview program installed.



Figure 4.3. Schematic diagram of the hybrid crossflow filtration system



Figure 4.4. Schematic diagram of the arrangement of hollow fiber membrane within a ceramic membrane.

The hybrid membrane filtration system that incorporates flow management to introduce rotational flow of the oil-water dispersion was assembled by installing a rotating tube upstream from the membrane unit (Fig. 4.3 and Fig. 4.5 (a)). The two swivels (Rotary Systems, Inc., RAMSEY, MN) were installed at the two ends of the rotating tube allowing for the free rotation of the tube but keeping other parts of the assembly stationary. The rotating tube was rotated by an electric motor via a

belt-and-pulley arrangement. Pulleys of several sizes were used to control the rotational speed of the tube. A unique attribute of this system is that the axial and rotational velocity of the flow can be changed independently of each other by changing the crossflow speed and the rotational speed, respectively. In Fig. 4.5 (b), the flow pattern inside the crossflow membrane filtration system is illustrated. The forced swirl of the oil-water dispersion helps separate the oil from water. The water permeates through the outer hydrophilic membrane while the oil droplets migrate towards the centerline where the inner hydrophobic membrane is located.



Figure 4.5. Schematic diagram of (a) hybrid crossflow membrane filtration unit and (b) the flow pattern inside the crossflow membrane filter in a hybrid filtration system.

By injecting air into the feed water immediately upstream from the membrane unit (see Fig. 4.3), the efficiency of air sparging in reducing membrane fouling by oil was
evaluated. During these experiments, an air injection line was installed close to the inlet of the rotational tube; air injected under pressure formed bubbles that were interspersed with the feed. Air pressure was controlled by a pressure regulator; air speed was monitored by an air flowmeter; and the air line was connected to a check valve and a shutoff valve.

The hybrid crossflow membrane filtration system as described above combines air sparging, hydrocyclonic separation and membrane separation processes (Table 4.1). As a result, the individual effects of each of the three processes, and effects of the processes applied in various combinations can be evaluated. For example, by injecting air into the membrane filtration system, we can evaluate the effect of air sparging on membrane filtration. By rotating the tube, we expect swirl motion of the emulsion to produce centrifugal separation similar to a hydrocyclonic operation.

 

 Table 4.1. Hybrid separation processes resulting from combining air sparging, hydrocyclonic separation and membrane filtration.

Fouling mitigation strategy	Without air sparging	With air sparging
Flow type		
Without swirl	Crossflow membrane	Air sparged crossflow
	filtration	membrane filtration
	(CFF)	(ACFF)
With swirl	Crossflow membrane	Air sparged crossflow
	filtration hydrocyclone	membrane filtration
	(CFFH)	hydrocyclone (ACFFH)

(H) implies hydrocyclonic separation and (A) implies air sparging

## 4.4. Results

4.4.1. The effect of membrane pore size, and the presence of surfactant on membrane filtration performance

The experimental results presented in this section were obtained with only membrane filtration without adding other hybrid technologies. A series of filtration experiments was carried out with ceramic membranes of three different pore sizes to evaluate the effect of membrane pore size on permeate flux and oil rejection. The experiments were conducted at different transmembrane pressures to make sure that the three membranes with different permeabilities have a similar initial permeate flux during oil-water separation tests. The measured permeability values for the three membranes are given in Table 4.2. The cross-flow velocity was 0.59 m/s with Reynolds number of 3,524. The produced oil droplet size was in the range of (1 to 100)  $\mu$ m when there was no surfactant present in the dispersion. The oil concentration in the retentate was 170-200 mg/L. Figure 4.6 (a) shows clearly that the 3.5 µm filter experienced the highest flux decline over the 15 min of filtration while in the tests with the 1.4 µm filter 30% permeate flux decline was observed over 15 min of filtration. The smallest pore size membrane (0.14  $\mu$ m) has shown complete oil rejection, however, this good rejection is a tradeoff between its lower performance in maintaining a high permeate flux as compared to the 1.4 µm filter. As for the oil rejection, the two larger pore sized filters rejected more than 90% of the oil, while the  $0.14 \,\mu\text{m}$  filter completely rejected the oil (Fig. 4.6 (b)).

Membrane pore size	Permeability (L/m2/hr/bar)
3.5 µm	1.1E+04
1.4 μm	9.6E+03
0.14 μm	1.9E+03

Table 4.2. Water permeability of different ceramic membranes



(b)



Figure 4.6. Permeate flux decline (a) and oil rejection (b) of three membrane during the filtration of oil-water dispersion without PVA

Another set of filtration experiments was conducted to evaluate the effect of PVA on permeate flux and oil rejection. The addition of PVA resulted in the following changes: 1) modification of oil droplet size and the oil concentration in aqueous dispersions; 2) filtration performance of hydrophilic ceramic membranes in terms of oil rejection and permeate flux; and 3) modification to the hydrophobicity of a hydrophobic polymeric membrane.

It was found that the addition of PVA does create an oil-water dispersion with a higher oil concentration in the aqueous phase and smaller oil droplet size. The difference in droplet size caused by adding PVA into the dispersion is illustrated in figure 4.7. Nanosized particles (< 0.1  $\mu$ m) were found in the oil-water-PVA dispersion.



Figure 4.7. Oil droplet size distribution with and without the presence of PVA in the retentate during the filtration of 3.5 µm filter

The three membranes (pore sizes  $3.5 \mu m$ ,  $1.4 \mu m$  and  $0.14 \mu m$ ) were tested with a dispersion that had PVA concentration of 0.2 g (PVA)/L. In experiments with the  $3.5 \mu m$  filter, the permeate flux decline was smaller than what was observed in the filtration of the PVA-free dispersion. But considering oil rejection data, it is clear that the improvement in permeate flux was due to the fact that a large proportion of oil passing through the membrane and not contributing to membrane fouling. In dispersions with PVA present (Fig. 4.7), most of the oil droplets were smaller than 1  $\mu m$ . As a result in the filtration with 1.4  $\mu m$  filter, oil droplets could potentially pass through the membrane pores and come out from the permeate stream; this is consistent with the observed oil rejection of less than 40% over the first 15 min of filtration. In contrast, the 0.14  $\mu m$  filter had the most severe flux decline among the three membranes and the final permeate flux after 15 min of filtration was much smaller compared to the permeate flux after the same duration of filtration of

PVA-free oil-water dispersion. However, there is still no oil permeating through, which means a 100% complete rejection of oil can be achieved with membrane filtration that has the nominal pore size smaller or equal to  $0.14 \mu m$ . So the significant fouling of 0.14  $\mu m$  filter occurred because all the oil droplets rejected by the membrane are being retained on the surface. This series of filtrations has shown a clear trend that gains in oil rejection can be realized but at the expense of large flux declines. And removal of the small oil droplets, which are produced when PVA is added, requires using the membranes that have pore size in the 0.1  $\mu m$  size range.



Figure 4.8. Permeate flux decline (a) and oil rejection (b) of three membranes during the filtration of oil-water dispersion with 0.2 g/L PVA

In addition to the effect of PVA on ceramic membrane filtration, an study of PVA adsorption onto a hydrophobic PVDF membrane (GVHP, 0.22  $\mu$ m, Millipore) surface showed that the adsorbed PVA significantly changes the surface contact angle of the membrane. In one series of experiments, an original membrane had an average water contact angle of 110°. Then the membrane was soaked in 0.2 g/L PVA aqueous solution for 24 h and rinsed with water gently and dried. The average contact angle became 40°. The exposure to PVA essentially changed a hydrophobic membrane into a hydrophilic one. We also tested oil permeability of this type of membrane. It was

found that the original PVDF membrane can easily filter out pure oil from an oil-water dispersion in a deadend filtration experiment. However, when the oil-water dispersion had PVA present, the membrane was no longer effective in removing oil.

#### 4.4.2. The performance of hybrid membrane filtration system

The hybrid system combines membrane filtration with two other processes to improve the oil and water separation performance (Table 4.1). The combination of membrane filtration and hydrocyclonic separation has a potential to achieve better oil water separation for two reasons. First, the membrane with appropriate pore size and surface chemistry can serve as a barrier for smaller oil droplets (e.g.,  $< 20 \,\mu$ m), which are difficult to remove from water by centrifugal separation within a typical deoiling hydrocyclone (also see section 4.4.1). Second, the rotational flow would result in centrifugal transport of oil away from the membrane surface leading to reduced membrane fouling by oil during separation. Basically, the two technologies would synergistically enhance one another.

The addition of air to the feed water upstream from the membrane module should result in a further mitigation of membrane fouling due to flotation and sparging effects. By attaching to oil droplets (flotation principle), air bubbles would facilitate the centrifugal transport in the hybrid system [226,236]. Sweeping of oil off the membrane surface by the air bubbles is also expected to contribute to fouling control [237].

To test the hybrid treatment system in different configurations, we have conducted filtration experiments under four different conditions (Table 4.1). During the filtration, we monitored the change in the size of oil droplets in the retentate stream (Fig. 4.9). Imposing rotation (CFFH process) did not seem to affect the size distribution of oil droplets. In contrast, the addition of air to the feed resulted in a shift of the peak of the size distribution of oil droplets to a larger size value.



Figure 4.9. Oil droplet size distribution measured for the retentate at 5 min (a) and at 30 min (b) of filtrations with 0.14 um filter at different hybrid conditions. CFF – crossflow filtration; ACFF – Air sparged crossflow filtration; CFFH – crossflow filtration



Figure 4.10. Permeate flux decline during the filtrations with 0.14 µm filter at different hybrid conditions.

The initial permeate flux is approximately 170 L/m<sup>2</sup>/hr. Transmembrane pressure is 11 psi.

The permeate flux appears to be affected by the introduction of additional features (Fig. 4.10). It should be mentioned that the oil concentration in the control experiment (160 mg/L) is lower than that in the other three experiments (280-330 mg/L). Thus we would expect a more significant permeate flux decline than what would happen in the control experiment if the oil concentration was similar to that in the other filtration experiments. Imposing rotation to the feed water did not help to the decrease the initial (i.e., over the first 20 min) permeate flux decline (Fig. 4.10) and the data actually shows that the permeate flux declined faster when rotation was introduced. After 20 min of filtration, there was no further permeate flux decline indicating that at this point, that membrane oil fouling had reached an equilibrium. As for the effect of

air sparging on crossflow membrane filtration, an improvement in flux decline became apparent after 15 min of filtration and air sparging became more beneficial in retaining a higher flux when rotation was applied. The final permeate flux values observed in experiments with the hybrid processes were higher than the final permeate flux value recorded in the control experiment (membrane filtration only), even though the oil concentration in the control experiment was smaller than the oil concentrations in the other experiments with hybrid processes. In none of the experiments was oil detected in the permeate line. The observation in oil droplets can be correlated to the results in permeate flux during the filtration experiments. The larger size oil droplets resulted from the addition of air (Fig. 4.9) can partially explain why air sparging is effective in maintaining relatively high permeate flux. Air bubbles seem to promote the coalescence of oil droplets, which in turn helps to reduce membrane fouling and thus maintain high permeate flux.

These preliminary results make a good starting point for further studies. It is also evident that the major flux decline occurred during the first 15 min of filtration; reduction of this flux decline rate to some extent by judiciously combining individual processes into one hybrid unit would perhaps result in the largest improvement of the overall performance.

### 4.4.3. The performance of dual membrane system

The dual membrane system has been tested to explore the potential of using membranes with different chemical affinities to separate an oil-water dispersion into two separate phases. The difference between a typical deoiling membrane filtration system and the dual membrane system is that the latter could extract oil from the dispersion. By doing so, oil concentration in the feed dispersion is lowered and thus help to mitigate oil fouling of the hydrophilic membrane.

50 ml kerosene stock solution was mixed in 1 L deionized water (4,400 mg/L) and ran the dispersion through dual membrane system (1.4  $\mu$ m ceramic membrane filter, PTFE hollow fiber (Fig. 4.11) operated at the transmembrane pressure of 10 psi and with the sweeping air flow rate of approximately 500 ml/min). The permeate coming out from the lumen of the hydrophobic membrane was approximately 2 ml of pure kerosene for the initial 15 min. Figure 4.12 shows the retentate, the permeate from the outer ceramic membrane, and the permeate from the inner hollow fiber membrane after 45 min of filtration.



Figure 4.11. SEM images of the outer surface (a) and cross-section (b) of the PTFE membrane



Figure 4.12. The images of samples of the retentate (sample on the left), the permeate from 1.4 µm ceramic membrane (3 samples in the middle) and the permeate from the hollow fiber membrane (sample on the right).

## 4.5. Conclusions

Three ceramic (TiO<sub>2</sub>) ceramic membranes of different pore sizes were tested as porous walls of a sparged hydrocyclone separating oil-water dispersions. The pore size was found to be a critical factor in determining permeate flux and oil rejection. The addition of PVA also had a profound impact on the separation performance. Although the complexity of the chemical makeup of produced water generated in the field necessitates tests of the developed hydrocyclone system with specific water compositions; the general trends in the separation performance with the membrane pore size and surfactant content are expected to hold.

The feasibility of affinity-based membrane separations of oil-water dispersions was also demonstrated. The demonstrated possibility of the recovery of oil can be prone to use in oil spill clean up application and produced water treatment operations.

## **Chapter 5. Summary and future work**

The development of nanotechnology can greatly benefit membrane-based separations for water treatment. In our study, we found that it was possible to design high performance polyelectrolyte multilayer membrane with high permeability and high selectivity using layer-by-layer deposition method. We also studied the interactions of nanoscale  $TiO_2$  and NOM molecules in aqueous solutions to explain the effect of ozonation in reducing NOM fouling of  $TiO_2$  ceramic membranes. Such understanding can result in better predictions of ceramic membrane fouling by NOM-containing waters as well as the fate and transport of  $TiO_2$  in the natural aqueous environment. Some prospects of future work are discussed below.

In the PEM study (Chapter 2), we have hypothesized that the improved separation efficiency with nanoparticle-fouled PEM films could be due to a change in the surface charge induced by the deposition of SiO<sub>2</sub> nanoparticles. To test this hypothesis, positively charged or neutrally charged nanoparticles can be filtered through PEM films and the change in rejection by the PEM films can be evaluated. In addition, PEM films can be modified with nanoparticles of different sizes and shapes (e.g., nanotubes, and nanoplatelets) to evaluate the importance of surface morphology on membrane separation performance. Considering that swellability of PEM films such as [PAA/PAH]<sub>n</sub> [62,238] and [PSS/PDADMAC]<sub>n</sub> [153] is strongly dependent on PEM deposition conditions (e.g., pH and ionic strength of the polyelectrolyte solutions), it is proposed to deposit a monolayer of nanoparticles with an average diameter comparable to the maximum swelling thickness of the film. In view of the possible use of deposited nanoparticles as catalysts in certain reactions, controlling the swellability can be used to adjust the access of nanoparticles to permeating species during the reaction. Finally, to improve the efficiency of PEM regeneration the backflushing can be optimized by a purposeful choice of the backflushing solution and by using auxiliary techniques (e.g., sonication) to remove the fouled PEM film before or after backflushing.

The NOM-TiO<sub>2</sub> interaction study (Chapter 3) can be taken further by applying XDLVO analysis to the interactions of TiO<sub>2</sub> nanoparticles with 1) various NOM size fractions and 2) under different water chemistries. To understand the contribution of non-XDLVO forces (steric forces and  $Ca^{2+}$  bridging effect) that are hypothesized to dominate TiO<sub>2</sub>-NOM interaction in the presence of calcium, modeling at the molecular scale is needed.

The design of the membrane-based crossflow filtration hydrocyclonic separation process can be greatly facilitated by using computational fluid dynamics as a predicting and diagnostic tool. Such simulation may be helpful to optimize the geometry of the system and identify the optimal combination of the many experimental variables (crossflow velocity, rotational velocity performance, air inflow rate, bubble size, etc). The dual membrane configuration has not been tested in the crossflow filtration hydrocyclone framework. It remains to be seen if the rotational flow can help in alleviating the fouling of the hydrophilic membrane by oil and enhancing the oil recovery by hydrophobic membrane. Perhaps most importantly, designing a fouling resistant superhydrophobic surface with nanotechnology can be what will ensure the commercial viability of the dual membrane system. The CFFH system should be tested with oil-water dispersions that contain additional components

(i.e., salts, colloids) as well as the real produced water.

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