A Thesis

entitled

Tailor-Made Polysulfone Ultrafiltration Membranes for the Study of the Effects of Metal Oxide Nanoparticles on Fouling

by

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Submitted to the Graduate Faculty in partial fulfillment of the requirements for the Master of Science Degree in Chemical Engineering

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December 2011
TiO$_2$ and ZnO nanoparticles are currently used in many consumer products, such as cosmetics, sunscreens, paint and many other applications. Therefore, with this increasing manufacture and application, it is inevitable that large amounts of nanoparticles are eventually discharged into the environment. Due to their size and high capacity to convey toxic substances, nanoparticles can have adverse effects on human health and the environment. Therefore, nanoparticles are an emerging class of contaminants that water purification technologies must be designed to remove when present.

Membranes are capable of separating species as a function of their physical and chemical properties when a driving force is applied, which enables filtration for removal of colloids, cells and molecules. Filtration processes, such as ultrafiltration (UF) and microfiltration (MF), play major roles in filtration of fresh waters, brackish and saline
waters, as well as wastewaters. A concern for membranes is the ability of nanoparticles to deposit within the membrane pores as well as on the membrane surface to foul the surface. Particles smaller than membrane pores can accumulate at the pore entrance to ultimately block the pore entrance and/or enter the membrane material matrix and adsorb to the membrane interior. Like larger colloids, fouling by nanoparticles is influenced by the solution chemistry (ionic strength, pH) and may therefore be controllable. However, the impacts of solution chemistry on the aggregation state and deposition mechanisms of nanoparticles have not yet been fully addressed.

Therefore in this work, hydrophobic flash-sheet polysulfone (PSf) membranes, chosen due to polysulfone’s high mechanical strength and thermostability, were casted via phase inversion to investigate the effects of two metal oxide nanoparticles on membrane fouling. First, membranes were cast using different casting dope concentrations in the presence/absence of a pore former (i.e. lithium chloride) with different thicknesses for characterization with respect to flux and salt (i.e. sodium chloride) rejection. The results revealed that with increasing dope concentration and membrane thickness, permeability decreased and subsequently salt rejection increased. Furthermore, compared to LiCl-free membranes, LiCl-containing ones were more permeable and displayed higher salt rejection, which was due to more porosity and smaller pore size caused by LiCl additives in membranes.

In the second portion of the study, the effects of two metal oxide nanoparticles, TiO₂ and ZnO, on membrane flux and salt rejection were determined. In this work, TiO₂ and ZnO were added to the filtration solution, also known as feed solution. Interestingly,
when TiO$_2$ was a part of filtration solution, higher filtration fluxes than pure water fluxes were obtained; on the other hand, ZnO presence in the filtration solution decreased the filtration flux. In other words, TiO$_2$ presence in the filtration solution increased the flux, while ZnO behaved, as expected, almost the same as filtration of only sodium chloride (NaCl) solution. The increase in flux was possibly due to TiO$_2$ agglomeration (despite sonication) and flocculation of TiO$_2$ nanoparticles in the presence of increasing ionic strength. It is hypothesized that at high ionic strength, zeta potentials would decrease due to double layer compression, which caused TiO$_2$ to tend to flocculate to form a more permeable fouling cake. The larger particles would also experience more hydrodynamic lift, which would lead to a thinner cake layer and thus higher flux during filtration.
To my beloved mother, Zohreh Khanbolouki and amazing father, Alireza Hakimelahi for their all boundless efforts and encouragements to help me make my dreams come true
Acknowledgements

This thesis would not have been possible without the love, support and patience of my family, friends and advisor.

Hereby I would like to thank my fantastic advisor, Professor Isabel C. Escobar who always encouraged me and gave me more confidence and strength during my master’s study in the US. I was very lucky to get a chance to have you as my advisor and work with you. Thank you for all your unsparing support and precious guidance.

My great gratitude to my amazing brother, Nima who was always there for me and helped me a lot through the dilemmas. I’m so thankful to my other siblings, Sara and Siavash for their perpetual love and heart-warming words.

I would like to express my appreciation to Dr. Cyndee L. Gruden and Dr. Yakov Lapitsky to kindly let me use the required equipments in their labs. Special thanks to my committee members, Dr. Maria Coleman and Dr. Yakov Lapitsky for their constructive comments.

My genuine appreciations to Dr. Tilak Gullinkala for showing me the initial set up required to start my project and thanks to Yan Huang to teach me how to use Zetasizer instrument. Finally, my sincere gratefulness to all my friends especially Zahra Karbaschi, Ehsan Izadi and Amir Motlagh for their friendship and support.
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<table>
<thead>
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<th>Description</th>
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<tbody>
<tr>
<td>A</td>
<td>Area</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>Avg</td>
<td>Average</td>
</tr>
<tr>
<td>BSA</td>
<td>Bovine serum albumin</td>
</tr>
<tr>
<td>CA</td>
<td>Cellulose diacetate</td>
</tr>
<tr>
<td>CEA</td>
<td>Chicken egg albumin</td>
</tr>
<tr>
<td>DI</td>
<td>Deionized/distilled water</td>
</tr>
<tr>
<td>DLC</td>
<td>Diamondlike carbon</td>
</tr>
<tr>
<td>DMA</td>
<td>N,N-dimethylacetamide</td>
</tr>
<tr>
<td>DMAc</td>
<td>Dimethyacetamide</td>
</tr>
<tr>
<td>DMAp</td>
<td>Dimethylaminopyridine</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethylsulfoxide</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy dispersive X-ray spectrometry</td>
</tr>
<tr>
<td>EtOH</td>
<td>Ethanol</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental protection agency</td>
</tr>
<tr>
<td>FO</td>
<td>Forward osmosis</td>
</tr>
<tr>
<td>FTIR-ATR</td>
<td>Fourier transform infrared spectroscopy in attenuated reflection mode</td>
</tr>
<tr>
<td>I</td>
<td>Ionic strength</td>
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<tr>
<td>IEP</td>
<td>Isoelectric point</td>
</tr>
<tr>
<td>LiCl</td>
<td>Lithium chloride</td>
</tr>
<tr>
<td>MBRs</td>
<td>Membrane bioreactors</td>
</tr>
<tr>
<td>MD</td>
<td>Membrane distillation</td>
</tr>
<tr>
<td>MES</td>
<td>2-(N-morpholino)ethanesulfonic acid</td>
</tr>
<tr>
<td>MF</td>
<td>Microfiltration</td>
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<tr>
<td>MW</td>
<td>Molecular weight</td>
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<tr>
<td>Acronym</td>
<td>Definition</td>
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<td>----------</td>
<td>-----------------------------------------------</td>
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<tr>
<td>TFC</td>
<td>Thin-film composite</td>
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<tr>
<td>NF</td>
<td>Nanofiltration</td>
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<td>NHS</td>
<td>N-hydroxysuccinimide</td>
</tr>
<tr>
<td>NMP</td>
<td>N-methyl-2-pyrrolidone</td>
</tr>
<tr>
<td>NNI</td>
<td>National nanotechnology initiative</td>
</tr>
<tr>
<td>PA</td>
<td>Polyamide</td>
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<td>PAA</td>
<td>Polyamic acid</td>
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<td>PAN</td>
<td>Polycrylonitrile</td>
</tr>
<tr>
<td>PEG</td>
<td>Polyethylene glycol</td>
</tr>
<tr>
<td>pH</td>
<td>Potential of hydrogen</td>
</tr>
<tr>
<td>PPESK</td>
<td>Polyphthalazine ether sulfone ketone</td>
</tr>
<tr>
<td>PSf</td>
<td>Polysulfone</td>
</tr>
<tr>
<td>PVDF</td>
<td>Polyvinylidene fluoride</td>
</tr>
<tr>
<td>PVP</td>
<td>Polyvinyl pyrrolidone</td>
</tr>
<tr>
<td>PWF</td>
<td>Pure water flux</td>
</tr>
<tr>
<td>PWP</td>
<td>Pure water precompaction</td>
</tr>
<tr>
<td>RO</td>
<td>Reverse osmosis</td>
</tr>
<tr>
<td>SAM</td>
<td>Self-assembled monolayer</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
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<td>SPES</td>
<td>Sulfonated-polyethersulfone</td>
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<td>UF</td>
<td>Ultrafiltration</td>
</tr>
<tr>
<td>V</td>
<td>Volume</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------------------------------</td>
</tr>
<tr>
<td>μm</td>
<td>Microns (micrometers)</td>
</tr>
<tr>
<td>ζ</td>
<td>Zeta potential</td>
</tr>
<tr>
<td>γ_{sg}</td>
<td>Surface energy of the solid</td>
</tr>
<tr>
<td>γ_{lg}</td>
<td>Surface tension of the liquid or casting dope</td>
</tr>
<tr>
<td>γ_{ls}</td>
<td>Surface energy of the solid at the solid/liquid</td>
</tr>
<tr>
<td>ρ</td>
<td>Density</td>
</tr>
<tr>
<td>α-Al₂O₃</td>
<td>Alumina</td>
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<tr>
<td>R_t</td>
<td>Total resistance</td>
</tr>
<tr>
<td>R_m</td>
<td>Intrinsic resistance of the membrane</td>
</tr>
<tr>
<td>R_c</td>
<td>Cake layer resistance</td>
</tr>
<tr>
<td>R_f</td>
<td>Resistance due to pore plugging</td>
</tr>
<tr>
<td>S</td>
<td>Spreading coefficient</td>
</tr>
<tr>
<td>Z</td>
<td>Charge number of the ion</td>
</tr>
<tr>
<td>1/k</td>
<td>Debye length</td>
</tr>
<tr>
<td>°C</td>
<td>Degrees celsius</td>
</tr>
<tr>
<td>cm</td>
<td>Centimeter</td>
</tr>
<tr>
<td>m²</td>
<td>Meter square</td>
</tr>
<tr>
<td>g</td>
<td>Grams</td>
</tr>
<tr>
<td>g/cm³</td>
<td>Gram per centimeter cubed</td>
</tr>
<tr>
<td>g/L</td>
<td>Grams per liter</td>
</tr>
<tr>
<td>J_w</td>
<td>Water flux</td>
</tr>
<tr>
<td>M</td>
<td>Molarity</td>
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<tr>
<td>hr</td>
<td>Hour</td>
</tr>
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<td>min</td>
<td>Minutes</td>
</tr>
<tr>
<td>ml</td>
<td>Milliliters</td>
</tr>
<tr>
<td>Mm</td>
<td>Milimolar</td>
</tr>
<tr>
<td>psi</td>
<td>Pounds per square inch</td>
</tr>
<tr>
<td>Wt%</td>
<td>Weight percentage</td>
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Chapter 1

1 Introduction

1.1 Need for Improved Water Treatment Processes

According to the National Academy of Engineering’s Report in 2011 [1], lack of clean water is responsible for more deaths than war in the world. The world water council reported that about 1 out of every 6 people living today do not have adequate access to safe drinking water, and more than double that number lack basic sanitation for which water is required. By some estimates each day nearly 5,000 children worldwide die from diarrhea-related diseases. This number would decrease significantly if sufficient water for sanitation were available [1].

Even though globally there are enough water sources, the problem is that many of those sources are not located where they are needed. In other words, “water, water, everywhere, nor any drop to drink”, (Samuel Taylor Coleridge, the English poet). Therefore, it is important to utilize existing water supplies as effectively as possible. In this regard membrane technology can be introduced as a solution in desalination, wastewater reuse or the other water treatment processes.
1.1.1 Membrane Technology

The use of membrane technology has fast increased over the past decennia due to higher efficiencies and with advances, lower energy requirements to address water scarcity and purification. As a result, many companies have started to utilize them as an alternative for many water purification processes.

Membranes may be composed of natural or synthetic polymers (plastic materials) or inorganic ceramic materials such as alumina, titania, zirconium oxides or some glassy materials. Current membrane filtration applications are listed below and shown in Figure 1-1:

Reverse osmosis (RO): In the osmosis phenomenon, water (solvent) passes through a semipermeable membrane from a side of lower solute concentration to a side of the higher solute concentration one in order to equalize the osmotic pressure between the two solutions. In reverse osmosis, by applying a pressure difference greater than the osmotic pressure difference, water flow direction changes from the higher concentration to the lower concentration solutions. By this method almost all the solid suspends, bacteria, viruses and other unwanted ions would be rejected, and a pure water would be achieved. Of note, forward osmosis (FO) is an emerging membrane process that behaves similar to RO and uses RO membranes, while filtration follows the osmotic pressure difference instead of the hydraulic pressure difference.

Nanofiltration (NF): Nanofiltration membranes are not as dense as reverse osmosis membranes and have pore diameters of 2 nm or less [2]. By employing them a fraction of monovalent ions and nearly all divalent can be removed.
Ultrafiltration (UF): Ultrafiltration membranes have pore sizes of approximately 0.01 micrometers. Macromolecules and viruses are removed by these membranes.

Microfiltration (MF): Microfiltration membranes have pore sizes of approximately 0.1 micrometers, and as a result rejection of bacteria and solid suspends from water is possible.

![Figure 1-1: Different types of membrane filtrations (Source: OzScientific.com [3])](image)

1.1.2 Nanoparticles In Water

TiO$_2$ and ZnO nanoparticles are currently used in many consumer products, such as cosmetics, sunscreens, paint and many other applications. Therefore, they are more often discharged to receiving bodies, such as waste streams and landfills, and eventually the environment. Nanoparticles (NPs) due to their size and high capacity to convey toxic substances can have adverse effects on human health and the environment. NPs can
deposit on the membrane surface to foul the membrane, and can deposit within the membrane pores to lead to pore plugging. Therefore, nanoparticles are an emerging class of contaminants that water purification technologies must be designed to remove when present. Because nanotechnology is still a young emerging technology, there is a great need for the development of designed treatment processes that would be able to reject nanoparticles from water.

For the study presented here, anatase (tetragonal crystal) structure of titanium dioxide (TiO$_2$) with the range size of 5-10 nanometers (nm) and hydrophilic ZnO of wurtzite (hexagonal close packing) form of approximately 20 nm were used as model NPs, as they are commonly used in consumer products. Anatase forms of TiO$_2$ nanoparticles (NPs) are very hydrophilic, photoactive and useful for a wide range of environmental applications, such as water and wastewater treatment, hazardous waste control and air purification [4]. TiO$_2$ has an isoelectric point (IEP) in the range of pH = 4.0 – 5.5 depending on manufacturer [5], while ZnO’s IEP is in the range of pH = 7.13 – 9.2 [6, 7, 8, 9]. IEP is the pH at which the zeta potential is zero.

1.2 Proposed Research

The aim of this research project was to investigate the effect of NPs on the performance of tailor-made ultrafiltration membranes. To this end, flash-sheet polysulfone (PSf) membranes (Figure 1-2), chosen due to polysulfone’s high mechanical strength, ability to withstand high temperature and stability against mineral acids, alkali in a wide pH range [10], were cast via phase inversion method. First, membranes were cast using different casting dope concentrations in the presence/absence of a pore former
(i.e. lithium chloride) with different thicknesses for characterization with respect to flux and salt (i.e. sodium chloride) rejection. In the second portion of the study, the effect of two metal oxide nanoparticles, TiO$_2$ and ZnO, on membrane flux and salt rejection were determined. In this work, TiO$_2$ and ZnO were added to the filtration solution, or feed solution.

![Polysulfone structure](image)

**Figure 1-2: Polysulfone structure**

### 1.3 Impact of Research

The motivation to pursue the study of NPs on membrane performance was the severe lack of information on the topic. In most of the previous works, NPs, especially TiO$_2$, was either entrapped or deposited on membranes [7-11], while the effect of NPs as components of feed water has not been the focus of much investigation. Little is known regarding the impact of TiO$_2$ or ZnO NPs on the membrane flux and salt rejection during filtration. According to previous studies, TiO$_2$ entrapped or deposited on membranes could be used to decrease fouling or increase the permeability and rejection. Hence, in this work, the impacts of the presence of NPs in the filtration solution were investigated.
Chapter 2

2 Literature Survey

2.1 Liquid Process Membrane Technologies

Membranes are capable of separating species as a function of their physical and chemical properties when a driving force is applied, which enables filtration for removal of colloids, cells and molecules. Membrane filtration processes play major roles in filtration of fresh, brackish and saline waters, as well as wastewaters. Currently there are several types of liquid membrane technologies available. These are categorized based on their pore size and also on the size of the materials they can reject (Figure 2-1). Based on decreasing pore size, membranes are divided into microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) membranes; while forward osmosis (FO) membranes generally lie within the NF/RO range.
2.1.1 Membrane Modules

Membranes are configured as modules, which consist of plate and frame, spiral-wound, tubular and hollow-fiber. Flat sheets can be either used in plate-and-frame modules with circular, square, or rectangle shape in cross-section or produced in spiral-wound modules [13]. Plate and frame is an open channel design that allows filtration of
products with very high viscosity, and it is particularly suited for high solids pharmaceutical and food applications (Figure 2-2). In laboratory scale flat-sheets are a good choice as they are easy to prepare and have surface area less than 1000 cm² [14].

Figure 2-2: Plate and frame membranes (source: GEA filtration [13])

Spiral membranes are flat-sheets sandwiched together with a feed spacer wound up around a punctured tube (Figure 2-3). Based on a report [13], these membranes are typically used for high-flow applications with minimal or no suspended solids. Their advantage is low hardware and operating costs. Tubular membranes are placed inside a tube made of a specific material, which also acts as the membrane support layer [14]. These membranes are highly resistant to plugging when processing streams with large amounts of suspended solids or fibrous compounds (Figure 2-4). However the low packing density of these membranes results in higher production cost [14].

Figure 2-3: Spiral membranes (source: GEA filtration [13])
Hollow fiber membranes offer high packing density, possibility of backwashing from the permeate side, and allow a high membrane surface area to be contained in a compact module (Figure 2-5). Hollow fibers have a diameter less than 0.5 mm while tubulars have larger dimensions (diameter is greater than 5 mm) that need to be supported [14].

2.1.2 Effect of Substrate on Membrane Casting

A substrate is the plate onto which flat-sheet membrane are cast. Therefore, the nature of the substrate influences the resultant membrane properties. To evaluate the extent of their impacts, substrates, such as cleaved mica (a hydrophilic silicate because of the presence of hydroxyl groups at the top side), glass plate, polyethylene coated paper (Rexam), diamond-like carbon (DLC) which is a plasma coated amorphous carbon layer
on a glass plate, and Teflon, were employed and compared [15]. Results revealed that Rexam and Teflon had the most strongly negative spreading coefficient values and subsequently more retraction and less permeability would be expected, while casting membranes on hydrophilic substrates like mica, glass and DLC resulted in less shrinkage and more permeability compared to hydrophobic plates such as Teflon and Rexam. That is, the properties of the resultant membrane are strongly controlled by the hydrophobicity of the casting substrate. Less pore size and permeability would occur due to the retraction of the casting dope on hydrophobic substrates.

2.1.3 Effect of Polymer Concentration and Different Additives on Membrane Properties

The dope, or casting solution, is made of the casting polymer, solvent and often one or more additives and/or pore formers. This solution is required to make the film or membrane. Increasing polymer concentration in the casting solution results in more polymer volume fraction, greater solution relative viscosity and in return decrease in porosity and flux [14]. Membranes are manufactured from a variety of polymers of different properties, such as cellulose acetate (CA), cellulose diacetate (CDA), cellulose triacetate, polyamide (PA), other aromatic polyamides, polyetheramides, polyetheramines, polysulfone (PSf), and polyetherurea. Thin-film composite (TFC) membranes are made from a variety of polymers consisting of several different materials for the substrate, the thin film and other functional layers.

Addition of different pore-formers to the casting solution is a useful method to improve membrane properties by changing the membrane morphology. Different materials such as ethanol, glycerol and lithium perchlorate (LiClO$_4$) have been added to
the casting solution to investigate their effects on the resulting polyvinylidene fluoride (PVDF) membrane performance [16]. With ethanol (EtOH) as an additive, the resulting membranes exhibited symmetric structures with uniform nodes, a trend that was attributed to the gelation provoked by crystallization before liquid–liquid demixing. In the presence of 2% LiClO₄ additive in the polymer solution, gelation of the polymer solution occurred, and the resulting membrane had a very irregular structure. On the other hand, with the addition of small amounts of glycerol to the casting solution, the membrane structure became more regular with fingerlike macrovoids, supported by a more porous substrate. Thus, the addition of glycerol is believed to have restrained the polymer interaction and favored liquid–liquid demixing.

In different study [17], lithium chloride (LiCl) was added to the casting solution containing polyamic acid (PAA) and N-methyl-2-pyrrolidone (NMP). That caused the formation of NMP-LiCl complexes, which decreased the interaction between NMP and polymer. Hence, reduction in NMP strength to interact with polymer led to aggregation of polymer chains in the casting solution resulting in fewer macrovoids on membrane. Thereby more porosity and more permeability, or in other words sponge-like asymmetric membranes, were obtained. Furthermore, other studies [18] on polyvinylidene fluoride (PVDF) membranes made of different solvents such as N,N-dimethylacetamide (DMA), N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO), and N-methyl-2-pyrrolidone (NMP) had already been performed. Once more, the same change in solvent strength due to LiCl effect was observed. That phenomenon decreased the membrane pore size which led to relatively higher salt rejection as well.
Moreover, different types of lithium halides such as lithium fluoride (LiF), lithium chloride (LiCl) and lithium bromide (LiBr) were added to casting dope consisting of polyethersulfone (PES) in DMF solvent in order to investigate their effects on the resulting hollow fiber membrane performances [19]. It was concluded that these additives change the membrane morphology and increase the pure water precompaction (PWP), with LiCl and LiF having similar permeation rates compared to LiBr. Additionally, it was found that adding more than 2% by weight LiBr yielded no additional increase in permeability. Polyethylene glycol (PEG) rejection results also revealed that introducing these additives to the casting solution enhanced the separation rates. Differences between lithium halides behavior was attributed to different halides’ molecular weights and viscosities, which can affect the non-solvent–solvent exchange and the velocity of phase separation.

2.2 Nanoparticles Impact on Membrane Performance

2.2.1 Nanoparticles discharges to the environment

Nanoparticles are a specific class of colloids, which as reported by Environmental Protection Agency (EPA) and the National Nanotechnology Initiative (NNI), have at least one dimension between 1 and 100 nm. They have been widely used in many consumer products and water and wastewater treatment systems due to their high surface to volume ratio. This high ratio provides nanoparticles with more reactive properties; thereby, the reaction between NPs and other molecules can be faster [20]. It has been reported that silver, carbon, titanium, silica, zinc and gold are the most wildly used NPs [21].
Industries manufacturing skin care products annually utilized 1,000 – 2,000 tons of NPs such as titanium dioxide, zinc oxide, silicon dioxide, aluminum oxide and iron oxide (Royal Academy of Engineering Report, 2004). Reported recent worldwide sales of products incorporating nanomaterials are €1.1 trillion, and are believed to increase to €4.1 trillion by 2015 [22]. Unfortunately, knowledge regarding NPs toxicity or impact on the environment has not increased at the same pace as their usage. There are no standard methods to measure nanoparticles in a soil or water sample; hence, little information is available on the presence of nanoparticles in these matrices. Therefore, it is difficult to study the effectiveness of current drinking and wastewater treatments to remove NPs, and it is subsequently hard to estimate population exposure to such particles through water [23].

Another rapidly growing use of nanotechnology is to aid in environmental applications, which is consequently expanding the volume of engineered NPs introduced to the environment. Therefore, NPs are widely released in receiving water bodies and must therefore be removed. One method that has the potential of removing NPs during water purification is membrane separations. However, particles smaller than membrane pores can accumulate at the pore entrance and ultimately plug the pore entrance and cause membrane fouling. That pore plugging would cause a flux decline [24]. NPs can also aggregate on the membrane surface to foul the membrane. That fouling might force more needs to frequent backwashing and other energy consuming processes. Thus, as different NPs would have different impacts on the resultant membrane performance, it is crucial to characterize the adsorption and aggregation abilities of different NPs.
2.2.2 TiO$_2$ entrapped membranes vs TiO$_2$ deposited membranes

Membrane bioreactors (MBRs), which are a combination of biological processes with membrane technology that replace activate sludge systems, have been widely used in wastewater treatment systems. However, like other membrane systems, fouling is a drawback. Fouling is growth of redundant materials on a solid surface, which can be divided into biofouling (living organism), and organic or nonorganic (non-living materials) fouling. In MBRs, the mixed liquor, which is the combination of wastewater and biological mass, can create biofilm and enhance membrane fouling. There are different methods to mitigate membrane fouling. One of them is either to introduce TiO$_2$ NPs to the casting solution in order to entrap the NPs within the membranes, or to deposit them on the membrane surface [11]. In their work, three different membranes with entrapped TiO$_2$ were made using dopes of polysulfone (PSf), polyvinylidenefluoride (PVDF) and polyacrylonitrile (PAN) in NMP solvent; then, different concentrations of TiO$_2$ NPs of 20 nm size were added to those dope solutions. Afterwards, flat-sheet membranes were cast via phase inversion. Membranes, made with TiO$_2$ deposited, were prepared by a dipping and pressurizing method. Cross-flow filtration tests using activated sludge as feed were performed with TiO$_2$ entrapped and deposited membranes. Membrane fouling was measured by calculating resistance in series model (Equation (1), [2]).

$$R_t = R_m + R_c + R_f$$  

Equation (1)

Where $R_t$ is the total resistance, $R_m$ is the intrinsic resistance of the membrane, $R_c$, is cake layer resistance formed on the membrane surface, and $R_f$ is caused by pore plugging and irreversible adsorption of foulants on pore wall or surface of the membrane.
Results of the study indicate that regardless the polymer dope, the presence of TiO$_2$ reduced cake layer resistance noticeably. Therefore, fouling mitigation was improved significantly. Furthermore, it was found that addition of TiO$_2$ decreased the contact angle, which resulted in more hydrophilic membranes. Lastly, TiO$_2$ entrapped and deposited membranes compared to neat membranes displayed less membrane fouling and flux decline. Comparison between TiO$_2$ immobilized membranes itself revealed that TiO$_2$ deposited membranes led to less fouling and higher flux than entrapped ones. This was explained by the fact that fouling mitigation is influenced by the surface area of NPs. In TiO$_2$ deposited method, more and larger NPs could be placed on the membrane surface and subsequently more reduction in fouling would be achieved.

Inserting TiO$_2$ to the casting dope formed a membrane with higher porosity and at the same time more blocked pores due to those NPs [11]. Higher porosity was explained by resultant increase in water-solvent inter-diffusion velocity in the coagulation bath, which was due to the hydrophilic nature of TiO$_2$. In other words, due to that hydrophilic nature of NPs, solvent diffusion velocity from the membrane to the water in the coagulation bath increased, which led to membranes with more porosity [25]. Furthermore, by comparing pure water flux data it was noticed that polymer material could affect permeability as well. For TiO$_2$ deposited membranes made of PVDF and PAN polymers, water flux values increased compared to pure polymer membranes, while for TiO$_2$ deposited membranes made of PSf, the flux decreased compared to pure PSf membranes. The difference could be due to the different materials of unlike nanoparticles, polymer and size of nanoparticles and their various impacts on different membranes.
In a different study, ultrafiltration TiO\textsubscript{2}-entrapped membranes were made of polyphthalazine ether sulfone ketone (PPESK) polymer in NMP solvent with polyvinyl pyrrolidone (PVP) as an additive via the phase inversion casting method [26]. It was determined that introducing up to 2wt\% TiO\textsubscript{2} into the casting solution increased the pure water flux, while beyond 2wt\% TiO\textsubscript{2} content led to flux decrease. This was attributed to the formation of larger pores on the membrane surface as a result of NPs aggregation. Contact angles and rejection of different solutes such as bovine serum albumin (BSA, MW 67,000), chicken egg albumin (CEA, MW 45,000) and lysozyme (MW 14,400) were measured to determine the effect of those nanoparticles on membrane morphology. The presence of TiO\textsubscript{2} in the casting solution decreased the contact angle and subsequently improved the membrane hydrophilicity. Lastly, the presence of TiO\textsubscript{2} in the casting dope up to 2wt.% increased the membrane rejection. Higher permeability and lower protein fouling were attributed to the increase in membrane porosity that caused less resistance against water permeation through the membrane and also more hydrophilicity, which reduced the interface tension of membrane-water and as a result more water molecules could be attracted to the membrane.

### 2.2.3 Fabrication of SPES/Nano-TiO\textsubscript{2} Composite Ultrafiltration Membrane

TiO\textsubscript{2} nanoparticles (NPs) with a range size of 5-42 nm were assembled on the sulfonated-polyethersulfone (SPES) membranes consisting of ether bond, sulfuryl group and sulfonic group [27]. To make those membranes wet UF membrane was rinsed in a sodium carbonate solution (0.2\% (by mass)) and then washed with deionized water. The neat SPES membrane with an area of 38.5 cm\textsuperscript{2} was dipped in the transparent colloidal
solution of TiO$_2$, stirred for 1 min by ultrasonic method and immersed for 1 h, and then washed with deionized water. Due to the strong electronegative oxygen in the ether bond, sulfuryl group and sulfonic group of the SPES, developing the composite UF membrane by the self-assembly between TiO$_2$ NPs and SPES previously mentioned groups could be done. Contact angle measurements revealed that hydrophilicity of these kinds of membrane has been improved significantly. Furthermore, scanning electron microscopy (SEM) and atomic force microscopy (AFM) images and separation experiments results verified that utilizing this method could lead to a membrane with much less fouling.

2.2.4 Microfiltration of TiO$_2$ Suspensions of Ceramic Membranes

In a study by Zhao et al [28], asymmetric tubular alumina ($\alpha$-Al$_2$O$_3$) microfiltration (MF) membranes were used to investigate the effect of pH and ionic strength (I) on TiO$_2$ microfiltration. In this regard, cross-flow MF tests of TiO$_2$ and different concentrations of NaCl solution on ceramic membranes were performed. The flux and zeta potential were measured for different ionic strengths and pH values. Results indicated that by increasing ionic strength, zeta potential would decrease, which was explained by equations (2) and (3) [29]:

$$I = \frac{1}{2} \sum C_i (Z_i)^2$$ \hspace{1cm} \text{Equation (2)}

$$I = 3.29 \sqrt{I}$$ \hspace{1cm} \text{Equation (3)}

Where I is ion concentration, $Z_i$, is, the charge number of the ion, and $1/ \theta$ is known as Debye length or thickness of the double layer. As can be found from the equations, when I increases, $1/ \theta$ increases as well which means $1/ \theta$ or the thickness of
double layer declines. In other words, zeta potential due to that diffuse layer compression decreases [28, 30, 31, 32, 33] 

According to reported flux data in that work, it was determined that the presence of TiO\textsubscript{2} in salt solution could lead to an increase in permeability. This trend was explained due to the flocculation of those particles at high ionic strength. The floc formation caused a more permeable cake because of the greater hydrodynamic lift and also higher shear-induced diffusion coefficient, which larger particles would experience [34]. In other words, with increasing ionic strength and decreasing pH in the salt solution, less cake resistance occurred, which led to higher permeate flux. However, TiO\textsubscript{2} results were in contrast with results from microfiltration of silica particles. MF results of silica resulted in higher permeate flux in lower salt concentration [35]. That contradiction was related to the different nature or structure of silica and TiO\textsubscript{2}; that is, unlike silica particles, TiO\textsubscript{2} flocculation happened [35].
Chapter 3

3 Investigation of the Effects of Thickness and Presence of Pore Former on Tailor-made Ultrafiltration Polysulfone Membranes

3.1 Abstract

Membranes are capable of separating species as a function of their physical and chemical properties when a driving force is applied, which enables filtration for removal of colloids, cells and molecules. In this work, flat sheet polysulfone ultrafiltration membranes were cast due to polysulfone’s high mechanical strength, thermostability and stability against chemicals. The main goal was to investigate the effects of dope concentration, membrane thickness and inorganic additive, lithium chloride (LiCl), on the filtration of different salt concentrations. The results revealed that with increasing dope concentration and membrane thickness, permeability decreased and subsequently salt rejection increased. Furthermore, compared to LiCl-free membranes, LiCl-containing ones were more permeable and displayed higher salt rejection, which was due to more porosity and smaller pore size caused by LiCl additives in membranes.
3.2 Introduction

Membrane technology has become an interesting, useful separation method over the past decades due to higher efficiencies and with advances, lower energy requirements for operation. As a result companies have started to utilize them as an alternative for many water purification processes. Membrane properties, such as permeability and rejection, are greatly influenced by the thickness of the membrane [36, 37, 38], the method of casting the membrane [39] and dope solution chemistry [24] which itself depends on many factors like dope concentration and additives or pore formers. Permeability and rejection are also influenced by the membranes filter solution.

For water purification processes, there are four major kinds of membranes currently used, reverse osmosis, nanofiltration, ultrafiltration and microfiltration. Membranes are manufactured from a variety of materials, such as cellulose acetate (CA), cellulose diacetate (CDA), cellulose triacetate, polyamide (PA), other aromatic polyamides, polyetheramides, polyetheramines, polysulfone (PSf), and polyetherurea; also, thin-film composite (TFC) membranes may be made from a variety of polymers consisting of several different materials for the substrate, the thin film and other functional layers. In this work tailor-made flat-sheet PSf membranes were used due to polysulfone’s high mechanical strength, thermostability and stability against chemicals.

Ultrafiltration polysulfone (PSf) membranes were chosen to investigate the effects of different casting solution (dope) concentrations, casting thickness, addition of pore-
forming additives, and subsequently, the membrane properties of permeability and salt rejection. Therefore, at first, PSf membranes with different concentrations and thicknesses were cast via immersion precipitation [40]. They were then precompacted with distilled water followed by the filtration of salt solutions of different concentrations. Then, the exact same membranes were cast with the addition of a pore-forming additive, lithium chloride (LiCl), to determine the significance of the addition of the pore former on the membrane’s permeability and salt rejection.

3.3 Experimental

3.3.1 Materials and Casting Instrument

Chemicals purchased, polysulfone (PSf, Aldrich, Mn: 22000), 1-methyl-2-pyrrolidinone (NMP, Alfa Aesar, 99%) and lithium chloride (LiCl, Sigma-Aldrich, 99%) were used as received. For membrane preparation, a BYK-Gardner film casting knife (provided by Paul N. Gardner Company) was used, and dial gauges were used to measure the thickness in different parts of the membrane to determine the average thickness.

3.3.2 Membrane Preparation

In either the absence or presence of LiCl, casting solutions (i.e. dopes) of different concentrations were made: 10, 12, 13, 15, 16 and 18wt% PSf. These dopes were prepared by adding PSf to NMP and stirring for about 24 hours. Then, by using an adjustable BYK-Gardner film casting knife, the dope was spread on a glass substrate at different thicknesses (optimal thickness range was found to lie between 120-240
micrometers). The formed film on the glass substrate was then put into a coagulation bath filled with deionized water (DI) to separate it from the glass surface. Therefore, flat-sheet membranes were formed via phase inversion [41, 42] The reason for using glass instead of Teflon or some other substrates was because of obtaining higher permeability due to less formed shrinkage [39]. All the flat-sheet membrane casting procedures are presented in Figures 3-1 through 3-4.

Figure 3-1: Casting of PSf dope on a mirror by using a film casting knife

Figure 3-2: PSf dope upon completion of casting
3.3.3 Precompaction and Filtration

For filtration experiments, dead-end filtration tests, in which applied pressure is a driving force and the only outlet for upstream fluid or feed is through the membrane, were performed using an Amicon 8010 stirred cell (Figure 3-5) with a rotating speed of about 300 rpm and an applied pressure of 70 psi (4.83 bar) was used. Small membrane samples of 4.1 cm$^2$ surface area were cut from similar locations on the cast membranes, and were precompacted by means of using DI water in the filtration cell for six hours.
After approximately 6 hours of precompaction upon reaching stable fluxes, filtration of salt solutions of different concentrations was started.

![Filtration Instrument (Dead-End Method).](image)

**Figure 3-5: Filtration Instrument (Dead-End Method).**

Sodium chloride (NaCl) solutions of different concentrations, also under 70 ps i pressure, were filtered for approximately six hours. Flux was measured for every 2 mL permeate volume; that is, time was measured for the filtration of 2 mL, while the filtration cell volume was 10 mL. In detail, the time to filter 2 mL from 6 to 4 mL was measured, which means both precompaction and filtration processes were run for 6 mL solutions separately. After gathering 4 mL DI water from running the test, the time was measured for the next 2 mL. The same was done for salt filtration in order to obtain reliable flux data. It should be noted that flux data reported (Figures 3-6 through 11) do not represent flux measurements evenly every 2 mL; instead, they show flux measurements for 2 mL from each run. That is, if precompaction lasted for 6 hours and 5 runs were needed, for each run the flux was measured for a 2 mL volume. This was done
because at the beginning flux was obviously high due to no precompaction, but after 4 mL the flux was more reliable and stable to be measured. This was verified by running different precompaction tests for membranes of same thicknesses.

Salt rejection was measured by using the following equation (4):

\[
\text{Rejection} = \frac{[(\text{feed conductivity}) - (\text{permeate conductivity})]}{\text{feed conductivity}} \quad \text{Equation (4)}
\]

Where the permeate conductivity is the average conductivity of permeate measurements obtained throughout filtration. Conductivity was measured by a portable conductivity meter Accumet® AP75 (Catalog No. 13636 AP75A, Fisher Scientific, PA).

3.4 Results and Discussion

3.4.1 Casting Solution Concentration

It was first determined that cast solutions of 10 and 12 wt% PSf led to inconsistent membranes that would tend to tear during filtration. Higher dope concentrations, such as 16 and 18wt%, were then tested. In such cases, casting of membranes was possible, but with resulting very low flux values even at a low thicknesses (for example, a thickness of 100µm led to a precompaction flux of 3 L/m²hr, which was deemed too low for adequate prolonged testing. Therefore, dope solutions of 13 and 15wt% were tested, and were found to be able to lead to consistent (i.e. reproducible) membranes with reasonable flux measurements for testing. Also, precompaction tests were performed at different pressures: 50-60 and 70 psi, and the fact
that with increasing the pressure, permeate flux increased, was verified and a pressure of 70 psi was chosen for testing. This is true in this study since the membrane used was ultrafiltration, so concentration polarization did not occur significantly to dominate the flux.

Precompaction and filtration flux data for 13wt% PSf dope solutions in the absence of LiCl for different thicknesses are shown in Figures 3-6 and 3-7. Both figures show that as the membrane became thicker, flux decreased due to the increased resistance to filtration, as expected. Furthermore, as the salt concentration increased, flux decreased. With membrane of higher thickness (220 µm), final flux values after filtration of 20 mM NaCl was about 5.3 L/m²hr while the resultant flux obtained from filtration of 100 mM NaCl of a thinner membrane (165 µm) was 16.2 L/m²hr (Table 3-1). In other words, although higher flux values are expected from filtration of lower salt concentrations, this study obtained higher fluxes from higher concentrations due to using membrane of lower thicknesses. Thereby, it can be concluded that membrane thickness displayed a more significant effect on flux than salt concentration.
Figure 3-6: Precompaction and filtration flux data for 13wt%PSf of relatively low thickness (µm).

Figure 3-7: Precompaction and filtration flux data for 13wt%PSf of higher thickness.
Figures 3-8 (A and B) and 3-10 show precompaction and filtration results for 15wt% PSf membranes of different thicknesses. Figures 3-8(A) and 3-8(B) show the precompaction and filtration, respectively, using 15wt% PSf dopes at lower membrane thicknesses, while Figure 3-10 at higher thicknesses. To show the reproducibility of the cast membranes, precompaction and filtration for membranes of the same thickness of 155µm were performed three times, and the resultant precompaction flux values were not significantly different (Figure 3-9). Similar conclusions to the 13wt% membranes were observed with the difference that more concentrated dopes led to lower flux values overall.
Figure 3-8: (A). Precompaction and (B). filtration flux data for 15wt%PSf of relatively low thickness.
Figure 3-9: Precompaction and filtration of membranes of 155 µm thickness.
As can be seen in all figures, the decrease in precompaction and filtration flux values over time always occurred. Mosqueda-Jimenez et al., 2004 reported [43], precompaction compresses the membrane, so membranes with more compressible structures, such as polysulfone, experience a reduction in flux during precompaction. The flux reductions are explained by more compaction and possible concentration polarization during the dead-end filtration of salt solutions, respectively.

Tables 3-1 and 3-2 show that membrane thickness and the concentrations of both the casting dope and the filtration (NaCl) solutions had a noticeable effect on the permeate flux. Higher thicknesses and casting dope solution concentrations lead to less permeability and subsequently higher rejection [36, 37]. Average flux in Tables means the average of fluxes once flux values became consistent, such as during the last 3 hours. That was done because precompaction and filtration were done for approximately 6 hrs each, but flux changes were not stable from the beginning”.

Figure 3-10: Precompaction and filtration flux data for 15 wt%PSf of higher thickness.
Table 3-1: Precompaction and Filtration flux data of 13 wt% PSf membrane in the absence of LiCl (Any “-” indicates tests were not performed for those thicknesses.)

<table>
<thead>
<tr>
<th>Thickness (µm)</th>
<th>145</th>
<th>155</th>
<th>165</th>
<th>180</th>
<th>182</th>
<th>220</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avg. Precompaction Flux (L/m²hr)</td>
<td>40.3</td>
<td>29.0</td>
<td>23.6</td>
<td>13.1</td>
<td>12.2</td>
<td>9.4</td>
</tr>
<tr>
<td>NaCl Concentration (mM)</td>
<td>_</td>
<td>10</td>
<td>100</td>
<td>_</td>
<td>_</td>
<td>20</td>
</tr>
<tr>
<td>Avg. Filtration Flux (L/m²hr)</td>
<td>21.5</td>
<td>16.2</td>
<td>5.3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3-2: Precompaction and Filtration flux data of 15 wt% PSf membrane in the absence of LiCl (Any “-” indicates tests were not performed for those thicknesses.)

<table>
<thead>
<tr>
<th>Thickness (µm)</th>
<th>125</th>
<th>135</th>
<th>137</th>
<th>155</th>
<th>184</th>
<th>186</th>
<th>200</th>
<th>220</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avg. Precompaction Flux (L/m²hr)</td>
<td>27.1</td>
<td>20.3</td>
<td>18.9</td>
<td>16.4</td>
<td>12.7</td>
<td>10.7</td>
<td>8.9</td>
<td>6.9</td>
</tr>
<tr>
<td>NaCl Concentration (mM)</td>
<td>20</td>
<td>10</td>
<td>20</td>
<td>35</td>
<td>20</td>
<td>100</td>
<td>_</td>
<td>_</td>
</tr>
<tr>
<td>Avg. Filtration Flux (L/m²hr)</td>
<td>24.7</td>
<td>17.7</td>
<td>17.5</td>
<td>14.4</td>
<td>11.9</td>
<td>8.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

All flux declines were rather low. It was during precompaction that the majority of the flux decline was observed and that was due to the compression of the PSf membranes. The trends of interest here were not the declines in flux due to the filtration.
of salt solutions; instead, the focus was the comparison of the effects of dope concentration, presence of LiCl and membrane thickness. The data in Figures 3-6 through 3-10 show that salt solutions had a low effect on flux decline but do provide information on the differences from dope concentration, LiCl and thickness. Based upon the data in Table 3-1, the 13 wt% membrane’s maximum and minimum flux values for the thickness range of 145-220µm were approximately 40 and 9 L/m²hr, respectively. For 15 wt% membranes, Table 3-2 shows that for thicknesses in the range of 125-220µm, the maximum and minimum flux values were approximately 27 and 7 L/m²hr, respectively.

### 3.4.2 Effect of LiCl Additive

Several studies have shown that casting solution properties have a significant influence on asymmetric membrane formation and subsequently its structure [19, 28, 35, 44, 45, 46, 47, 48]. To determine the effects of the addition of a pore-former, lithium chloride (LiCl), the 15 wt% PSf dope concentration was chosen since it displayed better behavior in comparison to 13 Wt.% Therefore, the ternary solution, PSf, NMP and LiCl (as a pore-former), was prepared to find out the effect of the pore former on membrane performance. In previous published research [17, 49], LiCl changed the membrane morphology and caused changes in permeability and rejection. In this work, the flux after precompaction and filtration was directly measured for the PSf membranes. Solutions of 1, 1.5 and 2 wt% LiCl were added to the solutions containing 15 wt% PSf in NMP. In this work, 2 wt% LiCl was found too viscous and it was difficult to obtain a smooth, flat-sheet membrane with no excessively large pores. With 2 wt% LiCl, there were noticeably porous on the surface.
Therefore in this work the maximum appropriate LiCl concentration was found to be 1.5 wt% with respect to obtaining higher flux and also being easier to be employed for membrane casting. In Figures 3-11 through 3-13, flux measurements for membranes cast using 15 wt% PSf dope including 1.5 wt% LiCl and with different thicknesses are presented.

![Graph showing flux measurements for membranes cast using 15 wt% PSf +1.5 wt% LiCl solution.](image)

Figure 3-11: Precompaction flux data for membranes of relatively low thickness cast by 15 wt%PSf +1.5 wt% LiCl solution.
Figure 3-12: Precompaction flux data for membranes of high thickness cast by 15 wt% PSf +1.5 wt% LiCl solution accompanying by two filtration data for 200µm.
Importantly all flat-sheets were cast under the same conditions, and all flux measurements were performed with the exact same procedure. Because of these measures to make data obtained reproducible, applicable and reliable, Figures 3-6 through 3-13 presented a smooth and gradual decrease in flux, with flux values falling on a single, characteristic line of flux vs elapsed time. The characteristic line indicated, as expected, that as membrane thickness increased, flux decreased due to increased resistance to flow. Furthermore, since tested membranes were ultrafiltration, the effect of concentration polarization from the filtration of salt solutions was not high, as it would be in the case of reverse osmosis or nanofiltration. Therefore, flux values obtained during the filtration of the salt solutions also fell on the characteristic line albeit at lower fluxes showing minor concentration polarization occurring.
From Figures 3-11 through 3-13, once more, the effect of thickness and filtration solution concentration on the membrane performance were observed. Flux values after precompaction and filtration (only NaCl solution) for membranes cast with LiCl in the dope are summarized in Table 3-3. When flux values were compared for 15 wt% PSf membranes of similar thicknesses with the only difference being the presence of LiCl in the dope (Tables 3-2 and 3-3), the effect of LiCl on membrane permeability can be observed. LiCl-free membranes of 155 µm thickness had average precompaction fluxes of 16 L/m²hr, while those containing the pore former (LiCl) in the casting dope and of the same thickness had average fluxes of 22 L/m²hr. As Lee et al [17] explained, the higher permeability can be elucidated by the interaction between NMP (solvent) and LiCl, which leads to a NMP-LiCl complex. This complex causes a reduction in solvent (NMP) strength that means the polymer (polysulfone) is less soluble in the solvent, and consequently, the polymer aggregates in the solution [17]. Thus, this aggregation reduces macrovoids formation, which means membranes with more porosities and, thus, higher fluxes [17, 36, 37, 44]. Fractional flux decline (calculated as the change in flux between precompaction and filtration divided by the precompaction flux) of the above membranes tabulated in Table 3-3 were measured by equation 5 and presented in Figure 3-14. From this figure, it can be seen that filtration of only NaCl always led to a decrease in the filtration flux.
Table 3-3: Precompaction and Filtration (only NaCl solution) flux data of 15 wt%PSf+1.5 wt %LiCl

<table>
<thead>
<tr>
<th>Thickness (µm)</th>
<th>~127</th>
<th>165</th>
<th>200</th>
<th>145</th>
<th>~170</th>
<th>200</th>
<th>202</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avg. Precompaction Flux (L/m²hr)</td>
<td>29.2</td>
<td>18.7</td>
<td>13</td>
<td>25.4</td>
<td>17.3</td>
<td>12.5</td>
<td>11</td>
</tr>
<tr>
<td>NaCl Concentration (mM)</td>
<td>20</td>
<td>20</td>
<td>35</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Avg. Filtration Flux (L/m²hr)</td>
<td>24.5</td>
<td>11.4</td>
<td>9.6</td>
<td>18.8</td>
<td>11.4</td>
<td>10.8</td>
<td>8.5</td>
</tr>
</tbody>
</table>

Figure 3-14: Flux decline of membranes casting by 15 PSfwt%+1.5 wt% LiCl solution
3.4.3 Rejection Measurements

Rejection of NaCl solutions by 15 wt% PSf in the absence of LiCl are presented in Table 3-4, while those for 15 wt% PSf in the presence of 1.5 wt% LiCl are shown in Tables 3-5 and 3-6.

**Table 3-4: Rejection data for 15 wt% PSf solution excluding LiCl**

<table>
<thead>
<tr>
<th>Thickness (µm)</th>
<th>NaCl Concentration (mM)</th>
<th>155</th>
<th>155</th>
<th>184</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>35</td>
<td>0.036±0.001</td>
<td>0.031±0.001</td>
<td>0.036±0.001</td>
</tr>
</tbody>
</table>

**Table 3-5: Rejection data from filtration of 100mM NaCl solution for 15 wt% PSf solution including LiCl**

<table>
<thead>
<tr>
<th>Thickness (µm)</th>
<th>145</th>
<th>160</th>
<th>170</th>
<th>203</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fraction Rejection</td>
<td>0.05±0.001</td>
<td>0.06±0.002</td>
<td>0.057±0.003</td>
<td>~0.07±0.002</td>
</tr>
</tbody>
</table>

**Table 3-6: Rejection data from filtration of 35mM NaCl solution for 15 wt% PSf solution including LiCl**

<table>
<thead>
<tr>
<th>Thickness (µm)</th>
<th>200</th>
<th>135</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fraction Rejection</td>
<td>0.08±0.002</td>
<td>0.046±0.001</td>
</tr>
</tbody>
</table>
According to the tables above, it was observed that as thickness increased, the resistance to permeability increased and the salt rejection increased. Furthermore, at higher salt concentrations, concentration polarization led to a decrease in filtration flux [50]. Based on the presented results, casting membranes using 15 wt% PSf dopes including 1.5 wt% LiCl showed the highest overall efficiency due to the increase in both permeability and NaCl rejection because of the change in membrane morphology. This trend can be explained as a result of higher porosity with lower pore size as a result of the LiCl additive [44]. However, since the membrane used was ultrafiltration, rejection of NaCl solutions was low, as expected. Rejection values were therefore not significantly different and just indicate a trend.

3.5 Conclusion

For ultrafiltration, it was found that 13 and 15 wt% PSf dopes produced membranes that were reproducible and able to be tested in a dead-end mode to exaggerate experimental conditions. Precompaction flux values for membranes cast using 13wt% PSf dopes were higher than those cast using 15 wt% PSf dopes. However, by employing 15 wt% PSf dopes, membranes of lower thicknesses could be obtained because of the more viscous dope. The 15 wt% membranes also displayed higher NaCl rejections, as expected, by denser membranes. It was also determined that membrane thickness affected flux; with higher thicknesses leading to lower fluxes and higher rejections. Moreover, adding LiCl to 15 wt% PSf dope decreased the interaction between NMP and polysulfone, which led to polymer aggregation that decreased macrovoids, and as a
result, enhanced the membrane porosity and subsequently the permeability. An increase in salt rejection for membranes cast with the addition of LiCl in the dope was also observed.
Chapter 4

4 Study of Two Metal Oxide Nanoparticles Effects on Polysulfone Ultrafiltration Performance

4.1 Abstract

With increasing manufacture and application of nanoparticles, it is inevitable that large amounts are eventually discharged into the environment and will ultimately be encountered in water and wastewater systems. Because of nanoparticle size and high capacity to convey toxic substances, nanoparticles can have adverse effects on human health and the environment. Therefore, nanoparticles are an emerging class of contaminants so that water purification technologies must be designed to remove when present. For the study presented here, two metal oxide nanoparticles, TiO$_2$ and ZnO, were used as model nanoparticles due to their wide use. Membranes are capable of separating species as a function of their physical and chemical properties when a driving force is applied, which enables filtration for removal of colloids, cells and molecules. Filtration processes, such as ultrafiltration (UF) and microfiltration (MF), play major roles in filtration of fresh waters, brackish and saline waters, as well as wastewaters. For this study, polysulfone (PSf) ultrafiltration membranes, chosen due to their high mechanical
strength, thermostability and stability against chemicals, were tailor-made via immersion precipitation with high flux values to study nanoparticle rejection and accumulation on the membrane. The central hypothesis was that, like other colloidal fouling, fouling by nanoparticles would be influenced by the solution ionic strength. Therefore, the impacts of solution chemistry on the aggregation state and deposition mechanisms of nanoparticles by changing the salt concentration were investigated.

4.2 Introduction

Nanoparticles are a specific class of colloids, which as reported by Environmental Protection Agency (EPA) and the National Nanotechnology Initiative (NNI), have at least one dimension between 1 and 100 nm. They have been widely used in many consumer products and water and wastewater treatment systems due to their high surface to volume ratio. This higher ratio provides nanoparticles with more reactive properties; thereby, the reaction between NP and other molecules can be faster [20]. In Table 4-1 common applications of nanotechnology and in particular NPs are provided. It has been reported that silver, carbon, titanium, silica, zinc and gold are the most widespread currently used NPs [21].
While commonly used to aid in environmental applications, NPs are also widely released in receiving water bodies and must therefore be removed. One method that has the potential of removing NPs during water purification is membrane separations. However, particles smaller than membrane pores can accumulate at the pore entrance and ultimately block the pore entrance and cause membrane fouling. This pore plugging would endow the membrane a flux decline [24]. NPs can also aggregate on the membrane surface to foul the membrane, which creates a need for more frequent backwashing and other energy consuming processes. Thus, it is crucial to characterize the adsorption and aggregation abilities of different NPs. For the study presented here, anatase (tetragonal crystal) structure of titanium dioxide (TiO$_2$) with the range size of 5-10 nanometers (nm) and hydrophilic zinc oxide (ZnO) of approximately 20 nm were used as model NPs, as they are commonly consumer products. Anatase forms of TiO$_2$ nanoparticles (NPs) are very hydrophilic, photoactive and useful for wide environmental applications, such as water and wastewater treatment, hazardous waste control and air purification [39]. TiO$_2$ has an isoelectric point (IEP) in the range of pH = 4.0 – 5.5 depending on manufacturer [5], while ZnO’s IEP is in the range of pH = 7.13 – 9.2 [6, 7, 8, 9]. IEP is the pH in which the zeta potential is zero.

Table 4-1: Nanotechnology applications (source: Mileyeva-Biebesheimer [21], nanotechproject.org [51]).

<table>
<thead>
<tr>
<th>Type of the products</th>
<th>Personal care products</th>
<th>Clothing</th>
<th>Cosmetics</th>
<th>Sporting goods</th>
<th>Sunscreen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of products in inventory</td>
<td>193</td>
<td>155</td>
<td>137</td>
<td>93</td>
<td>33</td>
</tr>
</tbody>
</table>
4.3 Experimental

4.3.1 Materials and Casting Instrument

Polysulfone (PSf, Aldrich, Mn: 22000), 1-methyl-2-pyrrolidinone (NMP, Alfa Aesar, 99%) and lithium chloride (LiCl, Sigma-Aldrich, 99%) were used as received. For membrane preparation, a BYK-Gardner film casting knife was used (Figure 3-1). Titanium dioxide (anatase phase) and zinc oxide NPs with purities greater than 98% and 99.8%, respectively were provided by Sun Innovations Inc., CA. TiO$_2$ and ZnO reported range sizes were 5-10 and 20 nm, correspondingly.

4.3.2 Membrane Preparation

Flat-sheet polysulfone membranes were cast using phase inversion with a dope composition of 15 wt% PSf and 1.5 wt% LiCl in NMP. The detailed casting procedure has been explained in Chapter 3.

4.3.3 Precompaction and Filtration

Membrane samples of 4.1 cm$^2$ surface area were punched out of the flat-sheet cast membranes, and were precompacted by means of using deionized water (DI) using a dead-end filtration cell (Figure 4-1). After precompaction, sodium chloride (NaCl) solutions of different concentrations in the presence of TiO$_2$ and ZnO were filtered. Both precompaction and filtration experiments were performed under 70 psi (4.83 bar) pressure and a rotating speed of about 300 rpm for approximately six hours. For each test, flux and rejection were monitored as explained in Chapter 3.
4.3.4 Scanning Electron Microscopy (SEM)

Scanning electron microscope (SEM, Hitachi S-4800, high resolution, made by Japan) uses an electron beam produced by high voltage (15-20 KeV) to visualize the sample as the light microscope uses the visible light produced by illuminating the source. Due to the application of electron optics, SEM results in a much higher resolution and greater depth of field in imaging a sample surface. In SEM, an electron gun produces a beam of monochromatic electrons. This beam passes through the first and second condenser lens resulting in a thinner and coherent beam, which is focused onto the sample surface through an objective lens. The finer electron beam thus focused on the specimen is scanned across the specimen surface. Sharpness of the image produced depends on the fineness of the beam diameter.

Energy Dispersive X-ray Spectroscopy (or EDS or EDX) is a chemical microanalysis technique used in conjunction with SEM. The EDS technique detects x-rays emitted from the sample during bombardment by the primary electron beam to characterize the elemental composition of the analyzed surface. The emitted X-ray has an energy characteristic of the parent element allowing for it to be specifically identified. The pattern obtained by this method contains peaks in various positions displaying the energy
levels of each scattered X-ray corresponding to a certain material/element. EDS data was obtained by Ultra Thin Window (UTW) Si-Li Solid State X-ray detector attached to XL 30 FEG SEM and used to quantify amounts of TiO$_2$ on the membrane.

4.4 Results and Discussion

4.4.1 Nanoparticles Size

Based on the information on nanoparticles size reported by the manufacturer (Sun Innovations Inc., CA), TiO$_2$ and ZnO had size ranges of 5-10 and 20 nm, respectively. However, according to transmission electron microscopy (TEM, Hitachi HD2300A, Hitachi High Technologies America, Schaumburg, IL) images of those nanoparticles, they had size ranges of 10-20 nm (Figure 4-2, [51]).
4.4.2 Filtration in the Presence of TiO₂ Nanoparticles

Filtration (or feed) solutions were made of TiO₂ at a concentration of 0.1 g/L and NaCl at concentrations varying between 20-100 mM. To make the filtration solution,
TiO$_2$ was added to DI water and shaken using an orbital shaker over night. To this TiO$_2$ solution, NaCl of different concentrations was added to make the filtration solution of pH of approximately 7.3. Resultant solutions were shaken again followed by sonication for approximately 18 minutes to minimize aggregation of the NPs. Afterwards they were used for filtration assays. All these procedures were repeated for the ZnO studies as well. The flux for TiO$_2$ NPs solutions in the presence and absence of NaCl are presented in Figures 4-3 through 4-6.
Figure 4-3 (A and B): Precompaction and filtration flux data of relatively thin membranes (Filtration solutions consist of TiO$_2$).

For the 155 µm thick membrane, filtration of the 20 mM NaCl and 0.1 g/L TiO$_2$ solution was performed accompanied by sonication every seven minutes to have a well-dispersed NPs solution (Figure 4-3(A)). The key observation from Figure 4-3(A) is that in the presence of TiO$_2$ NPs, the filtration flux was always higher than the final value of the precompaction flux. Other tests for membranes of lower thickness (143 and 145µm) using feed solutions of 100 mM NaCl and TiO$_2$ without sonication were also performed (Figure 4-3(B)). For the cases without sonication, the increase in filtration flux as compared to the final precompaction flux was higher than in the cases with sonication. This difference in behavior was associated with more NPs aggregation in case of non-sonication that affected membrane performance. In other words, sonication is performed...
to provide better dispersion and lower NPs aggregation, but aggregation still occurs. Therefore, unlike filtration of solutions containing only NaCl (presented in Chapter 3), addition of TiO$_2$ to the filtration solution increased the flux regardless of sonication. However, to support this hypothesis more tests were performed as presented in Figures 4-4 and 4-5.

**Figure 4-4: Precompaction and filtration flux data of relatively thick membranes (All filtration solutions consist of TiO$_2$).**

Filtration flux using a filtration solution containing 20 mM NaCl in the presence of 0.1 g/L TiO$_2$ for a membrane of 167 µm thickness with sonication is presented in Figure 4-4. Average flux values obtained from precompaction and filtration were 17.9 L/m$^2$/hr and 18.6 L/m$^2$/hr, respectively. The filtration of TiO$_2$ solution with 35 mM NaCl using a membrane of similar thickness (170 µm) and without solution sonication, also led
to a difference between final precompaction (17.1 L/m²·hr) and filtration flux (18.5 L/m²·hr). Notably the initial precompaction flux was higher for the thinner membrane, as expected. Additional studies using membranes of thicknesses higher than 180 µm (Figure 4-5(B)) and higher than 200 µm (Figure 4-5(C)) were performed. For all cases, resultant flux from filtration increased compared to pure water flux. That was attributed due to TiO₂ presence in the solution.
Figure B: ELAPSED TIME vs FLUX for precompaction and filtration of 180 μm particles.

Figure C: ELAPSED TIME vs FLUX for precompaction and filtration of 200 μm particles.
Experiments using a filtration solution of 35mM NaCl and TiO$_2$ for three membranes with similar thicknesses (180 µm) but from different flat-sheets were performed to investigate variability, as shown in Figure 4-5(B). Average flux from precompaction and filtration were respectively, 14.3±0.1 L/m$^2$h and 15.3±0.1 L/m$^2$h.

To investigate the effect of presence of TiO$_2$ on filtration flux, a comparison between feed solutions in the absence of TiO$_2$ (Table 3-3) and in the presence of TiO$_2$ (Tables 4-2 through 4-4) was performed using membranes of similar thicknesses cast using 15% PSf and 1.5% LiCl dope. In the absence of TiO$_2$, using the 165 µm and 20 mM NaCl (Table 3-3), the precompaction flux was 18.7 L/m$^2$h and the filtration flux
was 11.4 L/m²hr; on the other hand, in the presence of TiO₂, using the 167 µm and 20 mM NaCl (Table 4-2), the precompaction flux was 17.9 L/m²hr and the filtration flux was 18.6 L/m²hr. For the second comparison, in the absence of TiO₂, using the 200 µm and 35 mM NaCl (Table 3-3), the precompaction flux was 13.0 L/m²hr and the filtration flux was 9.6 L/m²hr; on the other hand, in the presence of TiO₂, using the 200 µm and 35 mM NaCl (Table 4-3), the precompaction flux was 13.2 L/m²hr and the filtration flux was 14.3 L/m²hr. For the last comparison, in the absence of TiO₂, using the 170 µm and 100 mM NaCl (Table 3-3), the precompaction flux was 17.3 L/m²hr and the filtration flux was 11.4 L/m²hr; on the other hand, in the presence of TiO₂, using the 172 µm and 100 mM NaCl (Table 4-4), the precompaction flux was 14.9 L/m²hr and the filtration flux was 15.9 L/m²hr. Therefore, the presence of TiO₂ in the feed solution led to increases in filtration flux as compared to precompaction flux regardless of salt concentration.

By comparing all the data from all Figures 4-3 – 4-5 (summarized in Tables 4-2 – 4-4), it was verified that by increasing NaCl concentration in the presence of TiO₂, the difference between precompaction and filtration flux increased. For example, all in the presence of TiO₂, for thickness of 178 µm and 0 mM NaCl, the filtration flux increased by 0.2 L/m²hr as compared to the precompaction flux; for thickness of 167 µm and 20 mM NaCl, the increase was 0.7 L/m²hr; for thickness of 170 µm and 35 mM NaCl, the increase was 1.4 L/m²hr (while for 180 µm, it was 1.0 L/m²hr); and lastly, for thickness of 176 µm and 100 mM NaCl, the increase was 1.7 L/m²hr (while for 172 µm, it was 1.0 L/m²hr). Furthermore, regardless of the NaCl concentration, the presence of TiO₂ in the solution always led to an increase in the filtration flux compared to pure water flux.
Table 4-2: Precompaction and filtration flux data (Filtration solution consists of either only TiO₂ or 20 mM NaCl +TiO₂).

<table>
<thead>
<tr>
<th>Thickness (µm)</th>
<th>178</th>
<th>207</th>
<th>210</th>
<th>155</th>
<th>167</th>
<th>210</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avg. Precompaction Flux (L/m²/hr)</td>
<td>15.4</td>
<td>10.9</td>
<td>9.3</td>
<td>21.5</td>
<td>17.9</td>
<td>9.1</td>
</tr>
<tr>
<td>NaCl Concentration (mM)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Avg. Filtration Flux (L/m²/hr)</td>
<td>15.6</td>
<td>11.0</td>
<td>10.4</td>
<td>21.8</td>
<td>18.6</td>
<td>9.4</td>
</tr>
</tbody>
</table>

Table 4-3: Precompaction and filtration flux data (Filtration solution consists of TiO₂ and 35 mM NaCl).

<table>
<thead>
<tr>
<th>Thickness (µm)</th>
<th>150</th>
<th>155</th>
<th>~170</th>
<th>~180</th>
<th>200</th>
<th>220</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avg. Precompaction Flux (L/m²/hr)</td>
<td>22.9</td>
<td>21.8</td>
<td>17.1</td>
<td>14.3</td>
<td>13.2</td>
<td>8.1</td>
</tr>
<tr>
<td>Avg. Filtration Flux (L/m²/hr)</td>
<td>23.7</td>
<td>22.7</td>
<td>18.5</td>
<td>15.3</td>
<td>14.3</td>
<td>8.9</td>
</tr>
</tbody>
</table>
Table 4-4: Precompaction and filtration flux data (Filtration solution consists of TiO₂ and 100 mM NaCl).

<table>
<thead>
<tr>
<th>Thickness (µm)</th>
<th>~127</th>
<th>143</th>
<th>~145</th>
<th>172</th>
<th>176</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avg. Precompaction Flux (L/m²hr)</td>
<td>29.4</td>
<td>26.2</td>
<td>24.5</td>
<td>14.9</td>
<td>15.6</td>
</tr>
<tr>
<td>Avg. Filtration Flux (L/m²hr)</td>
<td>31.3</td>
<td>29.1</td>
<td>26.9</td>
<td>15.9</td>
<td>17.3</td>
</tr>
</tbody>
</table>

In order to show the impact of TiO₂ on the final flux obtained after filtration, fractional flux decline (the change in flux from precompaction to filtration divided by the precompaction flux) versus membranes thickness was plotted (Figures 4-6). The first observation of this plot is that all fractional flux values were negative, which means flux increased during filtration, which verified that the presence of TiO₂ increased the filtration flux. Furthermore, higher salt concentrations (35 mM and 100 mM NaCl) always led to higher increases in final flux (i.e. consistently more negative values of fractional flux decline).
Zhao et al. (2005) proposed that at high ionic strength, the zeta potentials would decrease due to double layer compression, which caused TiO$_2$ to tend to flocculate to form a more permeable fouling cake. The larger particles would also experience more hydrodynamic lift, which would lead to a thinner cake layer and thus higher flux during filtration. Therefore, it is hypothesized here that, in the presence of TiO$_2$, the cake resistance was decreased and the permeate flux increased. Simply put, that increase can be explained due to TiO$_2$ impact on membrane morphology (that is, the compression of the electric double layer to decrease charge) and more TiO$_2$ flocculation. However, to
support these assumptions backwashing, scanning electron microscopy (SEM) and zetasizer analyses were performed.

Membrane fouling restricts the efficient use of the membranes. In this regard backwashing could be done to reduce that fouling. Backwashing is the reversing of filtration flow direction through the membrane; that is, pushing permeate water to the feed side to lift foulants that are not adsorbed to the membrane surface. The permeate turbidity is often an indication of when to backwash. In this work, backwashing for some of the experiments that used feed solutions containing TiO₂ was performed to identify the fraction of the TiO₂ accumulation that was reversible, and also to find the difference in resultant pure water after backwashing (Table 4-5). Here, it was determined that pure water flux after backwashing, which was measured instantaneously after filtration, was significantly enhanced. The interesting phenomenon observed was that the resultant pure water flux after backwashing was always higher than final precompaction flux. This supports the hypothesis that in the presence of TiO₂, the cake resistance was decreased and the permeate flux increased; that is, the cake became more reversible. Furthermore, it can be presumed that TiO₂ residuals left on the membrane surface even after backwashing had again affected the membrane morphology and its permeability.
Table 4-5: Backwashing flux data after 0.1 g/L TiO₂ and different NaCl concentrations filtration tests.

<table>
<thead>
<tr>
<th>Thickness (µm)</th>
<th>~170</th>
<th>~120</th>
<th>143</th>
<th>176</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avg. Precompaction Flux (L/m²hr)</td>
<td>17.1</td>
<td>29.4</td>
<td>26.2</td>
<td>15.6</td>
</tr>
<tr>
<td>NaCl Concentration (mM)</td>
<td>35</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Avg. Filtration Flux (L/m²hr)</td>
<td>18.5</td>
<td>31.3</td>
<td>29.1</td>
<td>17.3</td>
</tr>
<tr>
<td>Pure Water Flux After Backwashing</td>
<td>20.5</td>
<td>39.2</td>
<td>35.3</td>
<td>22.1</td>
</tr>
</tbody>
</table>

Scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDS) analyses were performed in order to identify TiO₂ aggregation on the surface. Representative SEM and EDS images are shown in Figures 4-7 through 4-12. All figures, with exception of Figure 4-6, which is in the absence of TiO₂, represent membrane surfaces after filtration of different concentrations of NaCl in the presence of TiO₂ NPs with sonication. Based on EDS analyses, particles that appear on the membrane surface are TiO₂. Therefore, despite sonication, TiO₂ aggregation happened, as these NPs had a range size of 5-10 nm before filtration process but here they are large enough to be visible under magnifications of 3.0 - 10.0 µm. Furthermore, by comparing the images, it was observed that by increasing NaCl concentration, more heterogeneous TiO₂ aggregates (i.e., varying shape and size) on the surface were detected (Figures 4-9 through 4-12, additional images shown in Appendix A). In case of only TiO₂, more
homogeneous aggregates (visually seeming to have similar shape and size) were observed (Figure 4-8).

From SEM images, it was observed that with increasing NaCl concentration in filtration solution, NP aggregate size on the membrane surface increased, which was believed to be associated with double layer compression. To envision the environment surrounding a charged colloidal particle and demonstrate how the repulsive forces and the ionic concentration vary with distance, a double layer model is normally used. In this model, a layer of ions is attached to and adsorbed onto a particle surface of opposite charge (known as the Stern layer). Beyond the stern layer, there is a second region (diffusive layer) enclosing the particle containing the free ions loosely associated with the surface. Both the Stern and the diffusive layers are referred to as the double layer. The thickness of this layer depends on the ions concentration in the solution [46]. In the double layer compression mechanism, large quantities of a neutrally charged salt are added. The salt then works by compressing the double layer around the particle to reduce the zeta potential, which is the potential at the interface of the Stern and the diffusive layers. When the outer layer is compressed, the repulsive energy barrier around the particle is decreased or eliminated, so that the van der Waals forces (attractive) dominate and coagulation takes place. This allows particles to combine and form larger aggregates [52, 53]. This is also in agreement with what can be found from equations (2) and (3) presented in Chapter 2. Therefore, the possible explanation here was that during filtration, TiO₂ nanoparticles agglomerate (Figure 4-8), while in the presence of increasing ionic strength (increasing NaCl concentrations), double layer compression occurred and TiO₂ nanoparticles flocculated to form larger particles. It is hypothesized
that these led to more permeable cake accumulations on the surface, which qualitatively resemble sponges on the surface.

Figure 4-7: Membrane surface after filtration of 100mM NaCl in the absence of TiO$_2$ NPs (membrane thickness: 200 $\mu$m)
Figure 4-8: (A) SEM image of membrane surface after filtration of only 0.1 g/L TiO\textsubscript{2} solution (membrane thickness: 210 µm), (B) EDS results of that surface.
Figure 4-9: (A) SEM image of membrane surface after filtration of 20 mM NaCl and 0.1 g/L TiO$_2$ solution (membrane thickness: ~161 µm), (B) EDS results of that surface.
Figure 4-10: (A) SEM image of membrane surface after filtration of 35 mM NaCl and 0.1 g/L TiO₂ solution (membrane thickness: 155 µm), (B) EDS results of that surface.
Figure 4-11: (A) SEM image of membrane surface after filtration of 100 mM NaCl and 0.1 g/L TiO$_2$ solution (membrane thickness: 200 µm), (B) EDS results of that surface.
Figure 4-12: (A) SEM image of membrane surface after filtration of 100 mM NaCl and 0.1 g/L TiO₂ solution (membrane thickness: 182 µm), (B) EDS results of that surface.

Lastly, a Zetasizer (Nano series, Nano-ZS, Malvern instruments, Worcestershire UK) was used in this work in order to measure nanoparticles (NPs) size in both feed and permeates. Zetasizer was used to monitor the NPs solutions and to characterize the nanoparticles with respect to three important characteristics: particle size, zeta potential...
and molecular weight. Zetasizer Nano-ZS can characterize NPs over 0.6 nm-6 µm size range. The zetasizer nano series performs size measurement employing a process called dynamic light scattering (DLS). DLS measures the Brownian motion by illuminating the particles with a laser and analyzing the intensity fluctuations in the scattered light by those particles. Here the average NP size obtained from filtration of identical solutions for membranes of same thicknesses using cumulant analysis by software is presented in Table 4-6. However, as the poly-dispersity index (PDI) values (equation 5) are relatively high (above 0.3), this single mode method can provide only a qualitative comparison between the particle sizes and cannot be taken at face value [54]. In other words PDI increases as the particle size becomes less uniform or sample contains large particles or aggregates, thus multiple narrow modes or multiple size distribution mode analysis would be more useful to employ (histograms of apparent size distribution of NPs presented in Table 4-6 are illustrated in Appendix B that show aggregations of NPs as well):

\[
PDI = \frac{\text{standard deviation in diameter}}{\text{mean diameter}}
\]

After each NPs size measurement using Zetasizer, two values were obtained: count rate and attenuator number for both feed and permeate solutions according to their concentrations. Count rate is the number of photons detected per second, which can also help to screen the sample quality. The attenuator number makes the comparison between count rates of two samples possible; that is, if a large difference between count rates of two samples exists, these can be compared by changing attenuator number in the software. In this work it was also tried to see if besides NPs size, the concentration of NPs in permeates could be determined. The concentration of particles in both feed and permeate solutions could have been compared by using the count rates. However, that
comparison was not possible since the particles sizes in both solutions were not similar and attenuator numbers of the solutions were not the same either. Therefore, only the comparison in nanoparticle size is shown (Table 4-6).

**Table 4-6: Average particles size of TiO$_2$ present in feed and permeate.**

<table>
<thead>
<tr>
<th>Thickness (µm)</th>
<th>210</th>
<th>167</th>
<th>150</th>
<th>180</th>
<th>200</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl Concentration (mM)</td>
<td>0</td>
<td>20</td>
<td>35</td>
<td>35</td>
<td>35</td>
<td>100</td>
</tr>
<tr>
<td>Avg. NPs size (diameter) in Feed solution (nm)</td>
<td>448</td>
<td>1449</td>
<td>1742</td>
<td>1742</td>
<td>1742</td>
<td>2700</td>
</tr>
<tr>
<td>Avg. PDI Value of Feeds</td>
<td>0.4</td>
<td>0.5</td>
<td>~0.5</td>
<td>~0.5</td>
<td>~0.5</td>
<td>0.7</td>
</tr>
<tr>
<td>Avg. NPs size (diameter) in permeate (nm)</td>
<td>237</td>
<td>241</td>
<td>407</td>
<td>304</td>
<td>284</td>
<td>914</td>
</tr>
<tr>
<td>Avg. PDI Value of permeates</td>
<td>0.5</td>
<td>0.4</td>
<td>0.5</td>
<td>0.4</td>
<td>0.4</td>
<td>0.6</td>
</tr>
</tbody>
</table>

From the data presented in Table 4-6, it was observed that with increasing NaCl concentration in filtration solution, NP size in both feed and permeate solutions
increased. This is in agreement with SEM images that show larger aggregates as NaCl concentrations increased (Figures 4-8 through 4-12). NP size in case of filtration of only TiO₂ was smaller than those using NaCl and TiO₂ solutions. In addition, the difference between NP size in feed and permeate using a TiO₂ only solution was lower than that in the presence of both salt and TiO₂. These results were consistent with flux data presented in Tables 4-2 through 4-4 and also explain why feed appearance was turbid in comparison to the permeate solutions in all cases. That is, it was hypothesized that during filtration, two phenomena would occur, first TiO₂ nanoparticles naturally agglomerate, and second TiO₂ nanoparticles flocculate in the presence of salt to form larger particles.

Rejection of feed solutions containing TiO₂ and different concentrations of NaCl was measured as described in Chapter 3, and results are shown in Table 4-7. According to rejection results, with increasing membrane thickness, rejection slightly increased, as expected due to an increase in resistance. Furthermore, there was no significant difference between rejection of NaCl in the presence (Table 4-6) and absence (Tables 3-5 and 3-6) of TiO₂. The low rejections of NaCl were expected as these are ultrafiltration membranes.
Table 4-7: Rejection data of filtration of different concentrations of NaCl in the presence of 0.1 g/L TiO₂

<table>
<thead>
<tr>
<th>Thickness (µm)</th>
<th>165</th>
<th>160</th>
<th>180</th>
<th>220</th>
<th>176</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl Concentration (mM)</td>
<td>20</td>
<td>35</td>
<td>35</td>
<td>35</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Rejection</td>
<td>0.12</td>
<td>0.045</td>
<td>0.06</td>
<td>0.116</td>
<td>0.05</td>
<td>0.06</td>
</tr>
</tbody>
</table>

4.4.3 Filtration in the Presence of ZnO Nanoparticles

While the target of the study was TiO₂ NPs, ZnO NPs were tested for comparison in order to determine if other NPs would also lead to increases in filtration flux. Precompaction and filtration of 0.1 g/L ZnO solutions in the presence and absence of different concentrations of salt (NaCl) were performed to determine the differences between these NPs effect on membrane permeability and TiO₂. All flux data is presented in Figures 4-13 and 4-14.
Flux values for membranes of relatively similar thicknesses (145 and ~147 µm) were compared. Precompaction and filtration of 100 mM NaCl and 0.1 g/L ZnO for 145µm membranes led to 24.2 and 23.1 L/m²/hr, respectively. For 0 mM NaCl and 0.1 g/L ZnO (that is, only ZnO feed solution), the 147 µm thick membrane displayed 24.7 and 24.4 L/m²/hr for the pure water and filtration fluxes, respectively. As expected, solutions consisting of both salt and ZnO NPs caused higher reductions in the filtration fluxes, consistent with feed solutions that contained NaCl only.

Figure 4-13: Precompaction and filtration flux data of thin membranes (All filtration solutions consist of 0.1 g/L ZnO).
Filtration and precompaction fluxes for ZnO solutions is summarized in Table 4-8 and Figure 4-15. Filtration of 100 mM NaCl and 0.1 g/L ZnO solution for membranes of higher thicknesses (176 and 215 µm) were also carried out. Precompaction and filtration results using the 176 µm membrane led to 15.2 and 13.2 L/m²·hr, respectively; while those for the 215 µm membrane were 7.1 and 5.7 L/m²·hr. Filtration of 35 mM NaCl and 0.1 g/L ZnO for the 220 µm membrane gave a flux of 7.3 L/m²·hr, while its pure water flux was 8.2 L/m²·hr. Precompaction and filtration of solution containing only ZnO for the membrane of 180 µm thickness resulted in 14.7 and 15.2 L/m²·hr, respectively. By comparing ZnO flux data, it was verified that filtration of solutions containing both salt and ZnO NPs led to relatively higher decreases in flux compared to fluxes obtained from

Figure 4-14: Precompaction and filtration flux data of thick membranes (All filtration solution consist of ZnO).
filtration of only ZnO solution. Furthermore, higher salt concentrations caused higher reductions. These results were consistent with results obtained from membranes of lower thicknesses. That is, unlike filtration using TiO$_2$ NPs, filtration of solution containing ZnO NPs led to reductions in flux. This was likely due to the different chemical properties of the two NPs used. Both TiO$_2$ and ZnO nanoparticles were hydrophilic under the conditions of this study, so hydrophilicity was not a factor in the different flux observations. In other words, the structures of those NPs (wurtzite nature of ZnO and anatase structure of TiO$_2$) might affect the interaction between NPs and membrane surface due to possible different van der walls attraction forces of those NPs.

Table 4-8: Precompaction and filtration flux data (Filtration solution consists of 0.1 g/L ZnO and different concentrations of NaCl (mM)).

<table>
<thead>
<tr>
<th>Thickness (µm)</th>
<th>~147</th>
<th>180</th>
<th>220</th>
<th>145</th>
<th>~176</th>
<th>215</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avg. Precompaction Flux (L/m$^2$hr)</td>
<td>24.7</td>
<td>14.7</td>
<td>8.2</td>
<td>24.2</td>
<td>15.2</td>
<td>7.1</td>
</tr>
<tr>
<td>NaCl Concentration (mM)</td>
<td>0</td>
<td>0</td>
<td>35</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Avg. Filtration Flux (L/m$^2$hr)</td>
<td>24.2</td>
<td>14.6</td>
<td>7.3</td>
<td>23.1</td>
<td>13.2</td>
<td>5.7</td>
</tr>
</tbody>
</table>
Figure 4-15: Flux decline vs. membrane thickness after filtration of ZnO solutions in the presence of different NaCl concentrations.

Furthermore, a comparison between the impacts of different filtration solutions and membrane thicknesses on the fractional membrane flux is presented in Figure 4-16, while a comparison of fractional flux decline in the presence/absence of NPs for one condition (145 µm thick membranes under 35 mM NaCl filtration) is shown in Figure 4-17. According to the figures, it can be observed that filtration of different concentrations of NaCl led to the highest fractional flux decline, which was likely due to more concentration polarization. Filtration in the presence of TiO₂ led to increases in filtration flux (as observed by the negative fractional flux decline values) since these NPs enhanced the filtration flux compared to pure water flux. The presence of ZnO
nanoparticles led to a reduction in fractional flux decline to a lower extent than in the absence of these NPs.

Figure 4-16: Flux decline vs. membrane thickness after filtration of only NaCl, NaCl NaCl+ TiO2 and NaCl+ZnO solutions
Figure 4-17: Flux decline after filtration of only 100mM NaCl, 100 mM NaCl+ TiO$_2$ and 100 mM NaCl+ZnO solutions of membranes of 145 µm thickness.

4.5 Conclusion

A concern for membranes is the ability of nanoparticles to deposit within the membrane pores as well as on the membrane surface to form dense cakes. The goal of this project was to study the effects of ionic strength (ranging from 0 – 100 mM NaCl) on nanoparticle membrane fouling. Two metal oxide nanoparticles, TiO$_2$ and ZnO, were used as they are widely used in products, and as a result, they are released to the environment. Polysulfone membranes were chosen as model membranes due to their high mechanical strength, thermostability and stability against chemicals. Polysulfone ultrafiltration membranes were cast via phase inversion.
Results showed that permeate flux increased during filtration of solutions containing TiO$_2$ nanoparticles, which was the opposite of what was observed when only NaCl was present in the filtration solution. During filtration, two phenomena occurred, first TiO$_2$ nanoparticles naturally agglomerated, and second TiO$_2$ nanoparticles flocculated in the presence of ionic strength to form larger particles. The larger particles experienced more hydrodynamic lift, which led to thinner cake layer and thus higher flux values during filtration. Therefore, it is hypothesized here that, in the presence of TiO$_2$, the cake resistance was decreased and the permeate flux increased. Therefore addition of TiO$_2$ to the filtration solution was able to reduce membrane fouling and increase the final flux. Moreover TiO$_2$ aggregation formed larger particles that could be better rejected. TiO$_2$ results were in contradiction with ZnO, as flux decreased during ZnO filtration. That difference was attributed to different chemical properties and consequently behavior of various nanoparticles.
Chapter 5

5 Suggestions for Future Work

1. pH Effect

The effect of pH should be investigated in nanoparticle filtration. As explained, both nanoparticles used had different isoelectric points; that is, particle charge was related to pH. As charge and double layer compression turned out to be significant factors in explaining the differences in behavior between TiO$_2$ and ZnO, the effects of pH on filtration should be determined.

2. SEM, EDS and Zetasizer (DLS) for ZnO

SEM, EDS and Zetasizer for membranes filtered with ZnO solution to further explain the different behavior of ZnO compared to TiO$_2$. There were not performed here since the main focus was on TiO$_2$ and its effect on membrane properties. ZnO filtration was only performed for comparison.

3. Cross-flow filtration

Use of cross-flow filtration would be a more realistic mode of filtration. In cross-flow filtration, the different feed and permeate flow directions leads to less fouling in comparison to the dead-end mode used here. Thus, it should improve the membrane
permeability significantly. Cross-flow filtration would also allow for runs to be extended over several days continuously, which would again provide more realistic conditions.

4. Use different membranes

In this study, only one membrane (hydrophobic polysulfone ultrafiltration) was used for investigation. While polysulfone membranes are widely used, the findings of the study are somewhat limited to one membrane only. Therefore, other membranes, of varying hydrophilicity should be tested. The membrane isoelectric points should also be measured to shed additional light into the effects of the nanoparticles. Lastly, it is expected that as pore size decreases (that is, nanofiltration and reverse osmosis membranes), the surface effects of nanoparticles would be more prominent, so these should be examined as well.
References


51. Mileyeva-Biebesheimer, O., “Applying fluorescence based assays to determine the impact of metal oxide nanoparticles on bacteria”, *PhD Dissertation*, 2011, 26


Appendix A

(A) SEM image of membrane surface after precompaction (membrane thickness: ~127 µm), (B) EDS results of that surface.
(A) SEM image of membrane surface after filtration of only 0.1 g/L TiO₂ solution (membrane thickness: 210 µm)
(A) SEM image of membrane surface after filtration of 35 mM NaCl and 0.1 g/L TiO₂ solution (membrane thickness: ~161 µm)
(A) SEM image of membrane surface after filtration of 35 mM NaCl and 0.1 g/L TiO$_2$ solution (membrane thickness: 155 µm), (B) EDS results of that surface.
(A) SEM image of membrane surface after filtration of 100 mM NaCl and 0.1 g/L TiO\textsubscript{2} solution (membrane thickness: 182 µm), (B) EDS results of that surface.
Appendix B

(A) Intensity VS particles size distribution for permeates obtained from filtration of only TiO2 solution for membrane of 210 µm thickness

Intensity %

size (d.nm)

210 µm-Only TiO2- Avg. size: 210.2 nm, PDI: 0.5

(B) Intensity VS particles size distribution for permeates obtained from filtration of only TiO2 solution for membrane of 210 µm thickness

Intensity %

size (d.nm)

210 µm-Only TiO2- Avg. size: 262.9 nm
167 μm-20mM NaCl+TiO2-
Avg. size:220.9 nm

167 μm-20mM NaCl+TiO2-
Avg. size:227.7 nm
(A B, C) Intensity VS particles size distribution for permeates obtained from filtration of TiO$_2$ + 20 mM NaCl solution for membrane of 167 µm thickness
150 μm-35 mM NaCl+TiO2-  Avg. size: 277.4 nm

150 μm-35 mM NaCl+TiO2-  Avg. size: 236.9 nm
(A B, C, D) Intensity VS particles size distribution for permeates obtained from filtration of TiO$_2$ + 35 mM NaCl solution for membrane of 150 µm thickness
(A) 180 µm-35 mM NaCl+TiO2- Avg. size: 274.4 nm

(B) 180 µm-35 mM NaCl+TiO2- Avg. size: 256.7 nm
(A B, C, D) Intensity VS particles size distribution for permeates obtained from filtration of TiO₂ + 35 mM NaCl solution for membrane of 180 µm thickness
200 µm-35 mM NaCl+TiO2- Avg. size: 223.3 nm

200 µm-35 mM NaCl+TiO2- Avg. size: 303.4 nm
(A, B, C) Intensity VS particles size distribution for permeates obtained from filtration of TiO$_2$ + 35 mM NaCl solution for membrane of 200 µm thickness.
(A, B) Intensity VS particles size distribution for permeates obtained from filtration of TiO₂ + 100 mM NaCl solution for membrane of 200 µm thickness
(A, B) Intensity VS particles size distribution for feed solution consisting of only TiO$_2$
(A, B) Intensity VS particles size distribution for feed solution consisting of 20 mM NaCl + TiO₂
(A, B) Intensity VS particles size distribution for feed solution consisting of 35 mM NaCl + TiO₂
Intensity VS particles size distribution for feed solution consisting of 100 mM NaCl + TiO$_2$

100 mM NaCl+TiO$_2$ Feed- Avg. size: 2700