A Dissertation

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Development of Low-Biofouling Polypropylene Feed Spacers for Reverse Osmosis

by

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Submitted to the Graduate Faculty as partial fulfillment of
the requirements for the Doctor of Philosophy Degree in Engineering

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Implementation of nanofiltration (NF) and reverse osmosis (RO) processes in treating traditional water sources can provide a steady-state level of removal that eliminates the need for regeneration of ion exchange resins or granular activated carbon. Moreover, RO can help meet future potable water demands through desalination of seawater and brackish waters. The productivity of membrane filtration is severely lowered by fouling, which is caused by the accumulation of foreign substances on the surface and/or within pores of membranes. Microbial fouling, or biofouling, is the growth of microorganisms on the membrane surface and on the feedspacer as present between the envelopes. The fouling of membranes has demanded and continues to demand considerable attention from industry and research communities. Many of these applications use membranes in a spiral wound configuration that contains a feed spacer.

The goal of this project was to develop low-biofouling polypropylene (PP) spacers through the functionalization of PP by a spacer arm with metal chelating ligands charged with biocidal metal ions, investigate the use of this metal-charged polypropylene (PP) feedspacers that target biofouling control, and to use some traditional and one novel techniques to autopsy the membranes after filtration to gain a better understanding of the biofouling mechanism and how the modified spacers are affecting it.

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List of Abbreviations

AA		Atomic Absorption
ATR		Attenuated Total Reflectance
BPO		Benzoyal Peroxide
DMA		Dynamic Mechanical Analysis
DMSO		Dimethyl Sulfoxide
DNA		Deoxyribonucleic Acid
DOM		Dissolved Organic Matter
DP		Depth of Penetration
dsDNA		Double Stranded Deoxyribonucleic Acid
DSC		Differential Scanning Calorimetry
EDS/EDX		Energy Dispersive X-ray Spectroscopy
EDTA		Ethylenediaminetetraacetic Acid
EPA		Environmental Protection Agency
EPS		Extracellular Polymeric Substance
FEG		Field Emission Gun
FTIR		Fourier Transform Infrared Spectroscopy
GMA		Glycidyl Methacrylate
GPC		Gel Permeation Chromatography

ICPMS	Inductively Coupled Plasma Mass Spectrometry
IDA	Iminodiacetic Acid
IMA	Immobilized Metal Affinity
IR	Infrared
MF	Microfiltration
MW	Molecular Weight
NF	Nanofiltration
NOM	Natural Organic Matter
PA	Polyamide
PP	Polypropylene
PS	Polysulfone
RI	Refractive Index
RO	Reverse Osmosis
SEM	Scanning Electron Microscopy
TFC	Thin Film Composite
TGA	Thermal Gravimetric Analysis
UF	Ultrafiltration
UV	Ultraviolet
XPS	X-ray Photoelectron Spectroscopy

Chapter 1

Introduction

Currently, about half of the world's population suffers from water shortages, and over the next 25 years, the number of people affected by severe water shortages is expected to increase fourfold [1]. In the developing countries that are most affected, 80-90% of all diseases and 30% of all deaths result from poor water quality [2]. In addition, modern economies cannot develop and thrive without sufficient access to water. There is growing recognition by governments and corporations that future peace and prosperity is intimately tied to the availability of clean, fresh water [3, 4].

Membranes possess the ability to treat a wide variety of source waters such as brackish and seawater for desalination, as well as low quality surface water and even wastewater. They can produce water that is of higher quality than traditional water treatment processes such as coagulation, flocculation, sedimentation, sand filtration, etc. For this reason, membranes and membrane processes have gained much popularity in recent years. Furthermore, like any high-tech product, membranes' performances have been consistently increasing while their costs have been consistently decreasing [5]. Ultimately, dwindling freshwater resources, more stringent water treatment standards, and the need to augment existing water supplies in growing urban areas are all driving factors for the expansion of membrane processes [6].

Membranes for water treatment are usually characterized into four main classifications that can be based solely on pore size. These classifications are, from the largest pore size (~1 micron) to the smallest (~0.001 micron): microfiltration (MF) and ultrafiltration (UF), which are considered low-pressure membranes, and nanofiltration (NF) and reverse osmosis (RO), which are considered high-pressure membranes. RO membranes have also been considered to be non-porous membranes resulting in a solution-diffusion based separation. These classifications can be seen in Figure 1.1. Much advancement has been made in membrane performance, permeability and durability, but there are still many problems with membrane performance and lifetime, which restrict them from more widespread uses. One such challenge, that is common to both low- and high-pressure systems, is membrane fouling [7].

Figure 1-1: The Filtration Spectrum

Fouling can be described as the undesirable accumulation and/or formation of deposits at the membrane surfaces, on the membrane pores, or within the pores. Just as it is with membrane classifications, there are four main categories of membrane fouling. These include: colloidal fouling, inorganic fouling, organic fouling, and biological fouling, which is often referred to as biofouling. The accumulation of foulants hinder the membrane filtration process by decreasing the flux of permeate and increasing the hydraulic resistance of mass transport. This accumulation can come in the form of cake/gel layer formation, concentration polarization, or physical pore blocking.

Biofouling is the accumulation and growth of microorganisms onto the membrane surface and on the feed spacer, which can be seen in Figure 1.2, as present between the envelopes in spiral wound reverse osmosis membrane modules. This accumulation of microorganisms, along with the presence of nutrients that are common in many membrane applications, forms biofilms. For spiral-wound reverse osmosis and nanofiltration membranes, biofouling is the major type of fouling leading to pressure drop [8-10]. It has been shown that biofouling causes a flux decline by increasing hydraulic resistance and by hindering back diffusion of salts, which further increase the concentration polarizations phenomenon [11, 12]. Furthermore, biofouling is particularly significant because membrane replacement due to fouling is the single largest operating cost in water separation [7]. For this reason, research on altering the chemical, and possibly antimicrobial, properties of the feed spacer is the focus of much attention.

Figure 1-2: Spiral wound membrane element [13]

In biofilms, organisms are embedded in a matrix of microbial origin, consisting of extracellular polymeric substances (EPS). These matrices are often very complex and difficult to remove. For this reason, much effort goes into the prevention of biofilm growth, rather than its removal. This prevention is usually attempted through the use of pretreatments, nutrient removal, maximizing shear forces at the membrane surface, and back-flushing. The problem with pretreatment methods is that even if 99.9% of microorganisms are removed, those left remaining can proliferate and cause irreversible fouling. Furthermore, biocides, such as free or combined chlorine, can only be used with certain chlorine-resistant membranes, and since biofouling is such a common problem, this has its downsides. Biofouling starts at the membrane/feedspacer interface suggesting that biofouling might be a feedspacer problem [14]. Because of this, research has gone into modification of the feedspacer to control biofouling. The geometry of the feedspacer

can be altered to control biofouling, but the traditional surface chemistry, which is typically that of polypropylene (PP), also has room for improvement.

The goal of this project was to develop low-biofouling PP, which can be used for numerous applications such as food packaging, medical devices, but mainly, reverse osmosis feed spacers, through the functionalization of PP. The functionalized PP contained a spacer arm glycidyl methacrylate (GMA) with a metal chelating ligand, iminodiacetic acid (IDA). Many studies have been conducted on the use of copper and silver ions to disinfect water against microbial biofilms [15, 16]. These ions are believed to interfere with enzymes involved in cellular respiration and bind DNA at specific sites [17]. For this reason, the metal chelating ligands were charged with either copper or silver ions to increase PP biofouling resistance.

Chapter 2

Literature Review

2.1 Introduction

Water purification can be achieved by membrane containing, pressure-driven processes such as ultrafiltration (UF), microfiltration (MF) nanofiltration (NF) and reverse osmosis (RO) resulting in a method that is straightforward, cost effective and versatile[18]. A basic schematic, describing how all pressure drive membrane processes function can be seen in Figure 2.1.

Figure 2-1: Basic Schematic of Pressure Driven Membrane Process[19]

The feed water is forced through the selective membrane using a pressure differential across the membrane as a driving force. Solutes of interest are, ideally, rejected into the concentrate and the solvent and other solutes pass through the membrane as the permeate. While this schematic represents the membrane as a flat sheet, many membrane configurations exist, each having their own pros and cons.

2.2 Types of Membranes

2.2.1 Tubular Membranes

Tubular membranes, which are typically ceramic and inherently strong, possess the ability to treat waters with high solid contents and large particles. This is due to the relatively large inner-diameter of the membranes, which can also allow for the use of high cross flow velocities to control fouling and aid in the ease of cleaning. On the other hand, this results in low packing density and high cost per square meter[20]. Figure 2.2 illustrates a few examples of tubular membranes.

Figure 2-2: Tubular Membrane Configuration[21]

2.2.2 Hollow Fiber Membranes

Hollow fiber membranes can produce high shear rates due to small inner diameter of fiber, have high packing density, low-pressure drop across the module and are commonly used for MF and UF. Unfortunately, the membranes can become plugged without proper prescreening and, also, problems can arise from large numbers of fibers in a single module[20]. Typical hollow fiber membrane modules can be seen in Figure 2.3

Figure 2-3: Hollow Fiber Membrane Modules[21]

2.2.3 High Pressure Membranes

Finally, spiral wound membrane elements can withstand high pressures, have a relatively high square meter of membrane to volume ratio, and, because of this, are commonly used for NF and almost always for RO. The feed spacer, which provides a space in which the feed water can flow, is the source of certain drawbacks of this configuration, such as areas of low shear, which results in fouling, as well as the ability to damage the membrane[20]. The remainder of this work will focus on this membrane configuration, which can be seen in Figure 2.4.

Figure 2-4: Spiral Wound Membrane Element[22]

2.3 Membrane Material

The majority of reverse osmosis and nanofiltration membranes are found in a spiral wound configuration and are polyamide(PA) thin-film composite (TFC) membranes [23], although cellulose acetate and cellulose triacetate are also used[24]. Other commercial materials of NF/RO membranes include: sulfonated polysulfone, sulfonated polyether sulfone, piperazine polyamide, and polyvinyl alcohol [25]. The TFC RO membrane usually consists of three structural components: polyester fabric, polysulfone (PS) support, and PA dense film layer [26]. A representation of TFC membrane can be seen in Figure 2.5.

Figure 2-5: Thin Film Composite RO/NF Membrane[27]

This type of membrane provides high flux and strength, coming from a loose and porous, yet mechanically strong, support layer and high rejection due to the thin selective polyamide layer.

2.4 Membrane Transport Mechanisms

In most membrane applications, and especially reverse osmosis, there is a concentration differential (osmotic pressure) that is a driving force in the opposite direction of the applied pressure. In these situations, this applied pressure must be greater than the osmotic pressure of the feed solution. Osmotic pressure (π_i) is a thermodynamic property of a solution and is related to the mole fraction of the solvent, X_{Bi} , as

$$\pi_i = - \left(\frac{RT}{V_B} \right) \ln X_{Bi}$$

(Equation 1.1)

where R is the universal gas constant, T is temperature and V_B is the volume of the solvent[28]. For dilute solutions, the osmotic pressure is found to obey ideal gas law, where C_{Ai} is concentration of solute, making equation 1.1 simplify to van't Hoff equation[28]:

$$\pi_i = C_{Ai}RT \quad (Equation 1.2)$$

Reverse osmosis transport models can be divided into three main groups [28]:

- (i) Irreversible thermodynamics models, where the membrane is treated as a black box whereby relatively slow processes proceed near equilibrium and fluxes of solute and solvent are assumed to be directly related to the chemical potential differences between the two sides of the membrane [29]. The permeate flux can be described by the following equation:

$$J = Lp(\Delta P - \sigma\Delta\pi) \quad (Equation 1.3)$$

Where J is the permeate flux, Lp is the pure water flux across the membrane, P is pressure, π is osmotic pressure and σ is a reflection coefficient.

- (ii) Porous models, which assume that transport through the membrane pores is due to both diffusion and convection through the pores and

- (iii) Nonporous or homogeneous membrane models, which assume that transport occurs between the interstitial spaces of the polymer chains or modules, typically by diffusion.

Similar to irreversible thermodynamics models, water flux through a membrane has been expressed by equation 1.4[30]:

$$J = \frac{\Delta P - \Delta \pi}{\mu R_{tot}}$$

(Equation 1.4)

Where μ is dynamic viscosity of the permeating solution and R_{tot} is the total resistance.

R_{tot} can be better defined by equation 1.5[30]:

$$R_{tot} = R_p + R_a + R_m + R_g + R_{cp} + R_i + R_d$$

(Equation 1.5)

Where R_p is resistance due to pore blocking, R_a is resistance due to adsorption inside the pores, R_m is hydraulic resistance of the membrane, R_g is resistance caused by the formation of a gel layer, R_{cp} is concentration polarization resistance, R_i is resistance caused by specific interactions, and R_d is resistance from deposits on the membrane. This definition of resistance factors in fouling that occurs during membrane operation and it can be seen that as fouling (pore blockage, adsorption, gel/cake layer formation, etc.) occurs, resistance will increase and flux will decrease if the pressure driving force is kept constant. The productivity of membrane filtration is severely lowered by fouling, which can be categorized into four basic types: colloidal, inorganic, organic, and biological.

2.5 Membrane Fouling

2.5.1 Colloidal Fouling

Feed water to membranes is generally pretreated for larger particles. Hence, colloids are generally the reason for particulate fouling in membrane systems. As its definition implies, when the term colloid is used in fouling, it covers a myriad of different materials or aggregates of materials, including organic, inorganic, and biological materials. An SEM image of such fouling can be seen in Figure 2.6.

Figure 2-6: Colloidal Fouling on Membrane Surface[31]

Low-pressure membranes such as micro and ultra filtration are usually discussed when colloid fouling is of concern. This is because these sorts of filtration are designed to reject such particles. The rejections of these particles result in cake/gel layers on or in the membrane pores. The layer has characteristics that may depend on the system operation parameters (flux and velocity levels), membrane characteristics (surface roughness and charge), solution chemistry (pH, ionic strength, ionic composition), and the

characteristics of the colloids (size, shape, charge, hydrophobicity). Particulate fouling has obvious impacts on the performance of a membrane system. The increase in deposition of materials on the surface can form a compact layer which can decrease flux and increase the pressure required for operation[32]. Colloidal fouling is typically assessed or evaluated in terms of transport, which is determined by convective forces such as permeate flux and crossflow velocity, and attachment, which is determined by electrostatic, van der Waals and hydrophobic interactions[33]. Colloidal fouling is most commonly dealt with via pretreatment of the feed stream and back-flushing of the membranes, but sometimes pH adjustment is used as well. Overall, little can be done to prevent colloidal fouling on a long term basis because, as previously mentioned, it is what some membranes are intended to reject[34, 35].

2.5.2 Inorganic Fouling

Inorganic fouling is caused by any material of inorganic origin. It may be the sole source of fouling but more commonly, it is in concert with other types of fouling[36]. This type of fouling is usually thought of as the precipitation of dissolved, sparingly soluble metals, as metal hydroxides, salts, and minerals onto membrane surfaces which results in scaling. Figure 2.7 shows an SEM image of this type of fouling.

Figure 2-7: Inorganic Fouling on Membrane Surface[37]

Inorganic fouling is usually encountered in desalination systems where salt concentration and their rejections are high. The phenomenon known as concentration polarization plays a large part in inorganic fouling, and more specifically, mineral scaling[38, 39]. In a concentration polarization layer, the concentration of chemical species (the inorganic compounds in this case) is higher at the membrane surface than in the bulk solution. Concentration polarization occurs because the rate of arrival of an inorganic species at the surface is larger than that of the diffusion of it back into the bulk solution. As Bhattacharjee and Elimelech[39] have shown, concentration polarization can affect membrane performance adversely outright, but what is more important is its role in the formation of mineral scaling. Mineral scale formation is almost always initiated within the concentration polarization boundary layer. This is due to the elevated salt concentrations in the concentration polarization layer relative to those in the bulk solution which can result in precipitation[39]. This precipitation and the subsequent mineral scaling occur when rejected salts or minerals become so concentrated at the membrane surface that they exceed their solubility limit. As is common with most types of fouling,

the properties of this scale are dependent on the chemistry of the bulk solution. More often than not though, the scaling is considered to be a hard or rock-like structure which grows from an initial nucleation site. This scale can contain its own microenvironment that can result in difficult removal and flow obstructions. There are many different forms of mineral scale that can occur simultaneously in a system and this can result in the formation of a very complex scale. Because of this, the chemistry of mineral scale removal is poorly understood and currently the topic of much research. pH adjustment through acid addition and the use of anti-scalants are the two most widely used pretreatment methods to avoid scaling in NF and RO processes[40]. Due to the weak pH dependence of the solubility of barium and calcium sulfate, it is difficult to control scaling due to it in membrane systems through pH adjustment alone. In these cases anti-scalants are required to prevent mineral scale formation. The mechanisms through which an anti-scalant works relies on its ability to interfere with the two principle mechanisms of scale formation: nucleation and crystal growth[40]. The four mechanisms through which this may occur are interference with the clustering process, dispersion, crystal distortion and chelation which results in a soluble salt[41]. Polycarboxylates and phosphonates, two types of polymeric organic compounds, are the most common anti-scalants used in membrane treatment[40]. Metallic ions have also been proposed to be an efficient anti-scalant for feed streams prone to calcium carbonate precipitation[42]. As far as pH adjustment goes, the most common form is acid addition to control inorganic scaling. However, alkalization has been utilized as another form of pretreatment[43].

2.5.3 Organic Fouling

Organic fouling generally results from the adsorption of dissolved organic matter onto the membrane surface, but can also result from deposition of colloidal organic matter. It is usually the first form and primary cause of chronic membrane fouling in most membrane systems. Organic foulants can include natural organic matter (NOM), algogenic organic matter, organic macromolecules, organic colloids, biopolymers, and microbially derived cellular debris. Typical organic fouling can be seen in Figure 2.8.

Figure 2-8: Organic Fouling on Membrane Surface[44]

Organic fouling is a ubiquitous problem throughout all membrane processes. Studies have shown that organic matter is the most prevalent membrane foulant, having accounted for nearly half of the foulants that were identified in membrane autopsies[41]. Organic fouling occurs through a variety of mechanisms, including adsorption, attachment, pore blockage, and cake or gel layer formation. The occurrence and progression of these different mechanisms are influenced by a host of parameters, including the properties of the organic matter such as size, hydrophobicity, and charge,

membrane characteristics such as hydrophobicity, charge, surface roughness, and pore size, water chemistry and operation parameters[45, 46]. As stated before, adsorption is the mechanism most commonly associated with organic fouling and for this reason, interaction between the membrane surface and organic foulant is of supreme significance. It is this interaction that has become the focus of much organic fouling control. As previously mentioned, surface characteristics play a large role in the adsorption of organic materials. If these can be altered, then the fouling can be controlled. Two of membrane surface characteristics that have shown promising results are decreases in surface roughness and increases in membrane hydrophilicity. Both have shown the ability to decrease organic fouling, probably by lessening the affect of adsorption of organic matter[47, 48].

2.6 Biofouling

2.6.1 Biofouling Introduction

Biofouling, which is the accumulation and growth of microorganisms and biofilms onto the membrane surface and on the feed spacer, causes a significant increase in differential pressure, is difficult to eliminate by routine cleaning procedures, and is ultimately endemic [49]. Biofouling can cause a flux decline by two methods: (i) an increase of the hydraulic resistance over the membrane and (ii) hindering the back diffusion of salts [50]. Microorganisms are present in nearly all water systems [51] and because of this biofouling and its control remains a major operating problem for many reverse osmosis (RO) plants as it occurs despite the use of pretreatment systems and the

addition of disinfectants. A membrane experiencing this type of fouling can be seen in Figure 2.9.

Figure 2-9: Biofouling on Membrane Surface[11]

Biofouling is especially problematic because biofilms occurring in membrane systems may cause severe loss of performance and the use of costly cleaning procedures to maintain output and quality. Frequently, the fouling can be so severe that operation cannot be maintained and membrane replacement is needed[49]. In spirally wound element biofouling is especially problematic due to the possibility for some sections of the flow channel to become blocked. Furthermore, biofouling can lead to other types of fouling, such as inorganic fouling, as these channeling issues causes rapid salt concentration in the affected areas. This leads to the precipitation of sparingly soluble salts and, ultimately, scaling [52].

2.6.2 Biofouling Mechanism

Biofouling of membrane surfaces occurs in a few general phases. Initially, the surface to which the biofilm attaches becomes conditioned with a range of organic

molecules that rapidly adsorb to the surface upon exposure to an aqueous environment. These molecules can include proteins, polysaccharides, nucleic acids, humic acids, lipids, fatty acids, pollutants, etc. [53] Then, primary colonization occurs where adhesion is essentially proportional to the cell density in the water phase and occurs owing to weak physicochemical interactions. It is thought that the cells that initially attach during this phase are often in starvation/survival phase and tend to be smaller in size and secreting a higher ratio of extra cellular polysaccharides [53]. It has been shown that higher amounts of EPS are directly related to cellular adhesion[54]. This primary colonization is then followed by the logarithmical growth phase, when cell growth on the surface contributes more to biofilm accumulation than does the adhesion of planctonic cells. Essentially, the cells which have attached to the conditioned surface can now feed off the nutrients which are concentrated at the membrane surface, due to rejection by the membrane's selective layer, and multiply[51]. Finally, a plateau phase, when biofilm growth (adhesion and cell multiplication) and cell detachment are in balance, occurs. This phase is controlled by the nutrient concentration and the resultant growth rate, the mechanical stability of the biofilm, and the effective shear forces. Also, it is independent of the concentration of cells in the raw water. It is also thought that during this stage subsequent production of extracellular polymers occurs [55].

2.6.3 Traditional Biofouling Control

Biofilm formation and biofouling are essentially unavoidable as some small percentage of microorganisms present can survive physical pre-treatment processes like coagulation, flocculation, sand filtration, ultra filtration and cartridge filtration [56].

More recent developments have led to technologies such as ultrafiltration membrane and UV pretreatment, but the former has a high capital and operational cost and the latter can lead to scale formation and has no residual effects. Both of these technologies are also ultimately incapable of completely removing microorganism. As a result, chemical pre-treatment of RO membrane units is required but is also shown to be ineffective in removing and/or completely destroying the complex multicellular structures [57]. Some common chemicals such as chlorine and ozone by alkaline treatment, tensides, enzyme, or complex-forming substances [58] have been used, as have been biodispersants [59]. Chlorine containing substances are notorious for chemical corrosion of RO membranes and can also form toxic disinfectant biproducts[55]. Recently, modifications to the membrane to prevent biofouling have been explored. These modifications usually look to reduce the formation of the conditioning layer via an increase in hydrophilicity [47, 60, 61] and decrease in surface roughness[48], or by coating/impregnating the membrane is antimicrobial metals[62, 63].

Conventional cleaning with toxic chemicals has an effect on the occurrence of biofouling in RO systems, but is not effective in really cleaning the RO system [56], as the biomass must be physically removed[64]. Because of this, methods of physically removing the biofilm layer have been investigated. Such methods include back flushing the membrane, air sparging[14, 65], and, more recently, modifications to the membrane feed spacer's size and geometry to increase shear forces[66].

2.6.4 Biofouling Control with Feed Spacers

Feed spacers, which usually have the form of non-woven crossed cylinders, serve to separate adjacent membrane leaves and create flow passages, but also to promote flow unsteadiness and enhance mass transport. Figure 2.10 is an example of a typical membrane feed spacer configuration.

Figure 2-10: Typical Feed Spacer Configuration[66]

By creating such turbulence, the undesirable fouling and concentration polarization phenomena are mitigated[66]. Research has also shown that little work has been focused on feed spacers for biofouling control by reporting the number of publications in journals satisfying the search criteria “biofouling” and “modified and/or adapted membrane” in the article title, abstract and keywords in the Scopus database of

March 2008, which amounted to 59. Conversely, the search criteria “biofouling” and “modified and/or adapted spacer” yielded no references at all [50]. The work that has been conducted on feed spacers has been focused on feed spacer geometry, generally to reduce pressure drop and increase permeate flux [66, 67]. These works have shown that altering the feed spacer geometry can alter wall shear stresses and that such stresses have maxima significantly higher than those corresponding to empty channels. The non-uniformity of shear stresses was also shown to have the ability to be manipulated which may have implications on membrane fouling. It is apparent that anti-fouling properties were not the primary focus of these studies and biofouling resistance, specifically, was not even mentioned. The only studies found regarding feed spacer surface modifications consisted of methods for bulk modifications of the entire membrane module/membrane/spacer rather than specifically the feed spacer [63, 68]. The lack of research being conducted on feed spacer modifications to control biofouling, coupled with the unique role the feed spacer plays in this type of fouling, has led to the research that has been conducted in this work.

Grafting of unsaturated vinyl monomers onto PP is a convenient route to develop new polymeric materials with synergistic properties[69]. Polymer-metal complexes have been extensively studied and successfully employed in several fields [70]. As in low-molecular-weight compounds, a polymer ligand must donate unshared electrons to the metal ion to form metal-ligand bonds. Among the multidentate ligands, iminodiacetic acid (IDA) possesses one aminopolycarboxylate and provides a reactive secondary amine hydrogen to react with alternate functional groups [70]. Hence, IDA can be more easily introduced to the side chain of a polymer or vinyl monomer via was is proposed to be an

SN2 epoxy group reaction of glycidyl methacrylate (GMA) and IDA [71]. This reaction has two advantages, (1) GMA is a commercial industrial material that is cheaper than any other vinyl monomers that possess an epoxy ring in the side chain; and (2) it produces a vinyl monomer that can be polymerized in the presence of an initiator and can be grafted to activated polymer surfaces. The chemical modification of polypropylene feed spacers to allow metal chelation, increase antimicrobial properties, and ultimately control membrane biofouling has been studied[71, 72]. In these studies, PP was functionalized with copper (Cu) to demonstrate that Cu-charged PP could be used to make low biofouling feed spacers for spiral wound elements. The functionalized PP contained grafted GMA with the metal chelating ligand (IDA) to which copper was chelated [71].

Many studies have been conducted on the use of copper ions to disinfect water against microbial biofilms with effective dosages of a few tenths of 1 mg/L [15]. Positively charged copper ions have an affinity for negatively charged microbial surfaces[73]. Copper is thought to be cytotoxic by causing changes in the plasma membrane permeability or efflux of intra-cellular K^+ during the entry of Cu^{2+} ions [74]. Also, it is known to coordinate with proteins, specifically through thiol groups[73] causing secondary and tertiary structural changes in the protein structure or in the protein active which may result in the inhibition or neutralization of the proteins' biological activities[75]. Copper is known to coordinate with Cys residues which, in turn, may lead to changes in enzyme activity and intracellular trafficking[76]. Plasma membrane function may be rapidly affected by copper ions, which was seen as an increase in K^+ efflux from excised roots of *Agrostis capillaries*. Similarly, it has been concluded that damage to the cell membrane, monitored by ion leakage, was the primary cause of Cu

toxicity in roots of *Silene vulgaris*, *Mimulus guttatus*, and wheat, respectively. Such damage could result from various mechanisms including the oxidation and cross-linking of the before mentioned protein thiols, inhibition of key membrane proteins such as the H^+ -ATPase, or changes to the composition and fluidity of membrane lipids[77]. Copper can also participate in Fenton-like reactions generating reactive hydroxyl radicals, which can cause cellular damage imparted via oxidative stress [74]. Silver ions also possess antimicrobial properties as they are known to have strong interactions with thiol (sulfhydryl, -SH) groups[78]. Cytoplasmic proteins and DNA are targets of silver through interaction with these thiol groups in proteins, causing enzymatic inactivation[79]. Additionally, cytosines in DNA form stable C-Ag-C structures[80].

Chapter 3

Research Objectives

It is obvious that maintaining high flux through the membrane during reverse osmosis (RO) filtration, while avoiding fouling, can decrease energy costs [47]. Hence, the objective of the present research was to functionalize polypropylene (PP) feed spacers to make them and, thus, the membrane less prone to biofouling. After functionalization, the PP feed spacers were characterized to verify the desired modification and evaluate its effect on the polymer's properties. Also, the performance of the modified, low-biofouling feed spacers was evaluated. Finally, the fouled membranes were autopsied to gain insight on the biofouling mechanism and how the modification was affecting it.

3.1. Functionalization of the PP

1. A poly-glycidyl methacrylate (GMA) spacer arm was graft polymerized to the PP surface through free radical initiation using benzoyl peroxide (BPO). The GMA was homopolymerized and the PP surface was activated simultaneously.
2. The metal chelating ligand, iminodiacetic acid (IDA), was bound to the GMA spacer arm.
3. Copper and silver ions were then chelated to the covalently bound IDA.

3.2. Characterization of the Modification

1. Fourier transform infrared (FTIR) spectroscopic analysis of virgin, as well as modified, PP was performed to determine the chemical and structural changes to the surface.
2. Scanning Electron Microscopy (SEM) coupled with X-ray energy dispersive spectroscopy (EDS) was used to determine the presence of chelated copper.
3. Gel Permeation Chromatography (GPC) was performed to gain insight about the length of GMA chains attached to the PP surface.
4. Differential Scanning Calorimetry (DSC) was used to determine the effects the modification had on the PP's crystallinity and to obtain information about the attached GMA.

5. Dynamic Mechanical Analysis (DMA) was performed to investigate the effect of the modification on the mechanical properties of the PP.

3.3. Evaluation of the Modification

1. Biocidal efficiency was evaluated by direct counts of cells which were detached from virgin and modified PP and stained with a dsDNA stain to show the degree of microbial attachment.
2. Determining the strength, stability and longevity of the copper and silver chelation was performed by monitoring the leeching of copper in a variety of solutions and/or during cross flow filtrations runs via atomic absorption (AA), inductively coupled plasma (ICP), and EDS analysis.
3. Performance evaluation of modified and virgin spacers was conducted in increased biofouling conditions via cross flow filtration runs monitoring flux and microbial growth on the membrane.
4. Performing autopsies of fouled membranes using live/dead cell counts of detached cells, SEM imaging and FTIR spectr-oscopy allowed for a better understanding of the biofouling mechanism and how the modified spacer affects it.

Chapter 4

Materials and Methods

4.1 Materials

4.1.1 Membranes

The membranes used were TFC-S polyamide membranes that were commercially available nanofiltration thin film composite (TFC) membranes manufactured by Koch Membranes (San Diego, CA). These polyamide membranes, described in greater detail in Chennamsetty and Escobar[48], consisted of a polysulfone support layer covered by aromatic polyamide selective layer. The functional groups were carboxylate/carboxylic acid. The film layer was approximately 1,000-2,000 angstroms thick and the molecular weight cutoff was around 200 - 300 Daltons[81, 82]. The membrane had a slight negative charge with a contact angle of 55°[83]. The typical operating pressure was 5.5 bar, with the maximum operating pressure being 24 bar. The maximum operating temperature was 45°C and the allowable pH range was 4-11. Chlorine tolerance was low, with the maximum continuous free chlorine concentration being less than 0.1 mg/l. A newer, but chemically identical membrane (verified using FTIR) was used in fouling studies using *Pseudomonas fluorescens* cells. This membrane was also from Koch Membranes, had a

typical operating pressure is 13.8-31.0 bar, with the maximum operating pressure being 44.8 bar, a maximum operation temperature of 50 °C, a pH range of 3-10 (1.8-11.0 during cleaning), and a free chlorine limit of 0.2 mg/L. The chemical structure of polyamide is shown in Figure 4.1.

Figure 4-1: Polyamide Thin-film Composite Structure

4.1.2 Polypropylene

Homopolymer polypropylene sheets of thickness 0.030 inches were purchased from Professional Plastics Inc. (Fullerton, CA) and were used as received unless otherwise noted. Homopolymer polypropylene 0.026" feed spacers, produced with 100% FDA grade (CFR 21) polypropylene, were donated by Delstar Technologies (Middleton, DE).

4.1.3 Chemical Reagents

Glycidyl methacrylate (GMA) was purchased from Fisher Scientific (Hampton, New Hampshire) and vacuum distilled before use. Sodium iminodiacetate disbasic (IDA) hydrate 98% and methylene chloride were purchased from Aldrich Chemistry (St. Louis, Missouri) and used as received. Humic acid was purchased in the form of a 50-60% sodium salt, as well as reagent grade tannic acid, from Acros Organics, New Jersey, USA. *Pseudomonas fluorescence* cells, ATTC#12842 were purchased from ATTC and were freshly cultured on R2A agar (BD, Franklin Lakes, NJ) before each inoculation.

Benzoyl peroxide, toluene, acetone, copper sulfate, silver nitrate, sodium chloride, calcium chloride, magnesium chloride, ferrous sulfate, sodium acetate, sodium thiosulfate, glucose, and ethylenediaminetetraacetic acid (EDTA) were purchased from Fisher Scientific (Hampton, New Hampshire) also used as received.

4.1.4 Glassware and Labware

All glassware (i.e., flasks, vials, bottles, etc.) was cleaned in a laboratory sink following a regime that involved a detergent wash, acid wash, and a minimum of three DI water rinses. The DI water was provided by a Barnstead Mega-Pure 1 System (Waltham, MA). The acid wash consisted of 4.25 mL of hydrochloric acid which was added to 250 mL DI water. Following the cleaning procedure, the mouth of the glassware was covered with aluminum foil and muffled at 550°C in a laboratory oven for a minimum of four hours in order to remove any organic contamination. After muffling, all glassware remained covered and was stored in a cabinet until use.

4.2 Chemical and Morphological Characterizations

4.2.1 Fourier Transform Infrared (FTIR) Spectroscopy

Infrared (IR) spectroscopy is widely used to assess the chemical nature of a substance including chemical bonds, molecular orientations, molecular energy levels and molecular interactions. In a standard experiment, light with a broad range of frequencies is directed through a sample while the transmittance of the light through the sample is measured. Two different techniques are used in IR spectroscopy. The first method uses a diffraction grating to spatially separate the spectrum. The frequency resolution of this spectrometer is a function of the fineness of the grating. A scanning mirror is used to

channel one wavelength of light into the detector. The second method involves using an interferometer to encode the spectrum in the measured signal. This method is called Fourier transform infrared spectroscopy (FTIR). An FTIR spectrometer uses a Michelson interferometer to modulate the optical signal and encode the spectrum information. A Fourier transform is performed on the resulting signal to retrieve the frequency/magnitude information. The basic operation of FTIR equipment depends on four important parts. They are source, interferometer, sample and detector, which are interconnected.

FTIR was used in attenuated total reflectance (ATR) mode to study the chemical nature of the membrane surfaces prior to and after modification. Digilab UMA 600 FT-IT microscope with a Pike HATR adapter and an Excalibur FTS 400 spectrometer (Randolph, MA) was used for all the analyses experiments conducted in this study. It was used to determine if chemical modifications resulted in the appearance of expected functional groups on the polypropylene surface. Also, fouled membranes were investigated using FTIR to obtain qualitative and quantitative information about the compounds present in the biofilm on the membrane surface[60].

4.2.2 Scanning Electron Microscopy (SEM) / Energy Dispersive X-ray Spectroscopy (EDS)

Scanning electron microscope (SEM) uses an electron beam produced by high voltage (15-20KeV) 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.

Figure 4-2: Specimen Interaction with Electron Beam[60].

When an electronic beam strikes the specimen, due to various interactions a variety of signals are generated as shown in Figure 4.2. Of these generated signals, the strongest region of the electron energy spectrum is due to secondary electrons. The secondary electron yield depends on many factors, and is generally higher for high atomic number targets, and at higher angles of incidence. Secondary electrons are produced when an incident electron excites an electron in the sample and loses some of

its energy in the process. The excited electron moves towards the surface of the sample undergoing elastic and inelastic collisions until it reaches the surface, where it can escape if it still has sufficient energy. Secondary electrons, by convention, are those emitted with energies less than 50 eV. This is only a small fraction of the electrons emitted from the sample. These secondary electrons are used for imaging in SEM[60].

SEM was used to visually observe the degree of polymer grafting and membrane fouling. The samples were coated with a thin layer of gold under an argon atmosphere using a SPI Module Sputter Coater with Etch mode, and were placed in the scanning electron microscope for analysis. Two electron microscopes were used in this project to study the modification and fouling associated with membrane filtration. A Philips XL 30 FEG SEM, located at EMAL at The University of Michigan, Ann Arbor, and a Hitachi S – 4800 SEM, located at Center for Material and Sensor Characterization at The University of Toledo, Toledo.

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 metal chelated on the modified polypropylene.

4.2.3 Micro Balance

The weights of the sheets were determined after being vacuum dried to a constant weight before modification (W_o) using a Mettler Toledo XP105DR Semi-micro balance that has a repeatability of 0.02mg. They were also determined, the same way, after modification where they were again vacuum dried to constant weight (W_f). The grafting level (GL%) of GMA onto PP was determined by using the following relation:

$$GL\% = \frac{W_f - W_o}{W_o} \times 100$$

4.2.4 Gel Permeation Chromatography

Gel permeation chromatography (GPC) was carried out on a SCL-10Avp Shimadzu high- performance liquid chromatography (Columbia, MD) to obtain the molecular weight distribution (MW) of the homopolymer GMA that was formed during the graft polymerization reaction. The homopolymer byproduct was collect from the reaction vessel, vacuum dried and then dissolved in methylene chloride. The eluent was HPLC grade methylene chloride and the column operated under flow rate of 1 ml/min. A calibration plot, constructed with polystyrene standards in the same methylene chloride in the range of 980- 500,000, was used to determine the molecular weights.

4.2.5 Dynamic Mechanical Analysis

A TA Instruments dynamic mechanical analyzer (DMA) Q 800 was used to measure thermal - mechanical properties of the virgin and modified polypropylene. In DMA, the sample is subjected to a dynamic strain and the resultant stress is recorded.

Storage modulus, loss modulus and tan delta were determined using a temperature ramp frequency sweep program with a tension clamp on thin sample films. Storage modulus is the measure of energy stored and loss modulus is a measure of energy lost under oscillatory strain. Tan delta is the ratio of loss and storage modulus, the peak of the tan delta curve was used as the glass transition temperature (T_g) of the sample. The samples were heated from room temperature to 100°C by using a ramp rate of 2°C/min and a frequency of 1 Hz. Sample preparation was done by cutting polypropylene sheets into thin strips and then entering the dimensions into the software. The sample dimensions were kept approximately constant from run to run to maintain consistency. No sub T_g transition was observed for any of the samples.

4.2.6 Thermal Gravimetric Analysis

Thermal gravimetric analyzer (TA Instruments, TGA Q50) was used to confirm functionalization of the polypropylene, obtain more information on the degree of functionalization and also study the degradation properties and thermal stability of the unmodified and modified polypropylene. The TGA runs will be performed in inert atmosphere (nitrogen gas) up to 600°C at the rate 5°C/min.

4.2.7 Differential Scanning Calorimetry

A Perkins Elmer Diamond Differential Scanning Calorimeter (DSC) was used to measure heatflow vs. temperature as a desired scan rate (in this case 20°C /min) This was done to determine the levels of crystallinity in the unmodified and modified polypropylene feed spacers as well as to investigate the affect the modification may have

on the thermal properties of the polypropylene. The DSC was equipped with a circulating liquid (Intracooler 1) cooling option which allowed for analysis to be performed between 0°C and 200°C.

4.2.8 Contact Angle Measurement

The effect of the modification on hydrophilicity was determined by measuring the contact angle of the PP surface using the Sessile Drop Half-Angle™ measuring method (U.S. Patent No. 5,268,733). The method dropped distilled water on the top surface of the PP sheet, and the angle formed between the drop and the surface was measured using a Cam-Plus Micro contact angle meter (Tantec Inc., Schaumburg, IL) as seen in Figure 4.3. The measurements were performed at room temperature. Contact angle measurements were taken on a 1cm² sheet of PP before and after each modification by which a relative change in surface hydrophilicity of the PP could be determined.

Figure 4-3: Contact Angle Measurement

4.2.9 Quantification of Metal in Solution

A Perkin Elmer Instruments AAnalyst 200 AA spectrometer, equipped with a Cu hollow cathode lamp, was used to quantify the amount of copper in solution during

leaching studies as well as during filtrations using virgin and Cu-charged feed spacers. Copper standard was purchased at 1000ppm in 2% nitric acid and diluted with DI water to 0.5, 1.5, and 4.5ppm for calibration before each sample run. Samples collected during filtration runs using Ag-charged feed spacers were sent to the United State Department of Agriculture Agricultural Research Service at the University of Toledo. The amount of silver in solution was quantified using a Thermo Scientific XSeries 2 ICPMS which is capable of accurately measuring silver in the parts per billion (ppb) range.

4.3 Experimental Methods

4.3.1 Preparation of Cu(II) Charged PP-graft-GMA-IDA

Polypropylene sheets were cut into squares with an area ranging from 2cm² to 4cm², or PP feed spacers were cut to the appropriate size, rolled and tied with Teflon tape, and sonicated in ethanol for 30 minutes to clean and remove anything on their surfaces. The sheets were then vacuum-dried at 60°C for 24 hours before being placed into the reaction vessel. A schematic of the reaction apparatus is shown in Figure 4.4. The nitrogen used was from a ultra high purity 300cc tank (Air Gas, Independence, OH).

Figure 4-4: Reaction Apparatus

The initial weights (W_o) of the sheets were determined before they were placed in a round bottom flask containing toluene as a solvent/interfacial agent, the radical initiator benzyol peroxide (BPO), and GMA. These reactions can be seen in Figure 4.5:

Figure 4-5: Graft Polymerization Reactions

According to the literature[84], polymerization occurs via C-C double bond cleavage and results in a graft material with the original reactivity of the epoxy ring. Thus, the

epoxy group can be effectively used to anchor the desired species. After the sheets soaked in the toluene/GMA monomer solution in which the toluene slightly swells and etches the PP, the reaction vessel was purged with nitrogen and the temperature was increased to 80°C to activate the BPO and the simultaneous homopolymerization of GMA and its grafting to PP was allowed to occur. The sheets were then taken out and washed with acetone to remove all unbound GMA homopolymer. The sheets were placed in a DMSO/H₂O solution containing iminodiacetic acid (IDA). The DMSO, as a polar aprotic solvent, stabilizes the transition state of the SN₂ reaction between the epoxy group of the GMA and the imine group of the IDA. Also, a mixed solvent system is used so that the IDA salt can be dissolved by the water. This reaction can be seen in Figure 4.6.

Figure 4-6: IDA Addition Reaction

After the reaction with IDA, DI water was used to rinse the sheets before they were vacuum dried and again analyzed by an ATR-FTIR spectrometer. The PP-graft-polyGMA-IDA sheets were placed into a 0.6M copper sulfate solution to allow IDA to chelate Cu(II) ions or in an equivalent solution of silver chloride to chelate Ag(II) ions.

This can be seen in Figure 4.7.

Figure 4-7: Metal Addition to Modified PP (Copper Shown)

4.3.2 Investigation of Antimicrobial Properties of Cu(II) Charged PP-graft-GMA-IDA

Two 150 mL Erlenmeyer flasks of LB Broth (Difco/Becton, Dickinson and Company, Sparks, MD) containing *E. coli* ATTC#10798 bacterium cells at a concentration of 3.0×10^5 cells/mL were prepared. Three sheets of both virgin PP and Cu(II) charged PP-graft-GMA-IDA were added to the each flask and they were then incubated at 35°C, which is near the maximum growth temperature of 37°C, to increase cellular growth. At 24 hrs, 96 hrs, and 168 hrs sheets were taken from each flask. Cells were detached from the sheets using a Stomacher 400 Circulator (Seward Ltd, London, England). Detached cells were stained with Quant-iT PicoGreen dsDNA stain and counted using an Olympus BX51 fluorescent microscope (Tokyo, Japan) and an Olympus DP-70 digital camera (Tokyo, Japan). Triplets of each sample were taken, counting ten fields each time.

4.3.3 Release of Chelated Metal Ions from Modified PP

a)Batch Studies: Surface Analysis:

Three 150mL Erlenmeyer flasks were filled with 100mL of DI water. To one flask, 2.67g of NaCl, 0.267g of MgCl and 0.267g of CaCl₂ were added. Another was prepared to contain 5mM EDTA at a pH of 11 (adjusted with NaOH). The final flask had its pH adjusted to 3.5 with HCl. One modified sheet which had been charged with Cu(II) was added to each flask and they were placed on a shaker table. After one week and two weeks, a sheet was removed from each solution, washed with DI water, vacuum dried overnight and analyzed using XEDS. Four areas were analyzed per sheet and compared to the initial amount of copper which was present on the PP surface. The study was then repeated with modified PP sheets which had been charged with Ag(II).

b) Batch Studies: Solution Analysis

Atomic absorption analysis was performed on solutions that had been exposed to the Cu(II) charged PP sheets in batch experiments. The batch experiments consisted of 2-cm² sheets of Cu-charged PP placed in 500-mL solutions of 5 mM EDTA, with pH adjusted to 11, and 50 mg/L ferrous sulphate, both of which were prepared in DI water. The solutions were shaken for 212 hours at room temperature. These solutions were chosen because the former is a common cleaning solution while the latter contains a divalent metal ion that could compete with copper for IDA chelation sites causing the potential copper to be displaced. 2-mL samples of the solutions were collected throughout the experiment, which ran for 212 hours, to be analyzed for copper content.

c) Cross flow Studies

Additionally, cross flow experiments were conducted to test copper leaching, as

shown in Figure 4.8. The apparatus consists of a feed bottle which is filled with solution of interest, a pump to flow the solution through a flow chamber that contains the modified PP, a collection bottle to collect nearly all of the solution which has passed over the modified PP (containing an average amount of copper leached), and a valve allowing for samples to be taken, at different time intervals, into a test tube.

Figure 4-8: Apparatus Used in Cross-flow Metal Leaching Studies[72]

Three separate solutions were prepared in DI water: one containing 5 mM EDTA at a pH of 11, one containing 10 mg/L of ferrous sulfate and one containing 8 ppm of dissolved organic matter (DOM) solutions comprised of 4 ppm of humic acid and 4 ppm of tannic acid. These solutions were then pumped, at a flowrate of 0.6 mL/min, through a flow cell (24 mm $\times$ 40 mm $\times$ 8 mm deep, Stovall Life Sciences Incorporated, Greensboro, NC), which contained a 1-cm² sample of Cu-charged PP. As mentioned, the solution that had flowed through the cell was sent to a collection bottle with samples collected in test tubes at different times. Analyses of the samples and the collection bottle were performed with AA. The motive behind the use of the first two solutions was described in the previous section, while that of the latter is the possible competition

between copper complexation with DOM and copper chelation to IDA. This study was not performed using Ag-charged PP because the previous batch studies sufficiently illustrated that silver's affinity to the IDA modified PP was far less than copper's.

d) Rechargability of the Modified Feed Spacer:

To qualitatively determine if the modified polypropylene could be recharged in the event that all or some copper was leached, a Cu-charged piece of feed spacer was placed in a nitric acid solution of pH 0.5. The purpose of this was to protonate the carboxylic acid and amine groups of the IDA and release the chelated copper. After this step, the feed spacer was washed with DI water and placed back into the 0.6M copper sulfate solution. Digital images were taken of the feed spacer when it was initially charged with copper, after being exposed to the nitric acid solution, and after being removed the 0.6M copper sulfate solution.

4.3.4 Performance of Modified Feed Spacers During Crossflow Filtration

a) Tap Water Studies:

The membrane was housed in a SEPA CF cross-flow filtration unit (Osmonics, Minneatonka, MN). The filtration unit was constructed out of 316 stainless steel and rated for an operating pressure up to 69 bar (1000 psi). The test unit was sealed by applying adequate pressure via a hand pump (P-142, Enerpac, Milwaukee, WI), which actuated a piston on the SEPA CF, sealing the membrane within the membrane cell. The feed stream was delivered by a motor (Baldor Electric Company, Ft. Smith, AR and Dayton Electric Manufacturing Co., Niles, IL) and M-03 Hydracell pump (Wanner Engineering, Inc., Minneapolis, MN) assembly. Flow valves controlled permeate and

retentate (also called concentrate) flow and the pressure acting on the membrane in the test unit. Due to the high pressures required by the membranes, it was necessary to control the temperature of the feed water using a chiller (Model KR60A, Cole-Parmer Instrument Company, Veenon Hills, Illinois) to keep it at approximately 20°C. A schematic of this setup can be seen in Figure 4.9.

Figure 4-9: Cross-flow Filtration Apparatus in Full Recycle Mode [48].

Cu-charged and unmodified spacers were tested in full recycle mode with the use of identical nanofiltration TFC-S membranes. In full recycle mode, a 55-L container was filled with feed solutions and tubes for the pump inlet, permeate outlet, and concentrate outlet placed into it. Water was pumped through a Poly Science KR-60A heater/chiller (Niles, IL) to maintain isothermal conditions. Tap water, which was dechlorinated with sodium thiosulfate and supplemented with 30 mg/L of sodium acetate, was used as a feed solution in all runs. After the solution was prepared, it incubated at room temperature for

12 hours before filtration began. Furthermore, each membrane was subjected to 8 hours of precompaction using DI water. The fluxes of membranes using both Cu-charged and unmodified feedspacers were measured throughout a 48-hour period of filtration.

To both verify the data received from this experiment and to test the properties of the Cu-charged spacer further, cross flow filtrations were performed exactly as described above but until the final flux was approximately 35% of the initial flux, or 51 hours in the case of the unmodified feedspacer and 286 hours in the case of the Cu-charged feed spacer.

b) Pseudomonas fluorescens Studies

The same protocol as in the previous studies was followed but at this time ($t = -16\text{hr}$) *Pseudomonas fluorescens* Migula cells, which were freshly grown on an R2A agar plate, were added to the reservoir so that the initial cell concentration was 10^6 cells/mL. Filtration was carried out at 34°C and 100psi. Again, each membrane was subjected to 8 hours of precompaction using DI water before filtration. The fluxes of membranes using Cu-charged, Ag-charged and unmodified feed spacers were measured throughout four filtration runs each: one four-hour run, one 24-hour run and two 48-hour runs (except in the case of the Ag-charged spacer which had one 48-hour run). Cell counts, following the same protocol listed for live/dead counting of cells detached from the membrane, were performed on the solution in the feed reservoir throughout filtration.

4.3.5 Fouled Membrane Autopsies

a) Cell Counts from Tap Water Studies

Samples of each membrane, one used with the unmodified spacer and one used with the Cu-charged spacer, were taken from identical locations on the membrane surface after the filtration period. Cells were detached from the samples using a Stomacher 400 Circulator (Seward Ltd, London, England). Detached cells were stained with Quant-iT PicoGreen dsDNA stain and counted using an Olympus BX51 (Tokyo, Japan) fluorescent microscope and an Olympus DP-70 digital camera (Tokyo, Japan). Triplets of each sample were taken, counting ten fields each time.

*b) Live/Dead Cell Counts of *Pseudomonas fluorescens* Studies*

Again, samples of each membrane, one used with the unmodified spacer and one used with the Cu-charged spacer, were taken from identical locations on the membrane surface after the filtration period. Cells were detached from the samples using a Stomacher 400 Circulator (Seward Ltd, London, England). Detached cells were stained with Quant-iT PicoGreen dsDNA stain (live cells) and propidium iodide (dead cells). They were then counted using an Olympus BX51 fluorescent microscope (Tokyo, Japan) and an Olympus DP-70 digital camera (Tokyo, Japan). Triplets of each sample were taken, counting ten fields each time.

c) SEM Imaging of Fouled Membranes

Samples of each membrane, one used with the unmodified/virgin spacer, one used with the Ag-charged spacer, and one used with the Cu-charged spacer, were taken from identical locations on the membrane surface after the filtration period. These membranes were vacuumed dried at ambient temperature to remove all water and were then coated using a gold-palladium target for 30 seconds to aid in electron imaging and prevent

charging. Scanning electron microscopy (SEM) imaging (Hitachi S-4800 High Resolution Scanning Electron Microscope, Japan) of membrane samples was performed.

d) FTIR Spectroscopy of Fouled Membranes

FTIR analysis using an attenuated total reflection Fourier transform infrared spectrometer (ATR-FTIR, Digilab UMA 600 FT-IT, Holliston, MA) microscope with a Pike HATR adapter and an Excalibur FTS 400 spectrometer, Ge crystal with a refractive index of 4.0 and a long wave length cut-off of 780cm⁻¹) was performed on an unfouled membrane, as well as membranes fouled using virgin and Ag and Cu modified feed spacers in twenty-one locations on each membrane and averaged. To determine the depth of penetration during ATR-FTIR, the Equation 1 was used[85], where DP is the depth of penetration of the evanescent IR wave, Θ is the angle of incidence (45°), λ is the wavelength (μm), n_1 is the refractive index (RI) of the Ge Crystal (4.0), and n_2 is the RI of sample being analyzed in this case polyamide with a RI of 1.56 [86]:

$$DP = \frac{\lambda}{2\pi n_1 [\sin^2 \Theta - \left(\frac{n_2}{n_1}\right)^2]^{\frac{1}{2}}}$$

(Equation 1)

This equation is valid when the refractive index of the sample is uniform throughout the depth of penetration. If one considers a case where there are two layers in the path of the IR penetration, as in the case of a biofouled membrane (biofilm and membrane layers), this equation must be altered to Equation 2, where n_3 is the refractive index of the biofilm layer, t_b is the thickness of the biofilm layer which is seen by the IR, and t_m is the thickness of the membrane, which is seen by the IR.

$$DP = \frac{\lambda}{2\pi n_1 [\sin^2 \phi - \left(\frac{n_2 \left(\frac{t_m}{DP} \right) + n_3 \left(\frac{t_b}{DP} \right)}{n_1} \right)^2]^{\frac{1}{2}}}$$

(Equation 2)

To determine t_m an FTIR spectra of an unfouled membrane must be acquired and a prominent peak that is characteristic of the membrane, but does not appear in the biofilm, is located. The peak at 1238cm^{-1} ($8.08\mu\text{m}$) was identified as such, and the area under it was determined. Once a biofilm layer of thickness t_b is accumulated on the membrane, the area under this peak decreases. The area under the peak of the fouled membrane is then divided by the area of the initial membrane, and the resulting value is multiplied by the DP calculated using the unfouled membrane to determine t_m . This is summed up in Equation 3, where A_1 is the area under the characteristic membrane peak of the unfouled membrane and A_2 is that of the fouled membrane.

$$t_m = \frac{A_2}{A_1} \times DP$$

(Equation 3)

The DP can simply substituted with $(t_b + t_m)$ in Equation 2, since the depth of penetration through the two-component system is obviously the sum of the thickness of penetration through both. From literature, n_3 , the refractive index of the biofilm, is 1.38[85]. It should be noted that this RI value was measured in the visible light range. The values of every variable except t_b are now known so it can be determined.

Once the thickness of the biofilm has been determined, information about the concentration of components in the biofilms can be investigated. The FTIR spectra of *Pseudomonas fluorescens* biofilms have been studied[85], and the locations of peaks for different components are known. A list of these components and their locations are shown in Table 4.1.

Table 4.1: FTIR Wavenumbers and Band Assignments of Biofilm Components

Wavenumber (cm⁻¹)	Band Assignment	Associated Biomolecule	References
970	C-O Stretch	Polysaccharides	[87]
1053	C-O or C-O-C Stretch	Polysaccharides	[87-89]
1380	Symmetric Stretch of Carboxylate Ion	Polysaccharides	[90]
1450	C-H bending of CH ₂	Lipopolysaccharides	[89, 90]
1535	NOH bend of Amide II	Protein	[87-92]
~1635	C=O Stretch of Amide I	Protein	[87-92]
1735	C=O Stretch of esters	Polysaccharides, fatty acids, phospholipids, lipopolysaccharides	[87, 89, 90]

For the peaks on the biofilm that do not interfere with peaks from the membrane, the area under a peak of interest can be determined by integration. Varian Resolutions Pro Version 4.1.0.101 was used to integrate under the peaks of interest and more information on this can be seen in Appendix B. This area is then divided by the thickness of the biofilm, t_b , on the membranes to get a concentration with units (amount/ μL). The unit in the numerator is not known since extinction coefficients are unknown, and therefore only *relative* quantitative information can currently be gained from this technique; that is, the concentration of a species in a biofilm on a membrane used with a

modified spacer versus that fouled with virgin spacer. Since Beer-Lambert's law states that concentration is directly proportional to absorbance, much insight about the difference in biofilm formation when using a copper-charged feed spacer can still be obtained. To determine the area under biofilm component peaks which do overlap peaks coming from the unfouled membrane, the absorption coming from the membrane in the specified region must be subtracted. To do this, the area of this region is determined from the spectrum of the unfouled membrane, multiplied by $\frac{t_m}{DP}$, and then subtracted from the area integrated under the same region on the fouled membrane.

Chapter 5

Results and Discussion: Method I

5.1 Preparation of Cu-Charged PP-GMA-IDA

Traditional melt-phase PP grafting often occurs at temperatures over 160°C. The use of PP powder or granules with a reaction temperature of 100-140°C has been shown to yield ~7% grafting [93]. For radical development, previous studies have shown that soaking of PP films with GMA and BPO in supercritical CO₂ for 10h and 130 bar at 70°C followed by thermal-induced grafting at 120°C yielded only 13.8% grafting [84].

The work presented here focused on the functionalization of polypropylene, first with a spacer arm and then with metal chelating ligands because these groups (i) are quite stable and easily synthesized, (ii) operate over a diverse range of conditions, (iii) have easily controlled binding affinities, and (iv) are well suited for model studies [94, 95]. For immobilized metal affinity (IMA) based separations, a chelate group is used to fix a copper ion to the polypropylene backbone via a spacer arm. Chelate groups are strong Lewis acids that form several coordinate bonds with the metal ion through the sharing of three or more pairs of electrons. The chelating ligands (IDA in this case) are bound to the polymer via a spacer arm (GMA) to make the chelating group more accessible. The over-

reaching goal of this study, however, was the attachment of copper to PP, so the results presented here focus on the polymer properties incurred by the addition of copper.

In this study, BPO was used as a radical initiator for the graft polymerization of GMA to the PP surface at a temperature of 80°C [71], or nearly half of temperatures outlined in the literature [84, 93]. Figure 5.1 displays the ATR-FTIR spectrum of a PP-graft-GMA sheet. The adsorption bands present at 1724 and 1253 cm^{-1} were caused by carbonyl stretching and ester vibrations of the epoxy group, respectively, indicating the attachment of GMA. Then, via an SN2 reaction, IDA was added to the PP-graft-GMA[71]. The mean grafting level (GL%) for all of the sheets was approximately 40%; that is, over 3-4 times higher than those associated with other studies [93, 95]. Figure 5.2 displays the ATR-FTIR spectrum of PP-graft-GMA-IDA. Adsorptions at 1589 and 3371 cm^{-1} were caused by carbonyl stretching from carboxylic acids and OH stretching from carboxylic acids present in IDA, respectively. The hypothesis for the high level of grafting observed in this study was proposed to be due to uncontrolled radically initiated polymerization with high concentration of GMA monomer, which agreed with other studies [96, 97]. Finally, after exposure to copper sulfate, x-ray energy dispersive spectrometry (XEDS, UTW Si-Li Solid State X-ray detector with integrated EDAX Phoenix XEDS system, located at the University of Michigan, Ann Arbor) was performed on the sheets, and it showed that there was $3.27 \pm 0.74\%$ by weight copper loading on the surface [71]. Also, as Figure 5.3 shows, mapping of the copper indicated uniform distribution over the surface of the sheets despite visual physical abnormalities present in SEM images.

Figure 5-1: FTIR Spectrograph of Virgin PP and PP-GMA

Figure 5-2: FTIR Spectrograph of Virgin PP and PP-GMA-IDA

Figure 5-3: EDS Mapping and SEM Images of Cu-Charged Polypropylene

A simple visual inspection of the sheets gives a clear indication that copper was chelated to the PP-graft-GMA-IDA. As seen in Figure 5.4, the PP-graft-GMA-IDA sheet turned blue when exposed to the 0.6M copper sulfate solution while a virgin PP sheet exposed to the same solution retains its original color (slightly opaque/white).

Figure 5-4: Image of Virgin and Cu-Charged Polypropylene

5.2 Characterization of Cu-Charged PP-GMA-IDA

5.2.1 Gel Permeation Chromatography of Glycidyl Methacrylate

Gel permeation chromatography was performed on the GMA homopolymer that remained in the reaction vessel after GMA addition reaction in order to gain insight on the molecular weight (MW) of the GMA which was grafted to the PP. While analyzing the homopolymer left in solution does not relate exactly to what was grafted the polypropylene surface, it provides a range and a maximum MW that has been graft to the surface. Two samples were analyzed and the weight average molecular weight was 153501 +/- 5787 and the number average molecular weight was 111754 +/- 11912, resulting in a polydispersity of 1.20 +/- 0.0035.

5.2.2 Dynamic Mechanical Analysis of Modified Polypropylene

To investigate the effects of the modification on the mechanical properties of the polypropylene, dynamic mechanical analysis was performed on virgin and modified sheets, as shown in Figure 5.5. At 30°C the virgin polypropylene had a storage modulus of 1729 MPa while the modified polypropylene had a considerably higher storage modulus of 2738 MPa. This was due to the higher storage modulus of the grafted glassy GMA. As the tan delta peak at ~80°C indicated, this grafted glassy GMA went through glass transition and became rubbery. As a result, the storage modulus decreased rapidly and became 236 MPa at 90°C, compared to 347 MPa of the virgin PP. While with increasing temperature, the modified polypropylene eventually displayed a lower storage modulus than the virgin PP, at or below maximum operation temperatures, which were usually around 50°C, the modified PP has a higher storage modulus.

Figure 5-5: Storage Modulus and Tan Delta of Virgin and Modified Polypropylene

5.2.3 Thermal Gravimetric Analysis of Modified Polypropylene

Thermal gravimetric analysis of modified polypropylene was used to confirm, along with the microbalance, the amounts of grafted GMA and chelated copper. Figure 5.6 shows the weight loss and its derivative vs. temperature. From this data, the ~40% grafting of GMA, which decomposed at approximately 340°C and produced a corresponding derivative weight peak, was verified. It was also seen that after all organic material had decomposed, around 480°C, there still was 111 µg of copper remaining. Knowing the surface area of this sample, 0.53 cm², the amount of copper was determined to be 0.21 g/cm². Also, the increased hydrophilicity of the modified polypropylene

caused it to adsorb moisture from the air resulting in a derivative weight loss peak starting around 100°C. This is not typically seen with polypropylene as it is considered to be hydrophobic.

Figure 5-6: Weight Loss vs. Temperature of Modified Polypropylene

5.2.4 Differential Scanning Calorimetric Analysis of Modified Polypropylene

Differential Scanning Calorimetry was used to determine the percent crystallinity of virgin and modified polypropylene. The resulting data can be seen in Table 5.1 The heat the fusion was determined to be 73.07 J/g +/- 6.80 for virgin PP. Dividing this by 146.5 J/g, which is the heat of fusion for 100% crystalline PP [98], it was determined that the virgin PP was ~50.0% crystalline. For modified PP, the heat of fusion was 40.47 J/g +/- 1.98 J/g. If normalized for the weight of PP, assuming the GMA accounted for 40% of the total mass, the modified PP was determined to be ~46.0% crystalline. This

decrease in crystallinity is thought to come from lower levels of crystallinity near the now modified surface of the polypropylene. Also, from this analysis, a glass transition in the modified polypropylene coming from the grafted GMA around 60°C was observed. This is similar to and compliments well the tan delta peak seen during dynamic mechanical analysis of the modified PP.

Table 5.1: Differential Scanning Calorimetric Data of Virgin and Modified Polypropylene

<u>% Crystallinity Virgin PP</u>	<u>% Crystallinity Modified PP</u>
49.8 ± 4.6	46.0 ± 1.3

5.2.5 Hydrophilicity Analysis of Cu(II) Charged PP-graft-GMA-IDA

After modifying the PP and chelating with copper, the contact angle decreased from 92.3±1.15° to 70.7±2.08°. A decrease in contact angle indicated an increase in hydrophilicity of the PP after modification. The contact angle was measured on the PP surface before and after the GMA was grafted, after the IDA was covalently bound, and after the copper was chelated. The contact angles were 92.3±1.15°, 89.0±2.00°, 52.7±1.15° and 70.7±2.08°, respectively, as shown in Figure 5.7. The decrease in contact angle was observed after the addition of IDA. This was expected, as the addition of IDA resulted in the presence of hydrophilic carboxylic acid groups on the PP surface. This is

an attractive property as hydrophilicity has been shown to decrease the likelihood of fouling [99].

Figure 5-7: Contact Angle of Virgin and Modified Polypropylenes

5.2.6 Antimicrobial analysis of Cu(II) Charged PP-graft-GMA-IDA

Figure 5.8 shows two of the fluorescence microscope photographs taken after 24hrs of incubation from each *e. coli* containing flask. For each sheet removed at the different time intervals, thirty of these images were taken. The number of cells attached to the PP-graft-GMA-IDA sheet after 24hrs was significantly less than those attached to the virgin sheets. Figure 5.9 shows the data collected over the entire 168hrs.

Figure 5-8: Images of Detached Cells from Virgin and Cu-charged Polypropylene

Figure 5-9: Counts of Cells Detached from Virgin and Cu-charged Polypropylene

After 24hrs, attachment was $2.9 \times 10^6 \pm 2.9 \times 10^5$ cells/cm² on the modified sheet versus $4.0 \times 10^7 \pm 2.1 \times 10^6$ cells/cm² on the unmodified sheet. Similar results were obtained at 96hrs, $3.1 \times 10^7 \pm 2.2 \times 10^5$ cells/cm² on the modified and $9.1 \times 10^8 \pm 3.9 \times 10^6$ on the unmodified, and at 168hrs, $4.5 \times 10^7 \pm 4.9 \times 10^4$ on the modified and $3.7 \times 10^8 \pm 1.1 \times 10^5$ on the unmodified. Therefore, the number of cells attached to the PP-graft-GMA-IDA sheets was consistently approximately an order of magnitude lower than those attached to the virgin sheets. While this order of magnitude decrease in cellular attachment may not translate directly to feed spacer performance, it does indicate an increase in antimicrobial properties of the Cu-charged PP.

5.2.7 Strength of Copper Chelation

a) *Batch Study: Surface Analysis*

Both batch and cross flow leaching studies were performed under specific conditions that may give insight into how problematic and to what extent copper may leach from modified feed spacers during filtration. Figure 5.10 shows that the release of copper after two weeks in concentrated common cleaning solutions was not drastic.

Figure 5-10: Fraction of Copper Remaining on Modified PP During Batch Leaching Study

The only two instances where a significantly different weight percentage of copper was observed was after two weeks in the 5mM EDTA solution at pH 11, and the HCl solution at pH 3.5 after both one and two weeks. The data collected indicated that common metal ions such as sodium, calcium, and magnesium do not displace the chelated copper. While the highly acidic solution and 5mM EDTA did appear to have some affect on the sheets after two weeks, the weight percent of copper remaining on the sheets after exposure was $3.26\% \pm 0.41$ and 3.89 ± 0.28 for the HCl and EDTA solutions respectively. As the experiments in this paper show, this weight percent of copper still acts affectively as a biocide.

b) Batch Study: Solution Analysis

A similar study using the same 5 mM EDTA with pH adjusted to 11 solution as well as a 50 mg/L ferrous sulfate solution was conducted, but instead of quantifying the copper remaining on the surface of the PP, atomic absorption was used to quantify it in solution. After approximately 5 days, the amount of copper displaced from the Cu-charged PP in the Fe(II) solutions was approximately 0.30 ppm. A similar trend was seen for the 5 mM EDTA solution, except the equilibrium concentration was approximately 0.17 ppm. This can be seen in Figure 5.11. While this equilibrium state is an artifact of these batch-style incubation experiments, only a small amount of copper leached from the feedspacers in both cases. However, it was seen that the iron solution caused more leaching than the EDTA.

Figure 5-11: Copper Displaced into Solution in Fe(II) and EDTA Solutions

c) Cross Flow Leaching Studies

Figure 5.12 presents the data obtained from the cross flow leaching experiments. The points on the graph represent samples taken in the test tubes at different times, while

the solid lines indicate the values of copper in the collection bottle after the 24-hr cross flow period. The latter value can be taken as the mean copper concentration that resulted from copper leaching. Again, copper concentrations taken at different times, as well as the average copper concentration, show that little copper leached from the Cu-charged PP and the concentrations were still below many drinking water regulations, which are 1.3 mg/L by the U.S. EPA [99], 4 mg/L by the Hong Kong government [100], and 2mg/L by the World Health Organization [101] and the European Union [102]. This might not be an issue for application; since this would be in the retentate stream since copper should be partially or completely rejected.

Figure 5-12: Cross-flow Copper Leaching Results

Lastly, copper leaching was also monitored during the bench-scale cross flow experiments using the Sepa CF cell. To ensure no copper was coming from the feed water itself, both the feed water and DI water were tested for copper and none was detected. Cross flow filtration was operated using a full recycle mode; that is, the permeate and concentrate streams were both recycled back into the feed stream basin. After 48 hours of

cross flow filtration, samples from the recycled stream, containing permeate and concentrate, were drawn and analyzed. Upon analysis, the recycled stream of the system with the unmodified spacer contained 1.063 ppm of copper. That is, copper appeared in the unmodified recycled stream. However, for the unmodified system, there were no sources of copper present in the DI or the raw feed water. Therefore, this was further investigated and found to be due to copper being introduced to the system either by the pump, which had a brass head, the chiller, which contained copper tubing, the heating element, or a combination of the three. From this data, it was contended that there was a background of copper present at all times. The recycled stream of the system with the Cu-charged PP spacer had a copper concentration of 0.63 ppm. Thus, there was no significant difference between the leaching of copper when Cu-charged PP spacers were used as compared to the use of unmodified PP spacers during the cross flow filtration.

d) Rechargability of Modified Polypropylene

To qualitatively determine if the modified polypropylene could be recharged in the event that all or some copper was leached, a Cu-charged piece of feed spacer was placed in a nitric acid solution of pH 0.5. The purpose of this was to protonate all the carboxylic acid and amine groups of the IDA and release the chelated copper. After this step, the feed spacer was washed with DI water and placed back into the 0.6M copper sulfate solution. Figure 5.13 shows that the modification does allow for recharging of polypropylene in case some or all of it has leached.

Figure 5-13: Images Showing the Rechargability of Modified Feed Spacers

5.3 Performance of Cu-Charged Feed Spacers

5.3.1 Tap Water Studies

Tap water, which was dechlorinated with sodium thiosulfate and supplemented with 30 mg/L of sodium acetate, was used as a feed solution in these runs. Permeate flux was measured throughout the 48-hour filtration experiments and normalized to the initial flux values, which were $38.46 \pm 1.35 \text{ L/m}^2\text{-hr}$ for the membranes using both unmodified and Cu-charged spacers, after precompaction, under a pressure of 6.89 bar. This can be seen in Figure 5.14.

Figure 5-14: Normalized Flux During Run One with Tap Water

Filtration experiments with both Cu-charged and unmodified spacers exhibited instantaneous flux declines, possibly due to particulate fouling. Immediately following this period, the flux remained relatively constant for both runs until approximately 15 hours. At such time, the flux of membrane system using the unmodified spacer began to decrease rapidly, possibly due to excessive microbial attachment. This trend continued for the unmodified spacer membrane system until the end of the filtration experiment. Conversely, the membrane system using the copper-charged feedspacer remained nearly constant after its instantaneous flux decline, indicating that if microbial attachment was the prevalent form of fouling, it could be controlled. During the second set of cross flow filtrations, as seen in Figure 5.15, which lasted 51 hours for the membrane with the unmodified feed spacer and 286 hours with the membrane using the Cu-charged feed spacer, a similar trend was observed over the initial 48-hour period.

Figure 5-15: Normalized Flux During Run Two with Tap Water

The initial fluxes for the membranes used with the unmodified and Cu-charged feed spacers in these experiments were $68.33 \pm 0.64 \text{ L/m}^2\text{-hr}$, after precompaction, under a pressure of 13.79 bar. A higher pressure was used to both make the experimental conditions more closely mimic real-life conditions and to make sure the results were not largely affected by pressure. Since the flux of the membranes using the unmodified spacer had been reduced to 20% of the initial value after 51 hours of filtration, the filtration was ended. Instead of stopping the membrane with the Cu-charged spacer at the same 51 hours, it was decided that its filtration would continue until it reached 35% of the initial flux. This took 286 hours, during which a rapid rate of flux decline was never observed. This lack of a rapid flux decline indicated that the mechanism by which the membranes with different feed spacers were fouling was not the same.

Following the filtration experiments, cells were detached from the fouled membranes and counted. After 46.25 hours and 286 hours of filtration using the Cu-charged feed spacers, there were $4.68 \times 10^5 (\pm 1.01 \times 10^4) \text{ cells/cm}^2$ and $6.24 \times 10^7 (\pm 3.88 \times 10^6) \text{ cells/cm}^2$

present on the membrane surfaces, respectively. After 47.5 hours and 51 hours of filtration with unmodified spacers, there were $5.44 \times 10^6 (\pm 1.24 \times 10^4)$ cells/cm² and $1.73 \times 10^7 (\pm 1.49 \times 10^6)$ cells/cm² present on the membrane surfaces, respectively. These values, and their standard deviations, are also presented in Figure 5.16 where the left side corresponds to the Cu-charged feed spacer and the right side to the virgin spacer.

Figure 5-16: Cellular Attachment Rate Using Virgin and Modified Spacers

From these cell counts, and the durations of the filtration experiments, a cell attachment rate was determined by simply calculating the increase of cells on the surface of the membrane from one membrane filtration time to the next. The attachment rate of cells to the membranes with the unmodified feed spacers was 3.39×10^5 cells/cm²-hr while that to the membranes with the Cu-charged feed spacers was 2.58×10^5 cells/cm²-hr; that is, over an order of magnitude lower. The cell attachment rate presented here assumed a linear rate of attachment, which the authors recognize as nonrealistic. While it is known that rates of cell proliferation and death are not linear over the filtration periods

investigated, presenting the attachment rate as linear allowed for a difference to be easily seen.

After observing drastically different cell attachment rates between the membranes using unmodified feed spacers and those using Cu-charged feed spacers, the attachment mechanisms were brought into question. To visualize microbial attachment, SEM images of membranes fouled while using the Cu-charged and unmodified spacers were taken. For this, the membranes, which were fouled during the 48-hour filtration experiments, were analyzed and the resulting images can be seen in Figure 5.17 where the right side corresponds to the Cu-charged feed spacer and the left side to the virgin spacer.

Figure 5-17: SEM Images of Membranes Fouled During Tap Water Filtration Runs Using Virgin Feed Spacers (left) and Modified Feed Spacers (right).

For both membranes, areas that were visually more fouled were chosen since the purpose of the imaging was to understand the mechanisms of fouling rather than any quantitative data collection. While cells were present on both membrane surfaces, it

appeared that the membrane fouled with the unmodified spacer also had a substantial amount of extracellular polymeric substances (EPS) within the fouling matrix that had been formed. Conversely, the membrane fouled while using the Cu-charged feed spacer appeared to only have cells on its surface. Furthermore, it appeared that the fouling by these cells resembled that of colloidal or particulate fouling, rather than the biofilm formation seen in the unmodified spacer image.

FTIR analysis was then performed to obtain a further understanding of the differences between the mechanisms of cell attachment and fouling occurring during cross flow filtration in the cases of the unmodified and Cu-charged feed spacers. Figure 5.18 shows FTIR spectra of the membranes fouled during the 48-hr experiments using the unmodified and Cu-charged spacers, as well as an unfouled membrane.

Figure 5-18: FTIR Spectra of Membranes Fouled During Tap Water Runs One

The spectrum of the membrane fouled with the Cu-charged spacer showed significant differences from the unfouled membrane, as it would be expected. The most prominent of these differences was the addition of the peak at a wavenumber of 1635cm^{-1} , which is indicative of a protein carbonyl stretch, and is commonly referred to as the Amide I peak [87-92]. When analyzing the membrane that was fouled with the unmodified spacer, four additional peaks were present. These peaks appeared at wavenumbers of 970, 1053, 1380 and 1735cm^{-1} and corresponded mainly with polysaccharides, but also to lipopolysaccharides, fatty acids and phospholipids [87-90]. A listing of these peaks, their band assignments and associated biomolecules can be seen in Table 5.2.

Table 5.2: FTIR Peaks of Interest, wavenumbers, band assignment, and associated biomolecule

<u>Wavenumber (cm^{-1})</u>	<u>Band Assignment</u>	<u>Associated Biomolecule</u>	<u>References</u>
970	C-O Stretch	Polysaccharides	[87]
1053	C-O or C-O-C Stretch	Polysaccharides	[87-89]
1380	Symmetric Stretch of Carboxylate Ion	Polysaccharides	[90]
~1635	C=O Stretch of Amide I	Protein	[87-92]
1735	C=O Stretch of esters	Polysaccharides, fatty acids, phospholipids, lipopolysaccharides	[87, 89, 90]

The FTIR analysis of the membrane fouled after 51 hours with the unmodified spacer, which can be seen in Figure 5.19, looked almost identical to the spectra of the membrane fouled after 48 hours also with the unmodified feed spacer (Figure 5.18), and it showed the presence of the same peaks.

Figure 5-19: FTIR Spectra of Membranes Fouled During Tap Water Runs Two

The FTIR spectra from the membrane fouled after 286 hours with the Cu-charged spacer (Figure 5.19) indicated that there was a thicker deposit layer on this surface. This can be observed by the lack of the peaks coming from the membrane itself showing through. Despite this, there were no peaks at 970, 1053, 1380 and 1735 cm^{-1} wavelengths, indicating again the lack of polysaccharides on the membrane surface. Therefore, FTIR evidence led to the conclusion that EPS formation was associated with the fouling of the

membranes that used the unmodified feed spacers but not with the membranes that used the Cu-charged feedspacers. This observation supports the role of the Cu-charged feedspacers in controlling biofouling.

5.3.2 *Pseudomonas fluorescens* Studies

Permeate flux was measured throughout one four-hour run, one 24-hour run and two 48-hour runs, and normalized to the initial flux values, which was $35.47 \pm 1.97 \text{ L/m}^2\text{-hr}$ for both spacer types, after precompaction, under a pressure of $\sim 6.89 \text{ bar}$. The same protocol as in the previous studies was followed but 16 hours prior to the filtration start, *Pseudomonas fluorescens* Migula cells, which were freshly grown on an R2A agar plate, were added to the reservoir so that the initial cell concentration was 10^6 cells/mL . Filtration was carried out at 34°C and $\sim 100\text{psi}$. The flux data can be seen in Figure 5.20. As expected, the flux declined significantly less in all cases with the modified feed spacer. This supported trends seen in earlier studies [71]. Interestingly though, filtration experiments with unmodified spacers exhibited much more instantaneous flux declines in the first four to ten hours, possibly due to cellular attachment coming from EPS secretion. This was investigated further. During the filtration runs, samples of the water in the feed reservoir were taken at 4, 24, and 48hrs and live/dead, as well as total, counts were performed on the cells in these samples. The total cell count can be seen in Figure 5.21 while the percentage of lives cells can be seen in Figure 5.22.

Figure 5-20: Normalized Flux Data for *Pseudomonas fluorescens* Containing Feed

Figure 5-21: Total Cells in Solution During Filtration

Figure 5-22: Viable Cells in Solution During Filtration

Following filtration, cells were detached from the membrane, stained with either PI or pico-green and imaged using a fluorescent microscope. An example of the images can be seen in Figure 5.23.

Figure 5-23: Cells Detached From Membranes During Filtration with *Pseudomonas fluorescens* Containing Feed Water

While this method was effective for measuring live and dead cells detached from the membrane fouled with the modified spacers, it was not capable of counting cells detached from the membrane fouled with the virgin spacers because of the high number of cells. Regardless of how diluted the samples to be stained were prepared, clumps of cells always appeared in the images even at early stages in the case of the virgin spacers. As can be seen in Figure 5.23, it qualitatively appeared that there was a higher concentration of live cells in all images taken of cells attached from the membranes fouled with virgin spacers. These results also pointed to high levels of EPS, resulting in cell “clumps”, on the membranes fouled with virgin spacers. It also showed that a different method should be used for a quantitative comparison of the membranes fouled with different spacers.

To visualize microbial attachment, SEM images of membranes fouled using both modified and virgin spacers were taken. For this, the membranes, which were fouled during the four-hour, 24-hour and one 48-hour filtration experiments were vacuum dried overnight, coated with gold-palladium and analyzed. The resulting images can be seen in Figure 5.24.

Figure 5-24: SEM Images of Membranes Fouled During Filtration with *Pseudomonas fluorescens* Containing Feed Water

Again, areas that were visually more fouled were chosen since the purpose of the imaging was to understand the mechanisms of fouling rather than any quantitative data collection, as this technique was largely qualitative by nature. The membrane fouled with the virgin spacer after four hours showed significant cell accumulation. After 24 hours, a biofilm covered the surface entirely, and a small amount of contour was observed in the biofilm. After 48 hours, the biofilm looked similar to what it did at 24 hours but the contour was much greater, indicating that the thickness of the membrane was likely greater. The membrane fouled with the modified spacer showed little or no cellular attachment after four hours, slightly more at 24 hours, and, at 48 hours, an image similar to the one taken from the membrane fouled with the virgin spacer after four hours was observed. When the flux from the membrane used with the virgin spacer after four hours was compared to that of the membrane used with the modified spacer at 48 hours,

there was visual agreement. Still, this autopsy was strictly qualitative and the need for more quantitative analysis remained.

A novel method allowed for monitoring of biofilm thickness versus filtration time and made it possible to compare biofilm component concentrations on membranes fouled with virgin and modified spacers versus time. This FTIR based technique has the ability to both absolutely quantify the biofilm thickness and quantitatively related biofilm components on fouled membrane surfaces. As can be seen in Figure 5.25, the biofilm thickness appeared to grow to the maximum measureable level (that is, when $DP = t_b$) at a faster rate when the virgin spacers were used.

Figure 5-25: Biofilm Thickness Vs. Filtration Time

When the polysaccharide (region from 900cm^{-1} to 1200cm^{-1}) amount was compared between the virgin and modified feed spacer, a higher amount after four hours of filtration with the virgin spacer was observed, as can be seen in Figure 5.26.

Figure 5-26: Polysaccharide Concentration vs. Filtration Time

This provided a quantitative verification of the qualitative trends observed by the previously described characterization techniques, and it indicated that the copper-modified feed spacers affected the cellular attachment of the bacteria by hindering the EPS (polysaccharide) secretion. This decreased cellular attachment ultimately resulted in lower flux decline observed.

5.4 Silver Charged Feed Spacers

Modified membrane feed spacers were also charged with silver(II), a known biocide [103], instead of copper. While it is known that silver(II) has a lesser affinity toward IDA than copper[104], is more costly than silver, and also has more stringent drinking water regulations[99], the biocide was investigated to observe how a feed spacer, charged with a metal which is more prone to leaching, would affect biofilm formation. This was done by simply placing the PP which has been modified to contain IDA in a 0.6M silver nitrate solution instead of the previously mentioned 0.6M copper sulfate solution.

5.4.1 Silver Leaching

To determine the extent to which the silver would leach from the feed spacers, compared to copper, as well as to determine that silver's affinity to the IDA modified feed spacer was indeed less, a batch study similar to that outline in section 4.3.3a was conducted. Modified PP that was charged with silver was exposed to the same three solutions (high salt, pH 3.5, and 5mM EDTA at pH 11) for one week. From Figure 5.27, it was observed that significantly more silver leached under identical conditions as compared to copper.

Figure 5-27: Fraction of Silver Remaining on Modified PP During Batch Leaching Study

While, after one week, both silver and copper did not appear to leach in the presence of the high salt solution, after exposure to solution at a pH of 3.5 and the 5mM EDTA solution at pH 11, only ~17% and ~32% of the silver remained on the surface of the modified PP. This was drastically less than ~75% of copper which remained after exposure to the same two solution for the same amount of time, indicating that silver had lesser affinity to the IDA modified PP and was more prone to leaching.

5.4.2 Performance of Silver Modified Feed Spacers

Permeate flux was measured throughout one four-hour , one 24-hour and one 48-hour experiments, and normalized to the initial flux values after precompaction under a pressure of 6.89 bar, similar to what was described previously, in section 4.3.4b, for copper charged feed spacers. *Pseudomonas fluorescens* Migula cells, which were freshly grown on an R2A agar plate, were added to the reservoir so that the initial cell

concentration was 10^6 cells/mL. Filtration was carried out at 34°C and ~100psi. The flux data, alongside the previously reported data, is shown in Figure 5.28.

Figure 5-28: Normalized Flux Data for *Pseudomonas fluorescens* Containing Feed Water with Silver Charged Feed Spacer

As the filtration data illustrates, the silver charged feed spacer appeared to control biofouling as well as, or better than, the copper charged feed spacer at short time increments (4hr or less). As filtration time increased, the ability of the silver feed spacer to control fouling and maintain a constant flux deteriorated, and after 48hrs the percentage of initial flux fell between that of the virgin and copper charged feed spacers (~47%). To investigate this performance, counts of live/dead, as well as total, cells in the feed reservoir were performed just as they were for the virgin and copper charged feed

spacer experiments. This total number of cells in solution vs. filtration time is shown in Figure 5.29, and the percentage of viable cells in the feed reservoir vs. filtration time can be seen in Figure 5.30. Both have been shown next to previously presented data (copper and virgin spacers) for comparison purposes.

Figure 5-29: Total Cells in Solution During Filtration with Silver Charged Feed Spacers

Figure 5-30: Viable Cells in Solution During Filtration with Silver Charged Feed Spacer

5.4.3 Membrane Autopsy After Using Silver Modified Feed Spacers

After filtration using silver charged feed spacers, membrane coupons were taken from identical locations on the membrane, vacuum dried, sputter coated with cold and imaged using a SEM. These images are shown in Figure 5.31.

Figure 5-31: SEM Images of Fouled Membranes Using Silver Feed Spacers

From these images, it appeared that the silver charged feed spacers caused more colloidal fouling of dead cells, rather than the EPS mediated biofouling (Figure 5.24) when the virgin feed spacer was used. This was consistent with the lower percentage of dead cells observed in the feed reservoir during filtration with the silver feed spacer. Also, this agreed with the amount of silver that was detected in the feed reservoir water vs. filtration time. As seen in Figure 5.32, the amount of free silver in solution is high after 4 hours of filtration time. The amount of free silver in solution then decreases with filtration time. It is hypothesized that the silver, having a lower affinity to IDA, leaches rapidly during the beginning hours of filtration, resulting in fewer viable cells in solution.

The amount of available silver on the feed spacer surface is then depleted, while the silver that has leached stays bound to components of dead bacteria. This results in less free silver in solution, a higher number of total cells in solution, a higher percentage of viable cells, and ultimately a faster rate of flux decline.

Figure5-32: Amount of Silver in Solution vs. Filtration Time

Biofilm thickness versus filtration time and was again calculated after cross-flow filtration runs with silver charged feed spacers. This allowed for a comparison in biofilm thickness, as seen in Figure 5.33, versus filtration time using the silver spacer against other spacers.

Figure 5-33: Biofilm Thickness vs. Filtration Time with Silver Charged Feed
Spacer

This slower increase in biofilm thickness during the early hours (<24hr) of filtration was also consistent with flux data, again pointing toward silver staying chelated and preventing biofilm formation in the similar fashion as the copper charged feed spacer. At later times (>24hr) however, the rate of biofilm thickness increased to greater than the copper charged feed spacers. This was consistent with the faster rate of flux decline seen during this period when using the silver charged spacer compared to the copper charged spacer. Once the biofilm thickness was calculated, the polysaccharide amount on the membranes fouled with the silver spacer could be calculated and

compared to previous virgin and copper charged spacer runs. This data is presented in Figure 5.34.

Figure 5-34: Polysaccharide Concentration on Membrane vs. Filtration Time with Silver Charged Feed Spacer

In contrast to the previous comparison, between copper-charged feed spacers and virgin feed spacers, the amount of polysaccharide on the surface of the membrane was not indicative of the extent of fouling, and ultimately flux decline, which had occurred. The amount of EPS present on the surface of the membranes fouled using the silver charged feed spacer was less, after 48 hours, than both the virgin and copper charged feed spacers. The flux decline, however, after 48 hrs was between that of when using copper charged and when using virgin feed spacers, pointing toward a fouling mechanism that was not dependent on EPS excretion.

As the cell counts observed in Figures 5.29, 5.30 and SEM images (Figure 5.31) indicate, a higher number of dead and total cells caused extensive colloidal fouling after

48hrs of filtration using the silver-charged feed spacer. The hypothesis to explain this was that the silver was leaching from the feed spacer, contaminating the feed reservoir and killing cells. This caused the number of dead cells to increase, but since there was an abundance of carbon source, the cells stayed in a log growth phase longer, resulting in an overall increase in cell numbers.

5.4.4 Comparison of Copper and Silver Charged Feed Spacers

Under the conditions used in these filtration experiments, the copper charged feed spacers were able to better control biofouling after 48 hours of filtration. This appears to be due to a weaker chelation of silver to IDA. The silver that is chelated to the surface of the modified feed spacer leaches rapidly, compared to copper, resulting in its inability to control biofouling at its origin (the membrane/feed spacer interface) after a few hours of filtration. Copper, on the other hand, does not leach as rapidly and is able to inhibit cellular attachment in this region for a longer period of time.

Chapter 6

Conclusions

The initial goal of this project was to develop a copper charged PP that could potentially be used as an antimicrobial/ low biofouling feed spacers for reverse osmosis spiral wound elements. To this end, PP was functionalized with metal affinity ligands via a spacer arm. Infrared spectroscopy verified that PP was successfully modified to become PP-graft-GMA-IDA at temperatures of 70°C as opposed to either higher temperatures or harsher conditions proposed in other studies. SEM and elemental analysis were used to show that the PP-graft- GMA-IDA was uniformly charged with copper(II). The modification method utilized simple a reaction apparatus, inexpensive straightforward techniques, and commonly used, readily available chemicals.

A second goal of this project was to show that this method, which could be used to produce copper-charged polypropylene feed spacers, can control membrane biofouling. As mentioned, polypropylene was functionalized with metal affinity ligands that could be charged with the biocidal metals, such as copper. This modification gave antimicrobial properties to the polypropylene feed spacer and also increased its hydrophilicity. Analysis showed that the number of cell attached to virgin PP sheets, over a 168 h time span, was approximately an order of magnitude higher than those attached to

the copper(II) charged PPgraft- GMA-IDA sheets. The chelation of copper to the feed spacer was determined to be preferential to Fe(II), EDTA and dissolved organic matter in both batch and crossflow leaching studies. Thus, environmental impacts from copper leaching when using Cu-charged PP feed spacers would be minimal. More significantly, use of the copper-charged feed spacer led to a consistently lower rate of flux decline during filtration. This increased resistance to fouling, and more specifically, biofouling, was hypothesized to be attributed to the hindrance of cell adhesion to the membrane/feed spacer interface. FTIR analysis verified the presence of greater levels of polysaccharides on membranes fouled while using the unmodified polypropylene feed spacers compared to membranes fouled using copper charged feed spacers. Polysaccharides are known to make up the largest portion of EPS, and are related to cell adhesion during initial stages of biofilm formation[54]. It is believed that the antimicrobial property, as well as the increased hydrophilicity, of the Cu-charged feed spacers aided in hindering cell adhesion and, consequently, biofilm formation and biofouling. Therefore, the use of copper-charged feed spacers have the potential to increase membrane life and decrease chemical cleanings associated with detrimental biofouling of membranes.

Also, it was desired to have a better understanding behind the mechanism by which the modified feed spacers were able to control biofouling. To investigate the role EPS plays in cellular adhesion and biofouling, a novel FTIR based technique was utilized to autopsy membranes which were biofouled with the use of virgin and antimicrobial, metal-charged feed spacers. Traditional methods such as live/dead cell counts and SEM imaging pointed to this hypothesis but lacked the ability to quantitatively relate the levels of polysaccharides on the membranes fouled with virgin and modified spacers. Because

of this, the FTIR based technique was implemented, and while it is limited to only analyzing a biofilm, or layer of biofilm, with a thickness equal to that of the depth of penetration (DP) of the IR evanescent wave, it resulted in a quantitative verification of this hypothesis.

Finally, the use of silver, as a chelated, antimicrobial metal, instead of copper was investigated as it is known to be biocidal. As expected, it was shown that silver does not chelate as strongly to the IDA modified PP as copper. Leaching studies showed much greater levels of silver release, compared to copper, when exposed to solutions a membrane and feed spacer will commonly encounter. During cross flow filtration using silver charged feed spacers, it appears that during the first few hours, before a critical amount of silver had leached from the feed spacer, the silver-charged feed spacers performed as well, or better than the copper charged feed spacers. After this time it appears that this increased leaching resulted in a higher percentage of dead and total cells in the feed reservoir compared to identical runs with copper charged feed spacers. This resulted in higher levels of colloidal fouling which ultimately resulted in a feed spacer whose performance fell between the virgin and copper-charged feed spacers during these studies. The presence of colloidal fouling, instead of traditional EPS controlled biofouling, was supported by FTIR analysis which showed lower levels of polysaccharides on the surface of the membrane fouled during the use of the silver charged spacer compared to other spacers.

Chapter 7

Recommendations

Although the chemical modification of PP feed spacers was successful, the process was done on a lab scale in batch processes and would not be feasible for large scale production. This is mainly due to the large amounts of GMA homopolymer which come out of solution during the GMA grafting step. To circumvent this, two recommendations have been made:

1. An alternate form of surface activation of the PP feed spacer, such as ozone, plasma, or UV, could localize the radical initiation and prevent homopolymer GMA from forming in solution. The spacer could be activated separately, and then ran through a bath of monomeric GMA. This would allow for a continuous process that would desirable in large scale production.
2. Large batches of feed spacer could be modified if the GMA homopolymer could be kept in solution. To keep the homopolymer in solution, the GMA molecular weight could be lowered by increasing the initiator (BPO) to GMA monomer ratio. Also, using a mixed solvent system could increase the solubility of GMA homopolymer, as could an increase in reaction temperature.

During bench studies which test the performance of copper and silver charged feed spacer, both appeared to reduce fouling but by different methods. To determine if these metal charged spacers would work in actual applications, two recommendations have been made:

1. Performing cross-flow filtration studies with a more realistic, one pass, feed, compared to running the filtration in full recycle mode would be beneficial. This would require either a large feed reservoir or a continuous feed source such as tap water that is constantly supplemented with carbon sources, micro organisms, etc.
2. Scaling up the project to produce full-scale spiral wound reverse osmosis/nanofiltration elements and using them at a desalination facility. This would be most ideal and would answer, definitively, which metal is better suited for controlling biofouling in a real-life application.

Finally, it should be determined if copper or silver have any affects on the relatively chemically fragile polyamide membranes. Lab studies with extended exposure to copper and silver solutions as well as real-life monitoring of membrane integrity in full size modules should be conducted.

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Appendix A

Flux Data

Actual flux data for tap water filtration runs seen in Figures 5.14 and 5.15 were presented in the following tables.

Table A-1: Flux Data Using Virgin Spacer During 100psi Tap Water Run

Time(hr)	Volume(mL)	ET (s)	Temp(°C)	PSI	BAR	Flux(L/m ² *hr)	Normalized Flux
0.00	30.00	176.79	20.00	100.00	6.89	39.41	1.00
2.00	30.00	192.54	20.00	100.00	6.89	36.19	0.92
3.00	30.00	204.87	20.00	100.00	6.89	34.01	0.86
4.00	30.00	209.34	20.00	100.00	6.89	33.28	0.84
5.00	30.00	214.20	20.00	100.00	6.89	32.53	0.83
6.00	30.00	225.80	20.00	100.00	6.89	30.86	0.78
8.25	30.00	224.40	20.00	100.00	6.89	31.05	0.79
12.67	30.00	239.78	20.00	100.00	6.89	29.06	0.74
23.00	20.00	169.09	20.00	100.00	6.89	27.47	0.70
25.00	20.00	176.24	20.00	100.00	6.89	26.36	0.67
28.00	20.00	182.90	20.00	100.00	6.89	25.40	0.64
30.00	20.00	195.07	20.00	100.00	6.89	23.81	0.60
34.25	20.00	203.81	20.00	100.00	6.89	22.79	0.58
48.00	15.00	296.52	20.00	100.00	6.89	11.75	0.30

Table A-2: Flux Data Using Cu-Charged Spacer During 100psi Tap Water Run

Time(hr)	Volume(mL)	ET (s)	Temp(°C)	PSI	BAR	Flux(L/m ² *hr)	Normalized Flux
0.00	15.00	92.90	20.00	100.00	6.89	37.50	1.00
2.00	15.00	93.46	20.00	100.00	6.89	37.28	0.99
4.00	15.00	103.46	20.00	100.00	6.89	33.67	0.90
5.00	15.00	106.07	20.00	100.00	6.89	32.85	0.88
9.00	15.00	113.69	20.00	100.00	6.89	30.64	0.82
11.25	15.00	114.80	20.00	100.00	6.89	30.35	0.81
23.00	15.00	116.93	20.00	100.00	6.89	29.79	0.79
25.50	15.00	117.46	20.00	100.00	6.89	29.66	0.79
28.25	15.00	121.48	20.00	100.00	6.89	28.68	0.76
35.00	15.00	125.16	20.00	100.00	6.89	27.84	0.74
48.00	15.00	125.27	20.00	100.00	6.89	27.81	0.74

Table A-3: Flux Data Using Virgin Spacer During 200psi Tap Water Run

Time(hr)	Volume(mL)	ET (s)	Temp(°C)	PSI	BAR	Flux(L/m ² *hr)	Normalized Flux
0.00	3.00	65.09	20.00	200.00	13.79	67.88	1.00
10.50	3.00	71.75	20.00	200.00	13.79	61.58	0.91
27.50	3.00	82.25	20.00	200.00	13.79	53.72	0.79
51.00	3.00	274.43	20.00	200.00	13.79	16.10	0.24

Table A-4: Flux Data Using Cu-Charged Spacer During 200psi Tap Water Run

Time(hr)	Volume(mL)	ET (s)	Temp(°C)	PSI	BAR	Flux(L/m ² *hr)	Normalized Flux
0.00	3.00	73.60	20.00	200.00	13.79	68.78	1.00
27.50	3.00	95.69	20.00	200.00	13.79	52.91	0.77
62.50	3.00	112.22	20.00	200.00	13.79	45.11	0.66
66.50	3.00	109.00	20.00	200.00	13.79	46.44	0.68
70.00	3.00	109.50	20.00	200.00	13.79	46.23	0.67
72.00	3.00	106.48	20.00	200.00	13.79	47.54	0.69
89.00	3.00	110.29	20.00	200.00	13.79	45.90	0.67

94.50	3.00	108.47	20.00	200.00	13.79	46.67	0.68
112.00	3.00	112.38	20.00	200.00	13.79	45.05	0.65
118.50	3.00	115.19	20.00	200.00	13.79	43.95	0.64
139.00	3.00	128.72	20.00	200.00	13.79	39.33	0.57
142.00	3.00	125.09	20.00	200.00	13.79	40.47	0.59
163.50	3.00	145.00	20.00	200.00	13.79	34.91	0.51
195.50	3.00	175.00	20.00	200.00	13.79	28.93	0.42
222.00	3.00	186.41	20.00	200.00	13.79	27.16	0.39
241.00	3.00	192.00	20.00	200.00	13.79	26.37	0.38
283.50	3.00	197.84	20.00	200.00	13.79	25.59	0.37
286.00	3.00	203.00	20.00	200.00	13.79	24.94	0.36

Actual flux data for filtration runs using *Pseudomonas fluorescens* containing feeds, seen in Figures 5.20 and 5.28, were presented in the following tables.

Table A-5: Flux Data Using Virgin Spacers During *Pseudomonas fluorescens* Runs

Time(hr)	Volume(mL)	ET (s)	Temp(°C)	PSI	BAR	Flux(L/m ² *hr)	Normalized Flux
0.00	10.00	250.00	28.00	100.00	6.90	40.00	1.00
1.00	10.00	310.00	31.00	100.00	6.90	32.26	0.76
1.75	10.00	318.00	31.50	100.00	6.90	31.45	0.73
3.25	10.00	293.00	34.00	120.00	8.27	34.13	0.63
21.25	10.00	408.00	35.00	120.00	8.27	24.51	0.44
27.75	10.00	421.00	36.00	120.00	8.27	23.75	0.42
48.00	10.00	480.00	35.00	120.00	8.27	20.83	0.38
0.00	10.00	289.00	28.00	100.00	6.90	34.60	1.00
20.50	10.00	376.00	35.00	120.00	8.27	26.60	0.55
22.50	10.00	398.00	35.00	120.00	8.27	25.13	0.52
45.50	10.00	532.00	36.00	120.00	8.27	18.80	0.38
47.50	10.00	556.00	36.00	120.00	8.27	17.99	0.37
48.00	10.00	562.00	36.00	120.00	8.27	17.79	0.36
0.00	10.00	320.00	25.00	100.00	6.90	31.25	1.00
4.00	10.00	360.00	35.00	100.00	6.90	27.78	0.72
7.00	10.00	342.00	36.00	130.00	8.96	29.24	0.57
20.50	10.00	335.00	37.00	150.00	10.34	29.85	0.49
21.50	10.00	407.00	37.00	125.00	8.62	24.57	0.49

24.00	10.00	421.00	37.00	125.00	8.62	23.75	0.47
0.00	10.00	288.00	26.00	120.00	8.27	34.72	1.00
1.00	10.00	329.00	29.00	120.00	8.27	30.40	0.82
2.00	10.00	369.00	33.00	120.00	8.27	27.10	0.67
3.00	10.00	351.00	33.00	125.00	8.62	28.49	0.68
4.00	10.00	369.00	33.00	125.00	8.62	27.10	0.64

Table A-6: Flux Data Using Cu-Charged Spacers During *Pseudomonas fluorescens* Runs

Time(hr)	Volume(mL)	ET (s)	Temp(°C)	PSI	BAR	Flux(L/m ² *hr)	Normalized Flux
0.00	10.00	300.00	25.00	100.00	6.90	33.33	1.00
0.50	10.00	285.00	27.00	100.00	6.90	35.09	1.01
1.50	10.00	261.00	30.00	110.00	7.58	38.31	0.94
19.50	10.00	257.00	35.00	120.00	8.27	38.91	0.79
22.50	10.00	270.00	35.00	120.00	8.27	37.04	0.75
24.50	10.00	280.00	35.00	120.00	8.27	35.71	0.72
26.50	10.00	280.00	36.00	120.00	8.27	35.71	0.71
42.50	10.00	330.00	36.00	120.00	8.27	30.30	0.60
44.50	10.00	335.00	36.00	120.00	8.27	29.85	0.59
48.00	10.00	339.00	36.00	120.00	8.27	29.50	0.58
0.00	10.00	567.00	26.00	110.00	7.58	35.27	1.00
0.75	10.00	553.00	29.00	110.00	7.58	36.17	0.96
1.50	10.00	525.00	30.00	110.00	7.58	38.10	0.99
5.00	10.00	500.00	33.00	110.00	7.58	40.00	0.96
24.00	10.00	556.00	35.00	110.00	7.58	35.97	0.84
25.50	10.00	572.00	35.00	110.00	7.58	34.97	0.82
28.00	10.00	582.00	35.00	110.00	7.58	34.36	0.81
29.00	10.00	590.00	35.00	110.00	7.58	33.90	0.79
45.00	10.00	690.00	36.00	110.00	7.58	28.99	0.67
47.00	10.00	700.00	36.00	110.00	7.58	28.57	0.66
48.00	10.00	709.00	36.00	110.00	7.58	28.21	0.65
0.00	10.00	712.00	23.00	110.00	7.58	35.11	1.00
6.00	10.00	568.00	34.00	120.00	8.27	44.01	0.90
24.00	7.00	389.00	33.00	120.00	8.27	44.99	0.94
0.00	10.00	278.00	25.00	120.00	8.27	35.97	1.00
2.50	10.00	283.00	27.00	115.00	7.93	35.34	0.98
3.00	10.00	284.00	29.00	110.00	7.58	35.21	0.98
4.00	10.00	288.00	31.00	110.00	7.58	34.72	0.92

Table A-7: Flux Data Using Ag-Charged Spacers During *Pseudomonas fluorescens* Runs

Time(hr)	Volume(mL)	ET (s)	Temp(°C)	PSI	BAR	Flux(L/m ² *hr)	Normalized Flux
0.00	22.11	300.00	31.00	95.00	6.55	61.42	1.00
0.50	23.95	300.00	33.00	95.00	6.55	66.53	1.04
2.50	24.16	300.00	37.00	95.00	6.55	67.11	0.97
7.50	24.14	300.00	37.00	105.00	7.24	67.06	0.88
20.00	19.17	300.00	36.00	95.00	6.55	53.25	0.78
24.00	18.01	300.00	36.00	95.00	6.55	50.03	0.74
27.00	16.79	300.00	36.00	95.00	6.55	46.64	0.69
44.50	12.16	300.00	35.00	95.00	6.55	33.78	0.51
48.00	20.05	514.00	35.00	95.00	6.55	32.51	0.48
0.00	24.98	240.00	27.00	102.00	7.03	62.45	1.00
3.50	27.07	240.00	32.00	102.00	7.03	67.68	0.97
5.00	24.86	240.00	32.00	102.00	7.03	62.15	0.89
9.00	23.12	252.00	33.00	102.00	7.03	55.05	0.77
21.00	18.46	238.00	33.00	102.00	7.03	46.54	0.66
24.00	18.43	242.00	33.00	102.00	7.03	45.69	0.61
0.00	13.76	240.00	22.00	110.00	7.58	57.33	1.00
0.50	14.59	240.00	25.00	110.00	7.58	60.80	0.99
4.00	16.45	240.00	32.00	110.00	7.58	68.55	0.96

*For all graphs, “ET” is the elapsed time for the “Volume” of permeate to be collected.

“Time” is the amount of filtration time at each point.

Appendix B

Determination of Area Under FTIR Peaks

The area under the peaks in the FTIR method presented in this study were determined by integration. Varian Resolutions Pro Version 4.1.0.101 was used to integrate under the peaks of interest. The method used has been previously described [[105]] and an example of this “corrected area” can be seen in Figure B-1.

Figure B-1: Corrected Area as Measured by Varian Software