MANUFACTURING AND PERFORMANCE OF ACTIVATED CARBON-COATED NANOFILTRATION MEMBRANES

A Thesis Presented to The Academic Faculty

By

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A journey of a thousand miles begins with a single step.

Laozi

For my mother,

whose success inspires me to dream big, work hard, and never give up.

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LIST OF ACRONYMS

- AC Activated Carbon
- AFM Atomic Force Microscopy
- ANOVA Analysis of Variance
- EDS Energy Dispersive X-Ray Spectroscopy
- FESEM Field Emission Scanning Electron Microscopy
- **GO** Graphene Oxide
- **HF** Hyperfiltration
- **IQR** Interquartile Range
- MF Microfiltration
- MILL Materials Innovation and Learning Laboratory
- NF Nanofiltration
- PAA Polyacrylic Acid
- PAC Powdered Activated Carbon
- PTFE Polytetrafluoroethylene
- **PVA** Polyvinyl Alcohol
- R2R Roll-to-Roll
- **RBS** Rutherford Backscattering Spectrometry
- **RO** Reverse Osmosis
- **SDS** Sodium Dodecyl Sulfate
- **SEM** Scanning Electron Microscopy
- SPM Scanning Probe Microscopy
- **UF** Ultrafiltration
- **XPS** X-Ray Photoelectron Spectroscopy

SUMMARY

Membrane-based desalination is becoming increasingly important due to rising global water scarcity. Both membrane systems and adsorption-based technologies are critical for most water treatment processes. Membranes are effective at removing total dissolved salts and particulate matter from water and adsorption-based technologies are ideal for removing organic and inorganic compounds. By combining adsorption and membranes together, there may be potential to create a lower energy treatment process with reduced system complexity, and therefore reduced cost. Merging adsorption and membranes together may also alleviate some of the limitations associated with each technology. Specifically, commercial membranes require high pressures and their salt removal capabilities tend to decline in harsh conditions. Activated Carbon (AC) is a highly adsorptive material that is used in wastewater treatment, but processing it with the wastewater can be a time-consuming and expensive process. Therefore, combining membrane technology and activated carbon adsorption into a single step may increase wastewater treatment efficiency and improve membrane performance.

This thesis seeks to understand the feasibility of manufacturing an activated carboncoated commercial Nanofiltration (NF) membrane in order to improve water treatment performance. Several coating methods were tested, including film coating and vacuum filtration coating, to determine the most suitable method for manufacturing the activated carbon-coated membranes. The concentration of activated carbon was varied to investigate the coating thickness's impact on membrane flux and salt rejection; these performance tests were carried out in a Sterlitech HP4750 dead-end cell with an aqueous magnesium sulfate solution as the feed solution. Characterization tests such as contact angle testing and Scanning Electron Microscopy (SEM) were carried out to develop a comprehensive understanding of the modified membranes.

The primary discovery is that activated carbon reduces a membrane's magnesium sul-

fate removal capabilities. Correlations between membrane performance and the concentration of coating on the membrane are reported. Testing showed that as the concentration of activated carbon in the coating increased, the flux through the membrane decreased. In addition, the salt rejection decreased with higher concentrations of activated carbon, and it was determined that this decreased rejection was likely due to the phenomenon of concentration polarization. Using lower concentrations of activated carbon for coating the surface of nanofiltration membranes led to the formation of an inhomogeneous AC-coated surface, resulting in less statistically significant data. In addition, contact angle testing proved that as the concentration of activated carbon increased, the membranes became more hydrophilic. The findings from this research can guide future experiments seeking to use coated membranes for other contaminant removal applications, such as the removal of pharmaceuticals or other micropollutants from wastewater [1].

Chapter 1 provides the introduction to the project along with the motivation for this work. By highlighting key background information and limitations of existing technologies, the importance of the work described herein becomes apparent.

Chapter 2 contains a literature review to give more detailed information about the key components of this work. The literature presented gives detailed information about manufacturing practices used for thin-film processing, activated carbon, as well as existing membrane technology. This section also contains information about previous studies conducted to improve membranes as well as the performance and characterization testing that takes place to discover important membrane characteristics.

Chapter 3 outlines the materials and methods used for this research. The first key challenge of this project was determining the most compatible manufacturing method to produce an activated carbon coating on a nanofiltration membrane. The experimental set-ups for the manufacturing processes are outlined in this chapter. After coating the membranes, the performance testing parameters and system used are given. This chapter also includes information about the characterization equipment used after performance testing. Chapter 4 describes the results of the performance tests and provides discussions about the outcomes from the studies. This chapter also includes ideas about why the outcomes were observed and compares the results to a model to support the claims. Furthermore, plots of the observed trends and images from characterization tests are included to explain the change in membrane performance with different AC concentrations.

Chapter 5 summarizes the key takeaways and conclusions from the experiments conducted.

Chapter 6 gives recommendations for future work related to this study. Several system improvements and future directions are suggested that would be interesting for future experimentation.

CHAPTER 1 INTRODUCTION AND MOTIVATION

The growing global population has contributed to the issue of water scarcity reaching an all-time high, exacerbated by the resource stress induced by climate change, industrialization, and water contamination [2, 3, 4, 5]. Different regions of the world experience water scarcity at varying levels, with more populous areas, such as India and China, suffering from more severe water scarcity [4, 6]. While many portions of the United States have access to clean drinking water and water sources for agriculture, there are still some areas of the United States that struggle with water availability due to the climate and other factors [4, 5, 6]. In addition, many different countries worldwide do not have the same easy access to freshwater, particularly those areas with large populations [4, 5]. A map showing the water stress severity in different regions of the world can be seen in Figure 1.1, where regions experiencing extreme water stress are highlighted in dark red [6].



Figure 1.1: Severity of water stress in different regions across the globe. Areas of high population typically have more extreme water stress compared to less populous regions [6]

Not only is the quantity of water in a given region a key contributing factor to water availability, but the quality of water and contamination sources in that region play a role in water scarcity as well [2]. As such, the need for efficient, reliable, and cost-effective desalination and contaminant removal technology is essential to ensure that people worldwide have access to clean water.

Membrane and adsorption-based systems have emerged as promising technologies for desalination and removing contaminants from water. However, there are limitations with each technology. Specifically, commercial membranes require high pressures, their salt removal capabilities tend to decline in harsh conditions, and there is a trade-off between achieving high salt rejection and high enough flux for the method to be feasible in large-scale desalination [3]. On the other hand, activated carbon is a highly adsorptive material that is used in wastewater treatment as well, but oftentimes it is mixed with the wastewater to remove contaminants and must be filtered out from the aqueous solution later, which can be a time-consuming, expensive, and inefficient process [7]. For this reason, integrating activated carbon adsorption with membrane technology, where the membrane is coated with an activated carbon layer, may improve wastewater treatment efficiency and efficacy.

In the work described herein, the primary goal was to manufacture an activated carboncoated nanofiltration membrane and evaluate the performance mechanism for salt and contaminant removal. A secondary goal was to compare the performance of an activated carbon-coated membrane to reverse osmosis membranes. By exploring these goals, this work sought to enhance membrane performance for wastewater treatment applications.

CHAPTER 2 BACKGROUND AND LITERATURE SURVEY

2.1 **Processing Techniques**

Thin film coatings have become an increasingly popular field of study in recent years due to their application to a vast number of industries. In order to meet this demand, many different processing techniques and strategies have arisen for a wide range of applications [8]. Depending on the needs for each experiment, a different coating technique may be more or less beneficial. Each of these different processes has significant advantages and disadvantages; therefore, it is important to weigh the pros and cons of each to select the correct strategy for a given application [8].

2.1.1 Overview of Coating Manufacturing Strategies

Although there are many processing techniques, most can be broadly categorized into continuous manufacturing strategies and batch production manufacturing strategies [9]. Depending on the application, each of these methods have distinct benefits. Continuous manufacturing practices are generally preferred when a process will be scaled-up in the future for an industrial size production load [10]. On the other hand, batch production can be used in industrial settings but is more often used as a small batch method, where a one-off product is being used for individual tests prior to large scale manufacturing [9].

Continuous Manufacturing

There are many different types of continuous manufacturing strategies, many of which are beneficial for mass production. For example, Roll-to-Roll (R2R) coating technologies such as slot die coating have been used for continuous high throughput manufacturing of thin films of uniform thickness [11]. Slot die coating has proven to be an environmentallyfriendly process for applications where speed and scalability are the main concerns [12]. In general, slot die coating consists of pumping a solution through a die and depositing it onto a moving substrate. The substrate is fed through the system by rollers which keep the substrate taught during the deposition process. Once the solution has been deposited, it cures on the substrate to form a solid coating. There are many parameters in slot die coating that can be changed in order to optimize the system, including the substrate speed, flow rate, height of die, and the physical die parameters [11]. Many of these parameters are independent of one another so one parameter can be changed without greatly impacting another. Because the roll-to-roll coating processes involve a single pass through the system, they are capable of delivering a high throughput and can easily be scaled up for mass production, as has been demonstrated in industrial applications [11].

Small Batch Production

On the contrary, a technique such as dip coating is more suitable for processing one product at a time. This method involves building a film layer-by-layer by dipping the substrate into a vat of the desired coating material, thus allowing for electrostatic forces between polymers to create a film after each iteration [11]. Excess solution drips off of the substrate back into the bulk solution as the substrate is removed. The solution then dries on the substrate and creates a uniform thin film. While this processing technique has been widely developed for large coverage areas, it is more difficult to scale this technique up for mass production [11].

Spin coating is one of the most commonly used techniques for creating thin films via the layer-by-layer method. It involves dispensing the liquid onto the center of the substrate, then rapidly spinning the substrate. This spinning motion causes particles of the solution to travel outwards and distribute homogeneously throughout the surface area of the substrate, thereby allowing precursors to react with each other on a molecular level [11]. Due to the fast rotational speed and additional washing steps, any unwanted molecules are removed from the substrate. The remaining material on the substrate is then left to dry and become a solid thin coating of uniform thickness throughout [11]. One benefit of this coating technique is that the thickness of the coating can easily be controlled by changing the spinning speed and concentration of the solution. It is also easy to scale up, as it is a rather simple method. A disadvantage is that because a large portion of the solution is removed from the coating during the spinning process, there is a significant amount of waste [11]. Spin coating has traditionally been used in photolithography or applications such as coating functional oxide layers on glass, when a thin film of uniform thickness is desired [11].

Spray coating is also an effective method for creating thin coatings. This process involves spraying a solution onto a substrate such that it forms an even, thin film. One of the main advantages for this method is that there is a lot of flexibility in the type of substrate that is compatible with this coating method [11]. Because the processing technique simply involves spraying the substrate, many different types of substrates can be used, including flexible substrates. This allows for further studies of the effects of bending on the coating. However, there are also disadvantages that come with the spraying technique. Because the solution is sprayed onto the substrate, there is the possibility for a lack of precision of the deposition technique due to the distance that the particles have to travel to arrive at the substrate and the possibility for spreading [11]. In addition, there could be waste due to the transfer of the material [11].

2.1.2 Tape Casting with Doctor Blade

For the specific application of this project, tape casting with a doctor blade was selected as the most ideal manufacturing technique. Tape casting is a method that involves evenly spreading a coating solution across a substrate using either a slot die or doctor blade [13]. The tape casting device can be set to run at different coating speeds and coating distances depending on the application [14]. The doctor blade allows for the user to select the desired thickness and adjust as necessary. The tape casting machine also includes a heated cover which can be used to assist in the drying process. For this project, speed and continuous manufacturing is not a priority, so therefore using the tape casting device to create one-off products is sufficient for this application.

Because this research seeks to understand how changing manufacturing properties impacts the effectiveness of coated membranes, the adjustability of the tape casting machine was highly appealing. This equipment can easily be adjusted to coat at different speeds and physical dimensions to allow for varied coatings. In addition, it does not require a specific substrate to be used, so a delicate substrate, such as a membrane, can be coated on without causing harm to the surface. All of these parameters can be quickly and easily changed between runs, allowing for a large variety of experiments to be conducted. The "film coater" described herein refers to the equipment used to perform the tape casting with a doctor blade.

2.1.3 Vacuum Filtration

Alongside tape casting, vacuum filtration was also a highly appealing manufacturing process to utilize for this research. Vacuum filtration is a very common method of filtration and can be easily adapted for different needs. Although there are many specific types of vacuum filters, all of them operate on the same basic principle: a vacuum on the filtrate side of the medium serves as the driving force to draw a solution through the medium, thereby allowing the liquid portion of the solution to pass through and the solid portion of the solution to be collected at the medium surface [15]. While vacuum filtration is oftentimes used as a method to separate parts of a solution, it has also been used as a manufacturing method for depositing thin films of a material on the medium used for the filtration [16, 17, 18]. Specifically, it has been proven to be a simple method to create thin, uniform, films of nanomaterials such as graphene oxide and carbon nanoparticles on a desired substrate [16, 17, 18]. Because vacuum filtration is very easy to modify, it is especially useful for small

batch production of thin films where scale-up is not a main concern [15].

For this project specifically, the membranes manufactured through the tape casting method were found to be incompatible with the performance testing cell. For this reason, vacuum filtration coating was investigated because of its flexibility in creating a coating of varying diameter. In this project, this adaptability was especially useful and allowed for the membranes manufactured to integrate properly with the dead-end cell used for testing.

2.2 Polymeric Membrane Technology

2.2.1 Overview of Membranes

Membrane technology has become the backbone of filtration and separation processes due to the large variety of types of membranes available for different applications. A driving force is used to push the feed solution through the membrane, allowing for the membrane to separate a target material out from the feed [19]. The driving force applied to the system can either be a pressure differential, potential gradient, or concentration difference, depending on the application [19, 20]. There are several common membrane configurations, including flat sheet membranes and hollow fiber membranes. Flat sheet membranes are flat and thin like a piece of paper, while hollow fiber membranes are shaped like tubes with a hole in the center [21]. Each membrane type is used for different applications, but flat sheet membranes are more commonly used in large scale industrial applications because they tend to be easier to manufacture than hollow fiber membranes [22]. Hollow fiber membranes are commonly used in gas separations and are growing in popularity for use in commercial applications such as desalination or use in the medical field [23].

In addition to the shape of the membrane, there are also several common morphologies and materials that create the structure of the membrane which in turn determines the membrane's function. Membranes can either be porous or dense, but for desalination and wastewater treatment applications, porous membranes are specifically of interest [19]. Porous membranes are typically characterized by their pore sizes, which dictate the type of particles that they are able to filter out [19, 21]. Several common porous membrane types are Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF), and Reverse Osmosis (RO) membranes, listed in order of decreasing pore size [19, 21]. The typical average pore size for each type of membrane for water treatment applications is given in Table 2.1 [24].

Table 2.1: Average pore sizes for the four main porous membrane types [24]

| Membrane Type | Pore Size (nm) |
|------------------------|----------------|
| Microfiltration | 100-1000 |
| Ultrafiltration | 5-50 |
| Nanofiltration | 2-5 |
| Reverse Osmosis | <1 |

Because of these differing pore sizes, each of these four main types of membranes is used to remove different contaminants from a solution (i.e. microbes, bacteria, organic pollutants, salts, etc.), as outlined in Figure 2.1 [25].

2.2.2 Types of Membranes

Microfiltration (MF)

Microfiltration membranes are oftentimes used as a wastewater pretreatment step to remove suspended solids from the solution because the pores are larger than other membrane types [21]. Because of these larger pores, MF is typically used for the removal of particles that are between 0.1-1 micron in diameter or larger [21]. Microfiltration methods are almost always followed by other separation techniques, especially for water treatment when the goal is to eliminate dissolved solids as well as suspended particles [21, 26, 27, 28]. Although there are other steps needed to achieve a high purity of water, microfiltration provides significant purification to water at a lower cost than other systems, making it a beneficial step in the water treatment process [28].



Figure 2.1: Outline of various membrane types and their filtration capabilities [25].

Ultrafiltration (UF)

Similar to microfiltration membranes, ultrafiltration membranes have relatively large pore sizes, so they cannot remove small dissolved particles like ions, but rather are used to remove larger suspended particles, colloids, and some large dissolved particles [21]. Typical UF membrane pore sizes range from 0.05-0.08 microns, though the exact pore sizes vary from membrane to membrane due to manufacturing parameters that cause the pores to form [21, 29]. One of the most important capabilities of ultrafiltration membranes in the water treatment industry is the ability of these membranes to remove pathogenic microorganisms, such as bacteria and viruses, from water [21, 30]. While many dissolved particles are still able to pass through ultrafiltration membranes, removing the bacteria and viruses makes the water safe for human consumption, though oftentimes ultrafiltration is used as a pretreatment step in industrial applications as well [30].

Nanofiltration (NF)

With pore sizes much smaller than MF and UF membranes, nanofiltration membranes are capable of filtering out dissolved particles on the order of 1 nanometer in diameter [21, 29]. Nanofiltration membranes are able to remove the same suspended particles as microfiltration and ultrafiltration membranes, in addition to other materials such as multivalent and monovalent ions [21, 31]. In wastewater treatment applications, ensuring that the water can be softened sufficiently to meet the standard for human consumption is extremely important, so nanofiltration membranes can be leveraged to find this balance [31].

Extensive prior research has been conducted on utilizing nanofiltration membranes for the removal of micropollutants, specifically those found in urine, as these salts, pharmaceuticals, and other compounds are found in and around wastewater treatment plants [32]. As these micropollutants enter the environment, they have the potential to cause significant harm to the surrounding ecosystems, including damage to animal and plant species, as well as cycling back to humans and causing health concerns [32, 33, 34, 35]. As such, nanofil-tration membranes have been of particular interest to combat the accumulation of unwanted contaminants because of the versatility of materials that they are capable of filtering from the water [32].

Reverse Osmosis (RO)

Reverse Osmosis (RO) membranes, also known as Hyperfiltration (HF) membranes, are the most selective membranes of the four discussed, and therefore are able to filter the smallest particles [21]. They are able to remove nearly all dissolved solids from the feed solution in addition to the larger particles that other membrane types are also able to remove [21, 32, 35]. These membranes are growing in popularity in municipal and industrial

wastewater treatment applications due to their purification capabilities [36]. Although reverse osmosis membranes are able to achieve very high water purity compared to the other membrane types, one key limitation is the high pressure required to operate reverse osmosis systems [37]. Because they rely on high pressures, reserve osmosis water treatment systems often consume a lot of energy and are not very efficient [37]. For this reason, it is of interest to investigate alternative methods that can achieve purity similar to reverse osmosis at a lower pressure and therefore lower level of energy consumption.

2.2.3 Membrane Materials

As there are many different types of membranes, there are also many different materials that can be used to make them. Synthetic membranes can be broken down into two main groups: inorganic and organic types. Inorganic membranes can be made of materials such as ceramics, carbons, or zeolites [38, 39]. Organic membranes, which are the focus of this research, are commonly made of polymers [38]. There are many different types of polymers that are suitable for use with different fabrication methods. They can be used to make commercial membranes compatible with each of the four aforementioned membrane processes. An outline of some of the most common membrane polymers and the membrane types that they can make is given in Table 2.2 [38].

Table 2.2: Examples of common polymers used for commercial membrane fabrication

| Polymer | Membrane Process |
|---------------------------|------------------|
| Cellulose Acetate | MF, UF, RO |
| Polyamide | MF, UF, NF, RO |
| Polysulfone | MF, UF |
| Poly(ether sulfone) | MF, UF |
| Polycarbonate | MF, UF |
| Poly(vinylidene fluoride) | MF, UF |
| Polyacrylonitrile | MF, UF |

For this research, polyamide membranes are of particular interest due to their use in wastewater treatment. When fabricating the membrane, the polymer is used as the active top layer of the membrane and is layered on top of a backing material [40]. An example of the layer configuration of a polyamide membrane is given in Figure 2.2 [40].



Figure 2.2: Structure of polyamide membrane layers [40]

To improve membrane efficacy, a thin active polymer film is desired, so the chemical synthesis process is very important [40]. For polyamide membranes specifically, an aqueous solution containing amine monomer is used for immersing the substrate [40]. It is then immersed in a hydrocarbon solution with acyl chloride monomer to obtain a thin film [40]. The organic structure of the polyamide membrane thin top layer synthesized in this way is shown in Figure 2.3 [40]. The composition of the polyamide layer is very important for membrane performance, and creating a polyamide with desired characteristics can greatly improve its effectiveness in the application of wastewater treatment [41].



Figure 2.3: Organic structure of thin film polyamide active top layer [40]

2.2.4 Performance Testing

Pressure-driven membrane systems undergo performance testing to quantify the effectiveness of the membrane. During testing, the membrane is secured in a test cell where certain parameters are measured. The feed solution is the solution that contains the contaminant of interest and passes through the membrane to be purified. The permeate is the resulting purified water that comes out of the cell once the solution has passed through the membrane. The effective membrane area is the membrane area through which the permeate flows, therefore performing the filtration [42].

The most important performance parameters are the membrane's contaminant rejection and the flux through the membrane. Rejection is a measure of how well the membrane is removing a contaminant of interest, whether it be a salt, pathogen, or suspended particle, and is given by a ratio of the concentration of the contaminant in the permeate to the concentration of the contaminant in the feed solution [32, 34, 42, 43, 44, 45]. Rejection (R) is given by Equation 2.1

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \cdot 100 \tag{2.1}$$

where C_p is the concentration of the contaminant in the permeate solution and C_f is the concentration of the contaminant in the feed solution [42]. The flux gives the rate at which the feed solution passes through the membrane and is dependent on the membrane's effective area, permeate mass, and time [42]. Flux can be measured in an instantaneous sense, where it is calculated between two successive points in time, or it can be calculated in an overall sense where it gives the trend compared to the start of the experiment. Instantaneous flux (J_i) is given by Equation A.1, which is provided in Appendix A.

Overall flux (J) is given by Equation 2.2

$$J = \left(\frac{m}{t \cdot A_{mem}}\right) \tag{2.2}$$

where m is the total mass of permeate collected at a certain point in time, t is the total elapsed time at that point, and A_{mem} is the effective membrane area. [42].

Typical testing for these membranes occurs in a dead-end stirred cell or cross-flow



(b) Crossflow Test Cell

Figure 2.4: Schematic of a dead-end stirred cell system and a cross-flow system. In a deadend stirred cell system, the feed flow direction is perpendicular to the membrane surface, whereas in a cross-flow setup it is parallel to the surface.

performance testing system. A comparison of a dead-end cell and a cross-flow cell is shown in Figure 2.4. In dead-end stirred cell systems, the flow of the feed solution is perpendicular to the membrane surface, and in cross-flow systems, the flow is parallel to the surface [46]. These dead-end cells contain a stirrer to emulate cross-flow performance [47]. Oftentimes in large-scale industrial testing applications, cross-flow processes are used to test large sheets of membranes at a high rate, while dead-end cells are more often used in smaller scale laboratory applications because they do not have the same scale-up capabilities [46].

2.2.5 Fouling

Membrane fouling occurs when contaminants are deposited on the membrane surface and build up over time, causing a decrease in flux and rejection performance [48]. This build-up occurs due to several different types of physical and chemical interactions between the membrane surface and the contaminants [49]. The deposited contaminants, known as foulants, can be biological, organic, inorganic, or particulate matter [49]. One of the biggest challenges of expanding the use of membranes in industrial water treatments plants is the tendency of fouling to decrease membrane performance, leading to increased membrane maintenance costs and system downtime [49, 50]. As such, discovering and developing innovative methods for reducing membrane fouling has become a principal focus in order to propel membrane technology forward [48, 49, 50, 51].

Because membrane fouling is such a common problem with membrane technology, many studies have been conducted to combat fouling [49]. A common method used to reduce fouling is utilizing "backpulsing," which involves reversing the transmembrane pressure for a brief period of time to clean the membrane and remove foulants [52]. Many works have also used surface modification to decrease the membrane's affinity for foulants and thereby reduce the amount of foulants that accumulate [52]. Oftentimes this surface modification consists of coating a material on the membrane surface to alter the surface chemistry, and in several studies, activated carbon has been used to reduce membrane fouling [52, 53, 54].

2.2.6 Concentration Polarization

For salt rejection membranes specifically, concentration polarization is a special type of fouling that can cause decreased rejection readings [48, 49, 55]. Because the rejected ions do not diffuse quickly away from the membrane, a buildup of ions at the membrane surface can cause the effective concentration at the membrane surface to be higher than that of the feed solution [48]. A schematic of this phenomenon is given by Figure 2.5.



Figure 2.5: Schematic of concentration polarization at the membrane surface. The increased concentration causes the apparent rejection, measured experimentally, to be lower than the true rejection capability [48].

Due to concentration polarization, the apparent rejection that is measured experimentally is lower than the true rejection capability of the membrane. The apparent rejection is the comparison of the concentration of the permeate to the feed solution, as given by Equation 2.1, while the true rejection is a parameter that can be modeled based on the osmotic pressure of the membrane and the flux through the membrane. The osmotic pressure in the permeate is given by Equation 2.3 [48]

$$\pi_{sl} = 2 \cdot c \cdot R \cdot T \tag{2.3}$$

where c is the molar concentration of the solute, R is the ideal gas constant, and T is the temperature (K). The osmotic pressure at the membrane surface can be modeled using the calculated osmotic pressure of the permeate and is given by Equation 2.4 [48]

$$\pi_{so,m} = \left(\pi_{sl} + \Delta P \cdot \left(1 - \frac{J_{w,salt}}{J_{w,pw}}\right)\right)$$
(2.4)

where ΔP is the transmembrane pressure, $J_{w,salt}$ is the flux through the membrane when using the salt feed solution, and $J_{w,pw}$ is the pure water flux through the membrane. The true rejection can then be calculated using this model and the two values of flux found experimentally. True rejection is given by Equation 2.5 [48]

$$R_{true} = \left(1 - \frac{\pi_{sl}}{\pi_{so,m}}\right) \cdot 100 \tag{2.5}$$

where π_{sl} is the permeate osmotic pressure calculated in Equation 2.3 and $\pi_{so,m}$ is the osmotic pressure at the membrane surface calculated by Equation 2.4 [48].

2.2.7 Characterization Techniques

Membrane characterization is an important step in gaining a holistic understanding of a membrane's structure and properties, specifically related to surface properties and possible surface defects. The membrane's structure, including physical and chemical properties, directly relate to its function; by examining certain aspects of a membrane's morphology such as roughness, hydrophilicity/hydrophobicity, pore size, and elemental composition, a more comprehensive understanding of a membrane's performance can be determined [56]. Many different techniques exist to target some of these parameters. Although not all of the methods discussed below were utilized in this project, it is important to note some of the other common technologies available for membrane characterization.

Atomic Force Microscopy (AFM)

Atomic Force Microscopy (AFM) is a common type of Scanning Probe Microscopy (SPM) used for determining a membrane's surface roughness, which is an important parameter to characterize as it can contribute to fouling and decreased membrane performance [56, 57, 58]. AFM utilizes a sharp probe to scan over a membrane surface and take 3-dimensional measurements [57]. It can either operate in a contact mode or a non-contact

mode, where the probe either makes physical contact with the surface to take these measurements or uses a feedback system to adjust a fixed distance between the probe tip and the surface [57]. AFM can either maintain a fixed distance and measure the current, or maintain a fixed current and measure the distance between the tip and the membrane surface [57]. The probe can measure the surface at varying resolutions depending on the amount of detail that is needed, making AFM a versatile and adaptable method for taking roughness measurements. Understanding the topography of the membrane can help to characterize the roughness and also help to identify surface defects or heterogeneity, all of which can contribute to a decrease or inconsistency in membrane performance [57].

Scanning Electron Microscope (SEM)

Another very common method used to characterize membrane surface properties is Scanning Electron Microscopy (SEM), which also includes Field Emission Scanning Electron Microscopy (FESEM). SEM can be used to understand the morphology of the membrane surface or cross section, as well as to investigate the fouling layer of the membrane, which is very valuable information to characterize the membrane [58, 59]. SEM was selected as one characterization method to use for this research, and the specific SEM equipment and the imaging parameters used for this project are described in detail in subsection 3.4.1.

When viewing the membrane surface, SEM can be used to get a closer look at the fouling layer, surface defects, and membrane pores, and it can also be used to measure these components [60]. Oftentimes, SEM is also paired with Energy Dispersive X-Ray Spectroscopy (EDS), X-Ray Photoelectron Spectroscopy (XPS), or Rutherford Backscattering Spectrometry (RBS), which are techniques that are used to determine the elemental composition of a membrane's surface [61]. These techniques are especially useful to determine the elements in the membrane's fouling layer [61]. These methods can be used to quantify the types of elements that are in the membrane and can also be used to focus on certain regions of interest [61].

In order to view a cross section of the membrane, oftentimes membranes are first fractured using liquid nitrogen to create a clean break where SEM can be used to view the membrane cross section. From these cross section views, the membrane thickness can be identified as well as thicknesses of individual layers of the membrane [56]. For instance, if a membrane is comprised of several different materials, such as an active layer and a backing layer, the SEM can help to identify the thickness and uniformity of the active layer on top of the backing [56]. In addition, examining the cross-section can help to identify interesting membrane morphologies, such as the finger-like structures observed by Liu et. al. [60].

Contact Angle Measurements

Contact angle measurement is used to determine the hydrophilicity or hydrophobicity of a material surface, which gives insight into the molecular interactions at the membrane surface [56]. For membranes, surface wettability is very important, as it influences performance characteristics such as flux, rejection, and fouling [62]. Contact angle measurements have also been found to relate to membrane surface roughness, which can contribute to higher rates of fouling and decreased performance when the surface is very rough [62]. For this reason, understanding a membrane's hydrophobicity or hydrophilicity not only gives insight into the molecular interactions with water, but also can give key insight into a membrane's performance. Examining contact angle at various points along a membrane can point to heterogeneity if the contact angle is not consistent across the surface of the membrane [62, 63]. Contact angle measurement was also selected as a characterization method to use for this research, and the specifications of the equipment used are described in detail in subsection 3.4.2.

A common contact angle measurement method is the Sessile Drop Method, where a drop of water or another liquid is deposited onto a surface and a camera is used to capture an image of the drop [64]. The contact angle can be calculated using Young's Equation, given by Equation 2.6

$$\cos(\theta) = \left(\frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}\right) \tag{2.6}$$

where γ_{SV} is the surface tension of the solid and vapor, γ_{SL} is the surface tension of the solid and liquid, and γ_{LV} is the surface tension at the liquid-vapor interface [56]. A contact angle greater than 90 degrees implies that the surface is hydrophobic, whereas a contact angle less than 90 degrees implies that the surface is hydrophilic [56]. The angle that is measured for contact angle tests is depicted in Figure 2.6 [58].



Figure 2.6: Contact angle measurements where a.) represents a hydrophobic surface and b.) represents a hydrophilic surface [58].

2.3 Membrane Coatings and Adsorption

Coating technology has gained popularity in a variety of fields. The manufacturability and versatility of different coating solutions have allowed for this field to grow and expand. When formulating a solution for coating, the microstructure, composition, and material properties have a significant influence on the resulting coated product [8]. Once the coating cures, the strength and flexibility of the resulting product are important properties to allow for a wide range of applications. Certain materials, such as MXenes, graphene oxide, and activated carbon, have proven to be promising materials for membrane coating applications. In addition, these materials exhibit adsorptive properties and have been used in
water treatment to remove contaminants.

2.3.1 MXenes

The family of MXenes includes a wide variety of 2D inorganic carbides, nitrides, and carbonitrides. Generally, these materials are represented as $M_{n+1}X_nT_x$ [65]. In this notation, M represents a transition metal, X indicates a carbide or nitride, T gives surface termination elements, and the value of n varies from 1 to 3 [65]. MXenes have proven to display high electron density, good water flux, and flexible mechanical properties, which makes them a highly promising candidate for conductive coatings; however, processing techniques have proven to highly impact the conductivity of MXenes [11]. This dependence highlights the importance for optimization of the manufacturing process to ensure that the material properties are not adversely affected. Because doctor blade coating is a highly adaptable technique, it is likely that the parameters of the coating process could be altered in a way that maintains the quality of the MXene [65]. MXenes have important applications in many different industries, including energy storage, optics, water treatment, and electronics [11, 65].

MXenes have been used in water treatment primarily for the removal of inorganic compounds, but recent developments have explored the use of MXenes for the removal of organic compounds as well [66, 67, 68]. MXenes have been of interest for removing contaminants such as pharmaceuticals and dyes due to material properties such as good stability, oxidation resistance, 2D structure, and hydrophilicity [66, 67]. Studies have shown that MXenes have good adsorption capacities for various contaminants, making them a promising material for water treatment applications [68].

2.3.2 Graphene Oxide

Similar to MXenes, Graphene Oxide (GO) has proven to be a widely-used material for membrane applications. In particular, graphene oxides have shown to be a barrier to

liquids and gases and are effective in separating organic solvents from water [69]. In addition, graphene oxides have been used for liquid and gas filtration applications [70]. Due to the mechanical and chemical stability of graphene oxides, they are compatible with high-pressures and solvent conditions that many other materials cannot withstand [71]. In addition, the resulting graphene oxide coating is lightweight and flexible, making it a good material for many applications. Slot die coating has been used for graphene oxide processing and has proven to be an effective method for depositing ultra-thin films [69]. In addition, slot die coating allows for a uniform coating, thereby enhancing surface properties and improving the overall performance of the graphene oxide coating [69].

In adsorption applications, graphene oxide has been investigated for the removal of contaminants such as dyes and heavy metals [70, 71]. Graphene oxide is also a desirable material for adsorption due to properties such as the presence of oxygenated functional groups, leading to high hydrophilicity and the ability to disperse easily in water [70]. In addition, GO is a cheap and efficient adsorbent, and it is easy to modify depending on the application, making it interesting to study for water treatment applications [71].

2.3.3 Activated Carbon

Overview and Use in Water Treatment

Activated carbon is a versatile and well-known adsorbent that has earned increased popularity in many different industries, including electrochemical fields as well as purification fields [72]. Due to its surface properties and adaptability to many applications, activated carbon is oftentimes used to adsorb pollutants from both gases and liquids; perhaps most notably, activated carbon has been used extensively for water treatment [72]. It has become an effective adsorbent for water treatment due to its desirable surface properties, namely its large surface area [73]. Several studies have investigated the application of combining carbon materials with membranes in order to improve water treatment applications [53, 74, 75, 76]. Specifically, studies have looked at using activated carbon to remove contaminants from the feed solution such as organic compounds and other contaminants, highlighting its effectiveness at purifying wastewater [1].

Formation and Chemistry

Activated carbon can come in many forms including powder, pellet, and granular forms, but the focus of this research is Powdered Activated Carbon (PAC) [72, 73]. These different forms can be purchased commercially or synthesized from various organic products; for example, Kallem et al. used orange peels to derive activated carbon [53]. Other organic sources that are commonly used to produce activated carbon are wood, coconut shells, and coal, which are turned into a char by burning them [73]. The char is then oxidized to form the internal pores, which is what distinguishes activated carbon from other forms of carbon [73].

Because many different types of source materials can be used to create activated carbon, the exact elemental composition varies, but generally is comprised of carbon, oxygen, sulfur, nitrogen, and hydrogen [73]. The most common functional groups in activated carbon are O–H, C=O, -CH2, and -CH3 [77]. The functional groups that contain oxygen are especially important in determining activated carbon performance because the oxygen greatly contributes to surface hydrophobicity [73, 77].

Membranes with Activated Carbon

Several studies have been conducted incorporating activated carbon with membrane technology to improve various aspects of the water treatment process. Some studies seek to synthesize a composite membrane with activated carbon while others have coated membranes with activated carbon. For example, Kallem et. al. created an activated carbon nanocomposite ultrafiltration membrane to increase membrane permeability and decrease fouling [53]. In this study, it was found that the activated carbon composite membrane achieved 4.6 times higher flux and a fouling reduction from 33% to 6%, indicating that the

activated carbon improved membrane performance in these areas [53]. Another study, as described in Shao et. al., sought to deposit activated carbon on ultrafiltration membranes to increase contaminant removal capabilities [78]. Through these prior works, it is evident that coupling activated carbon with membrane technology has been used to improve membrane performance and that there is potential for further improvement in these applications.

CHAPTER 3 METHODS

3.1 Activated Carbon Dispersion Preparation

The coating material was created by combining DI water and grade YP-50 Powdered Activated Carbon (PAC). Coatings of varying concentrations were made in 15mL test tubes with the weight percentages given in Table 3.1. Once both components were measured and put into the test tube, samples were mixed on a vortex mixer for 5 minutes and then sonicated for 60 minutes. Repeat samples were prepared for additional testing as needed following the same concentrations.

| Concentration (wt%) | DI Water (g) | PAC (g) | Total Weight (g) |
|---------------------|--------------|---------|------------------|
| 0.1 | 13 | 0.013 | 13.013 |
| 0.3 | 13 | 0.039 | 13.039 |
| 0.5 | 13 | 0.013 | 13.013 |
| 1.0 | 12 | 0.121 | 12.121 |
| 3.0 | 11 | 0.340 | 11.340 |
| 5.0 | 11 | 0.579 | 11.579 |

Table 3.1: Activated carbon dispersion concentrations by weight percent

3.2 Manufacturing Process Development and Method Selection

3.2.1 Preliminary Experimental Design and Testing

Film Coater

The film coater experimental set-up included the materials to create the activated carbon dispersions as well as the coating equipment. TriSep Flat Sheet TS-80 Nanofiltration membranes were used as the substrate for coating. MTI's Compact Tape Casting Coater with Vacuum Chuck and 110V Top Heating Lid (MSK-AFA-III) was used to create uniform

coatings on the nanofiltration membranes [79]. Along with this machine, an oil-less pump (AutoBo AP-1400C/V) was used to create a vacuum between the substrate and coater surface to ensure a flat and uniform coating region [79]. A 100mm doctor blade with manual micrometer adjustment knobs from DONNGYZ was used to ensure that each coating had a uniform thickness across the entire film. The doctor blade was placed on the coater surface in line with the machine's "travel pusher," which was driven by the machine to create the coatings [79]. After coating the membranes, each one was weighed to determine the mass of the carbon deposited during the coating process. The overall coating equipment setup can be seen in Figure 3.1 below.



Figure 3.1: Experimental setup of compact tape casting film coater machine with vacuum chuck. When turned on, the "travel pusher" moves horizontally to coat the substrate using the doctor blade. Once the membrane is coated, the drying cover can be lowered to heat the membrane, though it wasn't used for this project.

Activated carbon coatings were manufactured using the film coater in two ways. First, the membrane was coated using the film coater in the traditional sense as previously described, where the entire flat sheet membrane was placed on the surface of the coater and the doctor blade was used to cast activated carbon on the membrane. After coating, the flat sheet membranes were allowed to dry and then circular membrane samples were punched out using a 2 inch craft punch acquired from EK Tools. Several tests were completed to achieve an even coating on the membrane and the parameters were held constant, as given in Table 3.2.

| Parameter | Value |
|------------------------|-------|
| Concentration $(wt\%)$ | 5 |
| Volume AC (mL) | 1 |
| Gap Height (μm) | 50 |
| Coating Speed (mm/s) | 12 |

Table 3.2: Constant parameters for traditional film coater process preliminary testing

This method had several key limitations, such as the reproducibility of coatings between membranes as there was no way to measure the exact mass of activated carbon on each portion of the flat sheet membrane. In addition, the punching process bent the membrane and caused jagged edges on the membrane, which could interfere with its placement in the dead-end cell that would later be used for performance testing.

In order to mitigate some of these problems, the membrane preparation step for the film coater manufacturing process was modified to make it easier to reproduce the quantity of coating deposited on each membrane and eliminate the need for the craft punch. Each membrane was prepared according to manufacturer guidelines using the dead-end test cell's porous support disk as a guide to cut out a 49mm diameter membrane circle [47]; however, four tabs were included on the top, bottom, left, and right of the membrane circle measuring 1cm by 1cm. The uncoated membrane was then weighed and mass was recorded. A moisture-resistant polyester film was vacuumed to the film coater surface and the membrane was secured to the plastic by taping the tabs down. Activated carbon was then deposited in a semi-circle onto the membrane on the side nearest to the doctor blade. The doctor blade was then run and the coating was cast across the membrane. Once the membrane was coated, the polyester film was removed from the film coater and the membrane was coated, the polyester film was removed from the film coater and the membrane was coated to dry for 1 hour. The tape could then be removed from the membrane

to weigh the mass of the coated membrane. By subtracting the uncoated membrane mass from the coated membrane mass, the mass of activated carbon that was added to the membrane could be determined. The modified vacuum coater membrane preparation process is shown in figure Figure 3.2.



Figure 3.2: Modified membrane manufacturing process using film coater. The membrane was cut into a circle with four tabs which were then secured to a moisture resistant polyester film. Activated carbon was deposited onto the membrane in a semi-circle and then the doctor blade was used to cast the coating across the membrane. Once dry, scissors were utilized to cut the tabs from the membrane so that it would be compatible with the Sterlitech Dead-End Cell.

Several iterations of this process were completed to determine the optimal coating parameters to achieve a uniform coating across the membrane. After several tests, the parameters in Table 3.3 were held constant because they allowed the film coater to achieve a uniform coating without any visible defects.

Table 3.3: Constant parameters for modified film coater process preliminary testing

| Parameter | Value |
|--------------------------|-------|
| Concentration ($wt\%$) | 5 |
| Volume AC (mL) | 0.5 |
| Gap Height (μm) | 100 |
| Coating Speed (mm/s) | 12 |

Vacuum Filtration Coating

The vacuum filtering apparatus consisted of a conical flask with a filtering head attached to the top. A filtering cup was used to secure the membrane to the filter and hold the coating liquid. The TS-80 Nanofiltration Membrane was prepared according to manufacturer specifications by cutting it into a circle with diameter of 49mm using the dead-end test cell porous support disk [47]. Once cut, the membrane was weighed and then placed between the filtering cup and the filtering head with an O-Ring of the desired coating diameter. The filtering flask was connected to a Kozyvacu TA450 Vacuum pump to provide the necessary suction. The experimental set-up can be seen in Figure 3.3.



Figure 3.3: Vacuum Filter set-up used for coating activated carbon on membrane. Membranes were cut to 49mm to ensure compatibility with the test cell. The membrane was clamped to the flask with the filter cup which included an O-Ring to modify coating diameter. The filter was powered by a vacuum pump connected to the conical flask with a tube.

Initial coating experiments took place using a 5% activated carbon dispersion so that the results could be compared to the membranes prepared using the film coater. Manufacturing parameters were varied in order to identify the optimal operating conditions to achieve a coating compatible with the dead-end test cell. O-Ring size was altered in order to test varying coating diameters and a gasket was utilized to hold the O-Ring in place. In addition, the volume of activated carbon was altered so that full coverage could be achieved on the membrane. Lastly, the time that the samples underwent vacuum filtration was changed

to identify the amount of time needed for the activated carbon to fully dry. The constant parameters for preliminary testing are given in Table 3.4. After preliminary testing took place and the suitable manufacturing parameters were identified, coating concentrations were varied to create the full sample set while holding the aforementioned manufacturing properties constant.

Table 3.4: Constant parameters for vacuum filter coating process for preliminary testing

| Parameter | Value |
|--------------------------|-------|
| Concentration ($wt\%$) | 5 |
| Volume AC (mL) | 0.5 |
| O-Ring Diameter (mm) | 33 |
| Filtration Time (min) | 15 |

3.3 Performance Testing

3.3.1 Dead-End Cell Testing

Equipment Set-Up

Performance testing was carried out using a dead-end cell to measure the flux through the membranes and the salt rejection of each. A Sterlitech Test Cell model HP4750 was used for this testing [47]. An aqueous magnesium sulfate solution was used as the feed solution for experimentation. Compressed nitrogen was used as the driving force through the cell, and the nitrogen tank was connected to the test cell with high pressure tubing and a safety relief valve provided by Sterlitech. The stirred cell sat atop a magnetic stir plate (Fisher Scientific 1152049SH) which was set to 700rpm for the duration of experimentation. The permeate tube of the test cell deposited the permeate into a beaker which was placed on top of a balance (Mettler Toledo ML6001T/00). Continuous permeate weight measurements, which could then be converted to flux, were taken throughout the duration of the performance test runs utilizing the EasyDirect Balance software [80]. In addition, a Thermo Scientific Orion Star A212 Conductivity Meter with Orion 013005MD Conductivity Probe measured the permeate conductivity throughout experimentation, which was then converted to salt rejection [81]. The performance testing experimental setup can be seen in Figure 3.4. MATLAB was utilized for data processing to convert the raw data into usable metrics, and the MATLAB scripts used are provided in Appendix D.



Figure 3.4: Experimental setup of Dead-End Stirred Cell.

Relevant Parameters

In order to gain useful information from the data collected, MATLAB was used to calculate the salt rejection and the flux through the membranes. In this case, a 2g/L magnesium sulfate solution was used as the feed solution and conductivity was measured. Salt rejection (R) can be found using Equation 2.1, but because the salt makes the solution conductive, the equation can be updated to specifically measure conductivity in place of the

concentrations [42]. The specific salt rejection equation is given by Equation 3.1.

$$R(\%) = \left(1 - \frac{\sigma_p}{\sigma_f}\right) * 100 \tag{3.1}$$

where σ_p is the conductivity of the permeate solution and σ_f is the conductivity of the feed solution [42]. *R* is the percentage of salt that is present in the permeate solution compared to the feed solution, therefore describing the salt removed by the membrane.

The flux gives important information about the flow through the membrane at different times in the experiment. Flux for salt solutions is given by the instantaneous flux given in Equation A.1 and the overall flux given in Equation 2.2. For these tests, overall flux is specifically reported, so the flux values reported herein refer to the overall flux of the membrane. Flux is an important parameter to take into account when considering membrane efficiency, as the flux dictates the speed at which the feed solution can flow through the membrane and become purified [82].

3.3.2 Membrane Preparation, Conditioning, and Compaction

The membrane preparation steps consisted of membrane soaking, conditioning, and compaction. Once membranes were ready to be tested, whether in uncoated cases or coated cases, they were fully submerged in DI water overnight in accordance with manufacturer recommendations. After the soaking step was completed, the membrane was installed into the Sterlitech Cell and the cell was assembled. The conditioning step consisted of filling the cell with 200mL of DI water in order to flush out any preservatives and other residuals from the membrane [83]. The cell was then gradually pressurized by a nitrogen tank where the pressure was increased by equal increments every 2 minutes. This important step allowed for the membrane pores to close gradually to reduce the amount of feed solution that escaped through open pores [84]. If the compaction step is not performed, the membrane experiences high flux and low rejection in the beginning of testing because the pores are open and allow for increased flow through the membrane. The gradual compaction allows

for the flux to stabilize and for the membrane to compact and become ready for testing with the salt feed solution.

3.3.3 Performance Testing Parameters

In order to ensure that performance testing with the Sterlitech Dead End Cell was repeatable and comparable, several key parameters were chosen and held constant throughout experimentation. These parameters had to do with the equipment set-up as well as the test conditions and they were based on manufacturer specifications as well as test results from other studies [43, 44, 45]. The parameters that were held constant are given in Table 3.5.

Table 3.5: Parameters held constant for Sterlitech cell performance testing

| Parameter | Value |
|---|-------|
| Pressure (psi) | 100 |
| Stir Table Setting (<i>rpm</i>) | 700 |
| Effective Membrane Area (mm^2) | 900 |
| MgSO ₄ Concentration (g/L) | 2 |
| Feed Solution Volume (mL) | 200 |
| Permeate Volume Collected (mL) | 50 |

3.4 Membrane Characterization

3.4.1 SEM Testing

Scanning Electron Microscopy (SEM) testing was conducted in the Materials Innovation and Learning Laboratory (MILL) at Georgia Tech. A Phenom XL G2 SEM was used to conduct this testing. Samples were prepared by cutting pieces of the membrane at the center and edges of the membrane to inspect different regions. The samples were cut to a size that was compatible with the aluminum Ted Pella Sample Mounts, which are the standard size stubs available in the MILL [85]. The membrane sample was then fastened to the stub using carbon Ted Pella Pelco Tabs [85]. The samples were arranged on the sample holder stage and inserted into the SEM machine. The Phenom XL G2 SEM is capable of operating using a variable accelerating voltage in the range of 4.8kV to 20.5kV [85]. The magnification range of this machine is between 160x to 200,000x, and the equipment has a secondary electron detector (SED) as well as a 4-quadrant backscattered electron detector (BSD) [85]. For the imaging conducted in this project, a voltage of 10kV was used. Several different magnifications were used to look at the membrane, but the images included herein used a magnification of 440x to gain a better understanding of the general membrane topography rather than extremely magnified details. The imaging process consisted of viewing the surface properties of samples in the SEM machine and adjusting the magnification, focus, and lighting until regions of interest were brought into focus.

3.4.2 Contact Angle Measurements

Contact angle measurements were taken in the MILL at Georgia Tech using their raméhart contact angle goniometer equipment [86]. Samples were prepared by cutting pieces of each membrane and adhering them to a thin steel sheet to ensure that they laid flat for testing.

The contact angle testing consisted of depositing a 10 microliter drop of water onto the membrane and measuring it using the provided computer software. An image was also taken to post-process and to measure the contact angle between the water droplet and the membrane surface. Tests were conducted for both the uncoated and the coated membranes to inspect the difference between contact angles when the membrane was coated with different concentrations of activated carbon versus when it was uncoated. For each coating concentration, contact angle measurements were taken for three membrane samples.

CHAPTER 4 RESULTS AND DISCUSSION

4.1 Manufacturing Process Results and Evaluation

In order to determine whether the film coater or the vacuum filtration coating method was better for this application, coating repeatability tests were conducted. The film coater parameters were held constant at the values given in Table 3.3 and the vacuum coater parameters were held constant at the values given in Table 3.4.

To evaluate the modified film coater method, several membranes were created to confirm uniformity across the sample set of membranes coated using this method. The three membranes reported were weighed prior to testing and after being coated once the tape had been removed. The difference in coated mass and uncoated mass gives the mass of activated carbon coating deposited on the membrane. The recorded mass values are given in Table 4.1.

| Membrane Number | Uncoated Mass (mg) | Coated Mass (mg) | AC Mass (mg) |
|--------------------|--------------------|------------------|--------------|
| C5 | 260.11 | 458.49 | 198.38 |
| C6 | 257.96 | 454.52 | 196.56 |
| C7 | 257.39 | 454.37 | 196.98 |
| Average | 258.49 | 455.79 | 197.31 |
| Standard Deviation | 1.43 | 2.34 | 0.95 |

Table 4.1: Activated carbon mass deposited on membranes using the modified film coater method

Similarly, the vacuum filtration coating method was evaluated as well. After constant coating parameters were identified, the vacuum filtration coating method was analyzed for repeatability in depositing a uniform mass of activated carbon on each membrane. Uncoated membranes were weighed prior to coating, then they were weighed again after the activated carbon had been deposited on them. The results for three membranes that had

been coated using the same coating parameters are given in Table 4.2.

| Membrane Number | Uncoated Mass (mg) | Coated Mass (mg) | AC Mass (mg) |
|--------------------|--------------------|------------------|--------------|
| V5 | 204.02 | 352.89 | 148.87 |
| V6 | 205.27 | 347.27 | 142.00 |
| V9 | 206.24 | 358.81 | 152.57 |
| Average | 205.18 | 352.99 | 147.81 |
| Standard Deviation | 1.11 | 5.77 | 5.36 |

Table 4.2: Activated carbon mass deposited on membranes using the vacuum filtration coating method

4.1.1 Method Evaluation

The modified film coater method and the vacuum filtration coating method were compared to one another and evaluated to determine which manufacturing method would be best to move forward with for additional testing. First, the methods were compared on the basis of repeatability to ensure that the method selected would be capable of depositing a uniform mass of activated carbon onto each membrane. For the 5% activated carbon dispersion tests, the standard deviation of the modified film coater method was found to be 0.95mg as given in Table 4.1, while the standard deviation of the vacuum filter coating method was found to be 5.36mg as given in Table 4.2. The higher standard deviation of the vacuum filter coating method is likely due to the contact between the activated carbon and the O-Ring that is used to establish a smaller diameter; some coating dries on the O-Ring and is removed with the O-Ring after testing, caused a discrepancy between samples. A comparison of the two coating methods can be seen in Figure 4.1.

Because the standard deviation of the modified film coater tests was found to be lower than the standard deviation of the vacuum filter, these membranes were tested in the Sterlitech Cell for performance first. When these membranes were tested in the Sterlitech Cell, severe leaking was detected in several places on the test cell. First, leaking was found between the feed solution and the permeate stream, leading to very low salt rejection values. Troubleshooting steps were taken to determine the reason for the low rejection value, and



Figure 4.1: Activated carbon mass with different coating methods. The film coater was able to deposit more activated carbon on the membrane, while the vacuum coated deposited less, likely due to the O-Ring lifting some activated carbon off after removing it from the coating apparatus.

an in-depth description of the leaking troubleshooting tests, along with other troubleshooting measures that were taken, are given in Appendix B.

In addition, in several of the tests conducted with the film coated membranes, leaking was observed coming out of the bottom of the dead-end cell, indicating that the entire cell was not sealing properly. This was likely because of the increased thickness of the membrane due to the coating and an incompatibility between the O-Ring size and the thickness of the coated membrane. For these reasons, it was determined that the modified film coater method, though repeatable in the manufacturing process, was fully incompatible with the performance testing equipment that would be used. The standard deviation of the vacuum filtration coating method, albeit slightly higher than the modified film coater method, still proved that the vacuum filter was capable of creating uniform and repeatable coatings. Therefore, the vacuum filtration coating method was selected to move forward with for the remaining tests.

The vacuum filtration coating method was selected because it allowed for the user to manipulate the diameter of the coating deposited on the membrane; this meant that an uncoated border could be left around the perimeter of the membrane where the Sterlitech Cell O-Ring could achieve a proper seal with the membrane. Several coating diameters were tested and evaluated for their efficacy, and a 33mm diameter coating was determined to be the most compatible with the Sterlitech Cell. Leaking tests were conducted with the new coated membranes and no leaking was found around the O-Ring, indicating that the cell was now able to achieve a proper seal with the membrane and that the feed solution was not leaking into the permeate stream. Also, leaking out the bottom of the Sterlitech Cell was not observed during operation, leading to the conclusion that the vacuum filtration coating method was able to fabricate a membrane of compatible thickness with the Sterlitech test cell. These tests confirmed the hypothesis that the vacuum filtration coating method was then used to create coatings of various concentrations, as given in Table 3.1.

4.2 Membrane Performance Testing

4.2.1 Determination of the Triplicate Data Set

Evaluation of membrane stability and outlier analysis were conducted to identify the data points most suitable for further analysis and remove those that did not fall within acceptable ranges. First, the flux for each membrane was plotted against time. By looking at these plots, the membranes that reached steady state could be identified. Because a constant volume of permeate was collected for each test, some membranes that reached a higher flux value did not arrive at steady state in the amount of time that it took to collect the permeate. Tests that did not reach steady state were removed from the sample set because the flow through the membrane was not constant. The membranes that reached steady state values were considered for further testing. A flow chart of the process is given in Figure 4.2 to depict the logic of choosing the three most suitable points for each data set.



Figure 4.2: Membrane stability was determined by inspecting the plot of flux versus time and evaluating the steady state region. Outliers were determined using the interquartile range of the sample set. Tests that did not meet this criteria for either flux or rejection were removed from the final data sample set.

Outliers were then calculated using the Interquartile Range (IQR) of the full sample sets to determine which points fell outside the acceptable region. This method is shown by the box and whisker plot example given in Figure 4.3 [87].



Figure 4.3: Interquartile range is given by the region between the first and third quartiles of the data sample set. The upper and lower bounds are found by adding or subtracting $\pm 1.5 * IQR$ from the third or first quartile respectively, and any points that fall outside this range are considered outliers. [87]

The first and third quadrants of the data set were identified and the interquartile range was calculated by subtracting the first quadrant from the third quadrant as given by Equation 4.1

$$IQR = Q3 - Q1 \tag{4.1}$$

where Q3 represents the third quartile, or 75th percentile, of data, and Q1 represents the first quartile, or 25th percentile, of data. This IQR value was used to calculate the upper and lower bounds of acceptable data which would be used to isolate outliers. The lower bound of acceptable data points was calculated using Equation 4.2

$$LB = Q1 - (1.5 * IQR) \tag{4.2}$$

where Q1 is the first quartile of the data and IQR is the interquartile range given by Equation 4.1. The upper bound was calculated in a similar way, using Equation 4.3

$$UB = Q3 + (1.5 * IQR) \tag{4.3}$$

where Q3 is the third quartile of the data and IQR is the interquartile range given by Equation 4.1.

This process was repeated for both the flux and the rejection data for each test. Each point in the sample set was evaluated against these bounds, and if the point fell outside the bounds, then it was determined to be an outlier. If a given test had either a flux or rejection outlier, or both, it was considered an outlier and was not used for further analysis. This process allowed for three data points to be isolated from the full sample set.

4.2.2 Performance Testing Results and Discussion

After each triplicate set of data was isolated from the full sample set, the data was inspected and trends were found by averaging the triplicate data and calculating the standard deviations. A summary of the results for flux, apparent rejection, and true rejection for each coating concentration that was tested is given in Table 4.3.

| | Flux (lmh) | | Apparent Rej. (%) | | True Rej. (%) | |
|-----------------|------------|-----------|-------------------|-----------|---------------|-----------|
| AC Conc. (wt.%) | Avg. | Std. Dev. | Avg. | Std. Dev. | Avg. | Std. Dev. |
| 0% | 62.02 | 5.07 | 93.51 | 2.09 | 98.50 | 0.35 |
| 0.1% | 49.17 | 6.28 | 85.14 | 1.72 | 97.02 | 0.42 |
| 0.3% | 54.58 | 5.31 | 87.42 | 1.45 | 96.99 | 0.36 |
| 0.5% | 54.65 | 4.31 | 89.24 | 5.74 | 97.13 | 1.18 |
| 1% | 29.47 | 0.76 | 76.08 | 16.96 | 94.62 | 1.65 |
| 3% | 24.59 | 3.22 | 80.90 | 7.10 | 94.16 | 1.03 |
| 5% | 14.83 | 1.59 | 62.76 | 4.05 | 83.87 | 8.51 |

Table 4.3: Experimental results for membrane performance parameters including flux, apparent rejection, and true rejection for each coating concentration of activated carbon

This data can also be represented graphically. A plot of flux versus apparent rejection is given in Figure 4.4. It is important to see the relationship between flux and rejection when evaluating membrane performance because oftentimes membranes have a trade-off between these two parameters.



Figure 4.4: Plot of apparent rejection versus flux for triplicate sample sets of each coating concentration and the uncoated sample. Error bars are represented by the standard deviation of each sample set.

Figure 4.4 shows several unexpected trends in the data from testing. First, it can be seen that in general, as activated carbon coating concentration increases, both the flux and

apparent rejection values decrease. This was an unforeseen observation because the activated carbon was expected to improve membrane performance and increase the amount of salt that the membrane is able to reject due to its adsorptive properties. In addition, traditionally membranes show a trade-off between flux and rejection, where a lower flux corresponds with a higher rejection and a higher flux corresponds with a lower rejection. The activated carbon-coated membranes are showing a different trend, where an increase in coating concentration causes both a decrease in flux and a decrease in rejection. Therefore, it can be determined that the activated carbon coating is actually damaging the membrane and decreasing membrane performance.

Trends in Flux Data

To isolate these trends and further inspect the relationship between performance parameters and activated carbon coating, each parameter can be plotted against concentration. A plot of flux versus coating concentration is given in Figure 4.5.



Figure 4.5: Plot of flux versus activated carbon concentration for triplicate sample sets of each coating concentration and the uncoated sample

In this figure, the same aforementioned decreasing trend can be seen in the flux as the activated carbon concentration increases. It can be seen that the lower concentrations of activated carbon, such as 0.1%, 0.3%, and 0.5%, have error bars that overlap with the uncoated membrane, indicating that they do not, in fact, have a significant difference in flux values. However, the higher concentrations of activated carbon coatings, such as 1%, 3%, and 5% all show significantly different results, indicating that the trend of flux decreasing with higher concentration holds true. The statistical analysis conducted to determine and confirm the statistically different pairs is given in an in-depth discussion in subsection 4.2.3.

The decrease in flux due to the higher activated carbon concentration can be attributed to the increased membrane resistance caused by depositing a layer of carbon on the membrane surface. At these higher concentrations of activated carbon, more of the membrane surface is covered by activated carbon particles, therefore making it more difficult for the feed solution to interact with the membrane surface and pass through the membrane. A lower flux value is generally not desired for membrane processes because it means that the feed solution will take longer to pass through the system and will not be purified quickly. This oftentimes leads to a decrease in efficiency and higher energy requirements to achieve purified water; however, sometimes a lower flux value can be justified if the lower flux allows for the membrane to yield a higher contaminant rejection value. Oftentimes, if the feed solution is able to pass through the membrane more slowly, there is a higher level of contaminant removal, and this trade-off may make it worthwhile to have the higher energy demand to sustain a lower flux. Despite this potential benefit of a lower flux, the membranes tested experimentally did not have a higher rejection value paired with the lower flux, as previously mentioned in Figure 4.4, so the lower flux in this case is not justified.

While the final average flux given in Figure 4.5 is important in understanding membrane performance, the plot of flux versus time from the beginning of the experiment can also give valuable insight into membrane behavior throughout the duration of the experiment. The change in flux compared to time is depicted in figure Figure 4.6, where time is segmented into 10-minute increments and the corresponding flux values are given. Because it was previously determined that the flux values for the 0.1%, 0.3%, and 0.5% coatings are not statistically different from one another, only the 0.5% coating flux is plotted to better show the trend. The timespan shown in Figure 4.6 shows the amount of time that it took each membrane to reach 50mL of permeate collected, which was chosen so that each conductivity measurement was taken for the same amount of permeate and could be compared between sample sets more accurately.



Figure 4.6: Flux versus time for each membrane to reach 50mL of permeate collected.

There are several important trends of note in the flux versus time data. First, it can be noted that the uncoated and 0.5% sample have higher flux values than the other samples and reach the 50mL of permeate in less time. Because the values shown are averages of the triplicate sample set, the flux for these samples does not appear to achieve steady state, but when each individual test was inspected, they were determined to reach steady state. Therefore, this lack of linearity in these samples is simply due to averaging and sample variance. It can be noted though, that in both cases, the membranes spend less time in this steady state region compared to the samples of higher concentrations. The uncoated, 0.1%,

0.3%, and 0.5% samples all achieve the 50mL of permeate in under an hour of run time. It is important to note that this data was taken after the membrane had been compacted with DI water previously, so the total run time is longer than shown.

The higher concentrations of coatings, including the 1%, 3%, and 5% samples, clearly reach steady state in the time that it takes for them to achieve 50mL of permeate collected. In all three cases, the membranes achieved steady state in the first 30-40 minutes of operation and then maintained a steady value throughout the duration of the experiment. It is also interesting to note that the error bars for the higher concentrations of coatings are smaller than the error bars for the uncoated and 0.5% sample, indicating that there is less spread in the data at these higher coating concentrations. This also explains why the steady state trend can be more easily seen for the sample average as compared to the uncoated and 0.5% sample; because the data points are closer together in the sample set, the trend is more clearly displayed. This plot also highlights the problem of efficiency associated with having a lower flux. For the higher concentrations of membranes, it took double the amount of time to collect 50mL of permeate as compared to the uncoated and low concentration coated membranes. This is a problem because with this lower flux, the membranes did not achieve higher rejection, so the additional time required to filter the same amount of water is not justified in this application.

Trends in Rejection Data

The apparent rejection and true rejection are also important performance parameters to understand as they relate to activated carbon concentration. As previously mentioned, the apparent rejection is the experimental rejection found by comparing the permeate conductivity to the feed conductivity, whereas the true rejection gives a model for the rejection taking concentration polarization into account. A detailed explanation of this phenomenon is given in subsection 2.2.6. The values for apparent rejection and true rejection compared to activated carbon coating are given in Figure 4.7



Figure 4.7: Plot of apparent rejection and true rejection of $MgSO_4$ versus activated carbon concentration for triplicate sample sets of each coating concentration and the uncoated sample

In this plot, it can be seen that both apparent rejection and true rejection tend to decrease with increasing activated carbon concentration. The first important performance parameter to understand is the apparent rejection, which decreases with more activated carbon as previously mentioned. The apparent rejection is highest in the uncoated membrane, and is generally lower in the coated samples. This can be attributed to the activated carbon allowing more salt to pass through the membrane. It can be seen by the error bars that the uncoated apparent rejection sample is significantly different from the 0.1%, 0.3%, and 5% samples. The other coatings, including 0.5%, 1%, and 3%, have too large of a standard deviation to definitely state that they are different from the uncoated sample, but the average values do tend to be lower. More detailed information about the statistical significance of these results and which apparent rejection values differ from one another in a statistical sense can be found in subsection 4.2.3.

The next important parameter to consider is the true rejection as given by the concentration polarization model described in subsection 2.2.6. The true rejection tends to hold a relatively constant value for the uncoated sample and the lower activated carbon concentration samples, then decreases more sharply at the 1%, 3%, and 5% samples. The rigorous statistical analysis of the differences between true rejection pairs is given in subsection 4.2.3. At the higher concentrations, the true rejection is lower than the uncoated sample. This is likely because the model for true rejection takes into account the pure water flux as well as the salt water flux and the higher concentration of coatings show a smaller difference between flux values than the uncoated sample. This means that the contaminated water flows through the membrane at approximately the same rate as pure water, giving the membrane less opportunity to remove contaminants from the feed solution.

To better understand the impact of concentration polarization on each coating concentration, the difference between the apparent and true rejection values given in Figure 4.7 can be analyzed. Figure 4.8 shows the value obtained from subtracting the apparent rejection from the true rejection, highlighting the impact of concentration polarization.



Figure 4.8: Plot of the difference between apparent rejection and true rejection versus activated carbon concentration for triplicate sample sets of each coating concentration and the uncoated sample. The larger the difference between these two rejection values, the greater the impact that concentration polarization has on the salt rejection value.

The difference between the two rejection values gives insight into the impact of concentration polarization on each membrane sample set. If there is a large discrepancy between the true rejection and the apparent rejection, there is more concentration polarization, which caused the apparent (experimental) rejection to be lower. In general, the coated samples see a higher difference in rejection values and therefore a higher influence of concentration polarization when compared to the uncoated sample. This is likely due to the activated carbon attracting magnesium sulfate ions and allowing them to build up at the membrane surface. The ions do not diffuse back into the feed solution at a fast enough rate, causing the apparent rejection to be lower than the true rejection [48]. In addition, it can be seen that at some of the higher activated carbon concentration values, such as 0.5%, 1%, 3%, and 5% coatings, the error bars are much larger than in the lower concentrations or the uncoated sample. This indicates that there is a larger sample spread for these higher concentration samples than in the lower concentration samples.

4.2.3 Statistical Analysis of Performance Testing Results

Identification of Significant Differences Between Sample Sets

Statistical analysis was used to identify trends between data points and determine which points could be considered as statistically different and which ones were not significantly different. The triplicate sets of data that were isolated from the full data sets through the aforementioned analysis were used for the statistical tests described herein. The statistical methods utilized in this study were Analysis of Variance (ANOVA) and *t*-tests. First, an ANOVA test was conducted for the flux, rejection, and true rejection data to determine if statistically different pairs existed within the sample sets. Summaries of the relevant ANOVA results for the flux, rejection, and true rejection data are given in Table 4.4

For all three data sets, it was found that F is greater than F_{crit} and the p-value is less than α , indicating that there are statistically different pairs in all sample sets. Because an ANOVA test only identifies whether there are statistically different pairs but not which ex-

| Parameter | Flux | Apparent Rejection | True Rejection |
|------------------|------------|--------------------|----------------|
| Alpha (α) | 0.05 | 0.05 | 0.05 |
| P-value | 1.4315E-07 | 3.9099E-03 | 1.7046E-03 |
| F_{crit} | 2.8477 | 2.8477 | 2.8477 |
| F | 34.0489 | 5.5601 | 6.6600 |

Table 4.4: Relevant Results from ANOVA Testing for Flux, Apparent Rejection, and True Rejection Sample Sets

act pairs are different, t-tests had to be performed comparing each set in order to determine the different pairs. The results of the t-tests are compiled in Appendix C and discussed below.

The matrices shown in Figure C.1, Figure C.2, and Figure C.3 give the results of the t-tests for the flux, apparent rejection, and true rejection t-tests, respectively, along with the p-values determined for each. If the p-value between two tests was found to be less than the alpha value used (0.05) and t_{stat} was found to be greater than t_{crit} two-tail, the two data sets compared in the test were deemed to be statistically different from one another.

The matrix in Figure C.1 shows the t-test results for the flux data. For flux, it was found that the 0% coating is not statistically different from 0.1%, 0.3%, or 0.5% coatings. The 0.1% coating is not statistically different from 0.3%, 0.5% or 1% coatings. The 0.3% coating is not statistically different from the 0.5% coating. The 1% coating is not statistically different from the 0.5% coating. The 1% coating is not statistically different from the 0.5% coating. The 1% coating is not statistically different from the 0.5% coating. The 1% coating is not statistically different from the 0.5% coating. The 1% coating is not statistically different for the 3% coating. All other combinations of coatings were determined to be statistically different for their flux values. The key takeaways from the flux testing were that the lower concentrations of activated carbon coatings did not have a significant impact on flux when compared to the uncoated membrane. On the contrary, the higher concentrations, such as 1%, 3%, and 5% coatings all had statistically significant reduction of flux when compared to the uncoated membrane and the coated membranes of lower activated carbon concentrations. In addition, at these higher concentrations, the flux was found to be significantly different between both the 1% and 3% when compared to the 5% coating.

Apparent rejection t-test results are given in Figure C.2. It was found that the uncoated test is statistically different from the 0.1%, 0.3% and 5% tests. This indicates that the

coating at both low and high concentrations has a significant impact on the salt rejection capabilities of the membrane. The uncoated sample was not found to be statistically different from the 0.5%, 1%, and 3% samples due to the lack of consistency in these samples and therefore large variance. The 5% sample was found to be significantly different from all samples except the 1% sample, which had a large error bar and large variance for rejection. All other combinations of samples were not found to be significantly different in their apparent salt rejection capabilities.

A matrix summarizing the true rejection results is given in Figure C.3. From the true rejection t-tests, it was found that the uncoated sample is significantly different from the 0.1% sample and the 0.3% sample. The 3% sample is significantly different from the 0%, 0.1%, 0.3%, and 0.5% samples. All other combinations of samples did not show significantly different results for true rejection. As previously mentioned, the true rejection uses a model that gives an indication of what the rejection is when taking concentration polarization into account. The results of the t-tests show that in most cases, the membrane sample sets do not have significantly different true rejection values, indicating that they should have achieved similar rejection results when taking concentration polarization into account. Because the 0.1% and 0.3% samples have lower true rejection than the uncoated sample, this indicates that the flux induced by the activated carbon coating at low concentrations causes the true rejection of the membrane to be lower than the uncoated pristine membrane.

Standard Deviation Comparison and Analysis

Further analysis was conducted to understand how the standard deviation of the sample sets change with varying concentration. This analysis gives an indication of the repeatability of each coating concentration. Because the outliers and unstable points were already removed, the triplicate sets represent a set of data that should give repeatability without large variation. The plot in Figure 4.9 shows the standard deviation values for both the flux and rejection compared to the membrane activated carbon coating concentration.



Figure 4.9: Comparison of the standard deviation for each sample set at varying concentrations of activated carbon coating.

It was found that the flux standard deviation is the largest for the uncoated, 0.1%, 0.3%, and 0.5% concentrations of activated carbon. This fact indicates that the surface properties of the membrane cause flux variation whether it is uncoated or coated with a low concentration of activated carbon. Because the membrane surface was partially exposed at the lower concentrations, it is likely that the membrane surface itself impacts the flux repeatability from test to test. At the 1%, 3%, and 5% coating concentrations of activated carbon, the flux standard deviation is lower than the aforementioned cases, with a very low value less than 1 lmh at the 1% concentration. At these higher concentrations, the membrane surface is covered more completely by the activated carbon since a higher concentration is dispersed in the coating solution. It is interesting to note that the activated carbon coating seems to improve flux repeatability between tests, as can be seen by comparing the standard deviations of the higher concentration coatings to the uncoated membrane.

The salt rejection standard deviation seems to have an opposite trend, where the values are smallest at the lower concentrations of coating and the uncoated membrane but become larger at the higher concentrations. Notably, the rejection standard deviation for the 1% coating spikes to a value of 16.96%, indicating that there is large variability in the rejection values among the triplicate data set, while the uncoated membrane rejection has a standard deviation value of just 2.09%. In this case, it is likely that the membrane surface allows for a consistent amount of salt to be removed from the feed solution and the activated carbon coating inhibits this consistency. This could be due to surface interactions between the membrane and the feed solution that are altered by a large presence of activated carbon.

4.3 Membrane Characterization Tests

4.3.1 Scanning Electron Microscopy (SEM)

After completing performance testing, Scanning Electron Microscopy (SEM) was used to examine the membrane surface and gain a better understanding of the surface properties that may have led to the observed performance results. Initial SEM testing took place by viewing the 5% and 0.1% coated samples at two locations on the edge of the membrane and one location at the center of the membrane to determine whether or not there is an appreciable difference between the surface properties at the edge versus at the center. From this initial testing, it was determined that the deposition of activated carbon on both membranes showed similar results at the edges and at the center. Since there was no clear difference between the coating at the edge compared to the center, it was determined that the remaining SEM tests could be conducted at one sample in the center of the membrane. The images captured during SEM tests for each concentration of AC are given in Figure 4.10.

First, it is interesting to note that even the 0% uncoated membrane in Figure 4.10a shows surface irregularity and regions of inhomogeneity across the surface. These types of irregularities can come about in several different ways, such as the membrane manufacturing process, transportation and storage, or the effects of the performance testing itself on the membrane. This irregularity may also explain why there is a relatively high standard deviation for the observed flux values of the uncoated membrane, as shown in Figure 4.9.



(a) 0% Uncoated Membrane



(b) 0.1% AC-Coated Membrane



(c) 0.3% AC-Coated Membrane



(d) 0.5% AC-Coated Membrane



(e) 1% AC-Coated Membrane



(f) 3% AC-Coated Membrane

(g) 5% AC-Coated Membrane

Figure 4.10: Sample SEM images for each concentration. Note the irregular surface characteristics in the lower concentration AC coatings, while the higher concentrations show uniform coatings. Also note that the uncoated membrane shows surface irregularities too. If the feed solution interacted with areas of varying membrane resistance, there were likely some tests where the water could permeate through the membrane at a faster rate than in other tests, thus leading to differing flux values. Because the ions in the feed solution could still interact sufficiently with the membrane and its surface, this may explain why the rejection standard deviation remained low despite the high flux value.

It is also interesting to note the patterns of activated carbon deposited on the membrane at each concentration. At the lower concentrations, such as 0.1%, 0.3%, and 0.5%, there are clear "mountain peaks" of activated carbon formed that wind their way across the membrane surface, as shown in Figure 4.10b, Figure 4.10c, and Figure 4.10d, respectively. In these images, dark cloudy regions can also be seen, where it is likely that smaller particles of activated carbon were able to integrate themselves in the membrane surface without pil-ing up and causing the mountain peak feature that can be observed in some areas. Although the exact patterns of these peaks differ on each membrane, it is still very clear that there is an inhomogeneous coating deposited on these membranes. As such, these peaks and valleys would cause an increase in the surface roughness in the membrane, contributing to the decreased membrane performance and high variance between samples.

The irregular surface characteristics and varying membrane thickness could be responsible for the highly variable flux values observed for the membranes with lower concentrations of activated carbon coatings. Because the feed solution was interacting with a variable membrane surface, the flux would not be as regular as it would be if the membrane surface was smooth and consistent. In each of these cases, there are areas where the membrane surface is exposed or not completely covered in activated carbon, indicating that the feed solution was still able to interact with the polyamide surface. This ability to interact with the original membrane likely allowed the membrane to retain its salt rejection capabilities at these lower concentrations of coatings.

The higher concentrations of coatings show a stark difference compared to the lower concentrations of coatings. It is clear that the 1%, 3%, and 5% coatings, shown in Fig-

ure 4.10e, Figure 4.10f, and Figure 4.10g, respectively, show a much more uniform deposition of activated carbon than the lower concentrations of coatings. This suggests that these higher concentrations were able to achieve full coverage of activated carbon on the membrane surface compared to the lower concentrations using the vacuum filter coating method. This better coverage made the membrane surface more uniform and therefore allowed for the feed solution to interact with the membrane surface more consistently.

The improvement in uniformity explains the decrease in flux standard deviation at the higher coating concentrations, as given in Figure 4.9. The 1% and 5% concentrations seem to achieve more uniformity than the 3% concentration in the SEM images, which may explain the slight spike in variability in Figure 4.9. Regardless, the three higher concentrations achieved lower flux standard deviation compared to the uncoated membrane and the lower concentrations of coatings. Although the uniform activated carbon coating improved flux repeatability, the coating had an opposite effect on the magnesium sulfate rejection repeatability. This result is likely due to the fact that the feed solution was unable to interact with the original membrane surface as well as in the lower concentrations. In addition, the increase in activated carbon on the membrane surface led to higher rates of concentration polarization as explained in Figure 4.7 and Figure 4.8, making the membrane unable to reject as much salt as in the lower concentrations.

4.3.2 Contact Angle Measurements

Contact angle testing was performed to determine how the activated carbon coating impacted the hydrophilicity of the membrane and whether or not the concentration of coating caused a change in contact angle. Because a membrane's hydrophilicity or hydrophobicity impacts it's performance, this property is very important and can give insight into the reasons that certain results are being seen. The contact angle for each membrane was measured and the results are given in Table 4.5. This table includes the experimental results from the average of three samples for each activated carbon concentration that was tested. The membranes that were tested were the same membranes that were included in the triplicate data sets for the flux and rejection performance testing. This decision ensured that contact angle measurements were not taken from any outlier membranes in case the coating had an impact on their performance.

| | Contact Angle (°) | | |
|-----------------|-------------------|-----------|--|
| AC Conc. (wt.%) | Avg. | Std. Dev. | |
| 0% | 62.3 | 4.9 | |
| 0.1% | 46.0 | 2.6 | |
| 0.3% | 32.7 | 1.5 | |
| 0.5% | 23.3 | 6.4 | |
| 1% | 14.0 | 1.0 | |
| 3% | 6.0 | 1.0 | |
| 5% | 0.0 | 0.0 | |

Table 4.5: Experimental results for membrane contact angle measurements for each coating concentration of activated carbon

The same data that appears in the table is shown graphically in Figure 4.11 along with sample images captured during the contact angle testing. This figure shows the change in contact angle with coating concentration and the appearance of the water droplets.



Figure 4.11: Contact angle measurements for each activated carbon coating
Through contact angle testing, it was found that as the concentration of activated carbon increased, the contact angle decreased. This observation indicates that as the concentration of activated carbon increases, the membrane surface becomes more hydrophilic and there-fore attracts water more than the uncoated membrane. In addition, it was observed during contact angle testing that the AC-coated membranes absorbed the water droplet faster than the uncoated membranes. The droplets also spread much more quickly on the coated membrane and the spreading pattern was not uniform. In addition, the lower concentrations of coatings showed more variability in their contact angle measurements than the higher concentrations because there was an irregular distribution of activated carbon. It is interesting to note that the 5% activated carbon coated membrane experienced such rapid levels of spreading that the contact angle was too small to be measured, so therefore it was effectively 0 degrees for all three tests.

To fully understand the variation of contact angle with coating concentration and determine the significant measurements, statistical analysis was conducted. First, an ANOVA test was completed to determine whether or not there were statistically significant differences between the data. The results of the ANOVA test for contact angle measurements are given in Table 4.6.

Table 4.6: Relevant Results from ANOVA Testing for Contact Angle Measurements

| Parameter | Value |
|------------------|----------|
| Alpha (α) | 0.05 |
| P-value | 1.36E-11 |
| F_{crit} | 2.8477 |
| F | 135.9495 |

Through the ANOVA test, it was found that F is greater than F_{crit} and the p-value is less than α , indicating that there are statistically different pairs. The ANOVA test does not indicate which pairs are different, so t-tests were performed to determine which pairs of data are statistically significant. The results from the t-tests for contact angle measurements are given in the matrix provided in Figure C.4 along with the p-values for each combination of pairs. The t-test results show that the 0.5% coating contact angle is not statistically different than the 0.3% or 1% coating concentration contact angles. Other than this discrepancy, it was found that the contact angle for every other set of concentration pairs is statistically different. This result indicates that the observed trend of the contact angle decreasing with increasing concentration holds true and is a significant trend.

This trend is unexpected when considering the flux data observed in the performance testing described in subsection 4.2.2. Typically, a more hydrophilic membrane experiences higher flux values compared to a more hydrophobic membrane. In this study, it was observed that as activated carbon concentration increases, both flux and contact angle decrease. Although this is not a typical correlation, the decrease in flux is likely due to the increased membrane thickness caused by the higher concentrations of activated carbon coating. Because the higher concentrations achieve better coverage of the membrane, more particles of activated carbon are able to stack together, thereby increasing membrane thickness. This increase in membrane thickness would increase the membrane resistance and make it more difficult for the feed solution to permeate through the membrane, and therefore decrease the flux value.

CHAPTER 5 CONCLUSIONS

Through this research, the impact of activated carbon coatings of various concentrations on nanofiltration membranes was investigated. Commercial polyamide nanofiltration membranes were modified by depositing a coating of an aqueous powdered activated carbon dispersion on the surface and testing them in a dead-end cell.

The first key challenge was determining a suitable manufacturing procedure for depositing activated carbon on the membrane surface. A novel film coater method was developed to uniformly distribute the coating and allow for the coating mass to be measured. Although this modified film coater method could not be used for performance testing due to compatibility issues with the performance test cell, it proved to have very good mass distribution repeatability with low variation between samples. Instead, a vacuum filtration coating method was utilized to create coated membranes that were compatible with the dead-end cell that was used for testing. The vacuum filtration coating method was able to achieve high coating repeatability between samples and uniform coatings for the higher concentrations of activated carbon. This research proved that both the film coater method and the vacuum filtration coating method are viable candidates for depositing thin films of coatings onto membrane surfaces.

It was also determined that the activated carbon coating used in this research was not able to improve commercial nanofiltration membrane salt rejection. By observing the affects of coating concentration on flux and magnesium sulfate rejection, it was found that the activated carbon decreased flux and decreased salt rejection with increasing concentration. A model of concentration polarization helped to prove that this phenomenon is likely contributing to the decreased performance of the membranes, and may be responsible for the low apparent rejection values. The variability of the results obtained from performance testing also suggested that there were manufacturing inconsistencies between the membranes tested, and SEM imaging confirmed that the membrane surfaces differed greatly between concentrations of activated carbon. While the higher concentrations of activated carbon were able to achieve uniform coatings, the lower concentrations had "mountain peak" topography, which likely contributed to high flux variation and high standard deviations. In contrast, the uniform high concentration membranes achieved repeatable flux values. When compared to the uncoated membrane, the highest concentration of activated carbon (5%) showed better repeatability and lower standard deviation than the unmodified membrane. This conclusion suggests that if the activated carbon coating could be modified to enhance the salt rejection capabilities of the membrane, it has great potential to also improve the repeatability of the tests.

Lastly, contact angle testing determined that as the activated carbon concentration increases, the hydrophilicity of the membrane also increases. Because more hydrophilic membranes typically have higher flux values, it could be determined that the hydrophilicity was therefore not a contributing factor to the decreased membrane performance. Rather, it could be assumed that the increased membrane thickness due to the higher activated carbon concentration, in addition to concentration polarization, caused the modified membrane's lower performance.

CHAPTER 6 SUGGESTIONS FOR FUTURE WORK

The work presented in this thesis provided interesting insight into the manufacturing and performance of activated carbon coatings on nanofiltration membranes, and through this work, many limitations and future directions were uncovered. Although the coating did not show expected results, activated carbon is still a promising candidate to improve membrane performance due to its favorable material properties and widespread use in wastewater treatment plants. Several suggestions for future work are presented below to guide further experimentation and new research projects.

Although the activated carbon coated membranes did not improve magnesium sulfate rejection, it is possible that activated carbon could still improve membrane performance for the removal of other contaminants such as pharmaceuticals or other micropollutants [1, 32, 34]. One particular micropollutant of interest is 17α -ethynyl estradiol (EE2), which is released back into wastewater due to hormonal birth control pill use. This hormone is excreted in urine and, when found in wastewater, can have significant impacts on surrounding animal and plant ecosystems [1]. In addition, if EE2 circulates back to humans, it can lead to cancers or reproductive problems. EE2 was a contaminant of interest for this research, but due to limitations and lack of repeatability with the simple salt feed solution, the idea was abandoned to focus on a simpler contaminant. Even so, this would be a very interesting contaminant for future research to pursue removing with activated carbon-coated membranes.

The previously mentioned repeatability issues caused high standard deviations in the data and unpredictable results for some tests. Troubleshooting steps were taken to mitigate as many inconsistencies as possible, as outlined in Appendix B, but it would be interesting to conduct future testing with another system to see if more consistent results could be obtained. For example, utilizing a cross-flow system rather than a dead-end system may provide more consistent results for this particular membrane, as the manufacturer conducts their testing and creates specifications based on the use of a cross-flow system.

Lastly, utilizing a binder for the activated carbon coating may allow for the 3-dimensional structure to adhere to the membrane better and improve membrane performance. Other materials that are commonly used for coatings, such as graphene oxide, are 2-dimensional structures, and are therefore better able to coat the membrane. For this reason, the activated carbon coating in this study may have had problems because it was a binderless coating. Utilizing a binder such as Polytetrafluoroethylene (PTFE), Polyvinyl Alcohol (PVA), Polyacrylic Acid (PAA), or Sodium Dodecyl Sulfate (SDS) may help to stabilize the coating and allow it to bind to the membrane [88, 89].

Unexpected results do not necessarily imply the failure of a project, and the conclusions drawn from this research allowed for valuable information about activated carbon coatings to be gathered. The knowledge gained from the experiments presented in this thesis can allow for future experiments to improve upon the work already completed. Hopefully, future research can be done on activated carbon as a coating for nanofiltration membranes to allow for this technology to make an impact on wastewater treatment. Appendices

APPENDIX A

ADDITIONAL EQUATIONS

Instantaneous flux (J_i) is given by Equation A.1,

$$J_i = \left(\frac{m_i - m_{i-1}}{(t_i - t_{i-1}) \cdot A_{mem}}\right) \tag{A.1}$$

where m is the mass of permeate at a certain point in time i, t is the time at that iteration, and A_{mem} is the effective membrane area through which the solution is flowing [42].

APPENDIX B TROUBLESHOOTING STEPS

Several different troubleshooting steps were taken to ensure that the dead-end test cell was functioning properly. Leaking, both from liquid and gas, were the primary areas of concern for this system, so some of the troubleshooting tests that were conducted are described herein.

Leaking around the dead-end cell O-Ring was tested by aligning a cotton string around the outside perimeter of the O-Ring and using FD&C Blue 1 Food Coloring in the feed solution. After testing, the cotton string was observed to see if it had been dyed blue, indicating leaking. First, leaking tests were performed with the uncoated membrane and it was found that there was leaking around the O-Ring provided by the manufacturer. It was hypothesized that the membrane was too thin to be compatible with the provided O-Ring.

To test this theory, a thicker, non-porous membrane was tested in the cell to see if a seal could be achieved with the O-Ring provided. The string remained white during testing and no permeate came out of the cell, indicating that this thicker membrane was able to achieve a good seal. This result led to the conclusion that the nanofiltration membrane was too thin to be compatible with the O-Ring, so several thicker O-Rings were purchased and used in the cell. Once a compatible O-Ring was found, it was used for all future tests.

Leaking was tested with the coated membranes as well. In the tests using the coated membranes that were manufactured using the film coater, the string was found to be blue, leading to the conclusion that the activated carbon coating was interfering with the O-Ring's ability to seal to the surface of the membrane. Because of this leaking, it could be determined that the membranes fabricated from the film coater were not compatible with the test cell due to leaking.

Some of the observed inconsistencies in data were theorized to be due to pressure dif-

ferences between tests. This could either be due to nitrogen escaping out of the cell during testing or inconsistent applied pressure. To mitigate these problems, all tests were run at a constant pressure of 100psi and the cell was tested for nitrogen leaking. This troubleshoot-ing step involved pressurizing the cell with the membrane inserted and then submerging the test cell in a bath of water. Once submerged, the cell was observed for 5 minutes to see if any air bubbles escaped from the bottom of the cell. Using the new O-Ring that was compatible with the nanofiltration membrane, no leaking out the bottom of the cell was observed. It could then be concluded that the nitrogen pressure was maintained in the cell and none was escaping from the bottom.

APPENDIX C

T-TEST RESULTS

| Flux | | | | | | | | |
|------|----------|----------|----------|----------|----------|----------|----------|--|
| | 0% | 0.1% | 0.3% | 0.5% | 1% | 3% | 5% | |
| 0% | | p=0.0758 | p=0.1539 | p=0.1240 | p=0.0082 | p=0.0017 | p=0.0042 | |
| 0.1% | p=0.0758 | | p=0.2792 | p=0.7033 | p=0.0543 | p=0.0169 | p=0.0183 | |
| 0.3% | p=0.1539 | p=0.2792 | | p=0.5092 | p=0.0149 | p=0.0036 | p=0.0064 | |
| 0.5% | p=0.1240 | p=0.7033 | p=0.5092 | | p=0.0453 | p=0.0137 | p=0.0169 | |
| 1% | p=0.0082 | p=0.0543 | p=0.0149 | p=0.0453 | | p=0.1250 | p=0.0007 | |
| 3% | p=0.0017 | p=0.0169 | p=0.0036 | p=0.0137 | p=0.1250 | | p=0.0181 | |
| 5% | p=0.0042 | p=0.0183 | p=0.0064 | p=0.0169 | p=0.0007 | p=0.0181 | | |

Figure C.1: T-Test results comparing all sets of the flux data. P-values for each comparison are included in the cell. If the p-value is less than the α value of 0.05, the pairs are considered to be significantly different and the matrix cell is colored green. If the p-value is greater than 0.05, then the pairs are not significantly different and the cell is red.

| Apparent Rejection | | | | | | | | |
|--------------------|----------|----------|----------|----------|----------|----------|----------|--|
| | 0% | 0.1% | 0.3% | 0.5% | 1% | 3% | 5% | |
| 0% | | p=0.0059 | p=0.0143 | p=0.3129 | p=0.2194 | p=0.0981 | p=0.0013 | |
| 0.1% | p=0.0059 | | p=0.1541 | p=0.3574 | p=0.4547 | p=0.4203 | p=0.0031 | |
| 0.3% | p=0.0143 | p=0.1541 | | p=0.6477 | p=0.3679 | p=0.2590 | p=0.0022 | |
| 0.5% | p=0.3129 | p=0.3574 | p=0.6477 | | p=0.3310 | p=0.1884 | p=0.0028 | |
| 1% | p=0.2194 | p=0.4547 | p=0.3679 | p=0.3310 | | p=0.6811 | p=0.3167 | |
| 3% | p=0.0981 | p=0.4203 | p=0.2590 | p=0.1884 | p=0.6811 | | p=0.0311 | |
| 5% | p=0.0013 | p=0.0031 | p=0.0022 | p=0.0028 | p=0.3167 | p=0.0311 | | |

Figure C.2: T-Test results comparing all sets of the apparent rejection data. P-values for each comparison are included in the cell. If the p-value is less than the α value of 0.05, the pairs are considered to be significantly different and the matrix cell is colored green. If the p-value is greater than 0.05, then the pairs are not significantly different and the cell is red.

| True Rejection | | | | | | | | |
|----------------|----------|----------|----------|----------|----------|----------|----------|--|
| | 0% | 0.1% | 0.3% | 0.5% | 1% | 3% | 5% | |
| 0% | | p=0.0094 | p=0.0065 | p=0.1944 | p=0.0580 | p=0.0205 | p=0.0969 | |
| 0.1% | p=0.0094 | | p=0.9335 | p=0.8949 | p=0.1352 | p=0.0212 | p=0.1160 | |
| 0.3% | p=0.0065 | p=0.9335 | | p=0.8659 | p=0.1361 | p=0.0463 | p=0.1164 | |
| 0.5% | p=0.1944 | p=0.8949 | p=0.8659 | | p=0.0994 | p=0.0306 | p=0.1161 | |
| 1% | p=0.0580 | p=0.1352 | p=0.1361 | p=0.0994 | | p=0.7083 | p=0.1647 | |
| 3% | p=0.0205 | p=0.0212 | p=0.0463 | p=0.0306 | p=0.7083 | | p=0.1732 | |
| 5% | p=0.0969 | p=0.1160 | p=0.1164 | p=0.1161 | p=0.1647 | p=0.1732 | | |

Figure C.3: T-Test results comparing all sets of the true rejection data. P-values for each comparison are included in the cell. If the p-value is less than the α value of 0.05, the pairs are considered to be significantly different and the matrix cell is colored green. If the p-value is greater than 0.05, then the pairs are not significantly different and the cell is red.

| Contact Angle | | | | | | | | |
|---------------|----------|----------|----------|----------|----------|----------|----------|--|
| | 0% | 0.1% | 0.3% | 0.5% | 1% | 3% | 5% | |
| 0% | | p=0.0149 | p=0.0099 | p=0.0011 | p=0.0036 | p=0.0027 | p=0.0021 | |
| 0.1% | p=0.0149 | | p=0.0048 | p=0.0110 | p=0.0003 | p=0.0001 | p=0.0011 | |
| 0.3% | p=0.0099 | p=0.0048 | | p=0.1343 | p=0.0004 | p=0.0001 | p=0.0007 | |
| 0.5% | p=0.0011 | p=0.0110 | p=0.1343 | | p=0.1309 | p=0.0439 | p=0.0243 | |
| 1% | p=0.0036 | p=0.0003 | p=0.0004 | p=0.1309 | | p=0.0006 | p=0.0017 | |
| 3% | p=0.0027 | p=0.0001 | p=0.0001 | p=0.0439 | p=0.0006 | | p=0.0091 | |
| 5% | p=0.0021 | p=0.0011 | p=0.0007 | p=0.0243 | p=0.0017 | p=0.0091 | | |

Figure C.4: T-Test results comparing all sets of the contact angle data. P-values for each comparison are included in the cell. If the p-value is less than the α value of 0.05, the pairs are considered to be significantly different and the matrix cell is colored green. If the p-value is greater than 0.05, then the pairs are not significantly different and the cell is red.

APPENDIX D MATLAB SCRIPTS FOR DATA PROCESSING

The following pages include the MATLAB scripts that were used for the data analysis in this project. The first script was used for the membrane conditioning step. It manipulates the mass data from the scale and calculates the flux of the membrane and then creates an upper and lower bound in which the flux should fall to be deemed stable. The second script was used for the actual performance testing flux. Similar to the conditioning script, it converts mass to flux. In addition, it created plots of the data and writes the data into an Excel file. The third script was used to compare flux between tests for each coating concentration. This script was especially useful in observing the membrane stability and determining which membranes were unable to reach steady state in the time given.

```
% Converts conductivity from CSV file with text in cells to data file with numbers only
clear;clc;clf;close all
%% MANUAL ENTRY:
% Insert File Names:
weight file=['C:\Users\jotom\Desktop\School\Research\SummerFall 2021 Research\Data\2.
Benchmark Testing Data\' ...
   'test 96 cal.csv']; %file to pull weight data from
target file=['C:\Users\jotom\Desktop\School\Research\SummerFall 2021 Research\Data\2.
Benchmark Testing Data\'...
   'Full test 96 write 2.xlsx'] ; %target file to put new data
% Test parameters:
m beaker1= 66.2; %Mass of beaker 1 [g]
% Constants:
timestep=1 ;
unit time='min';
P= 6.89476; %pressure [Bar]
A mem=.000907; %Active membrane area [m^2]
%% Open files
%Weight Data:
weight table=flip(table2cell(readtable(weight file)));
date time2=weight table(:,2);
m perm=cell2mat(weight table(:,4));
stability=weight table(:,8);
date time string2=cellfun(@char,date time2,'UniformOutput',false);
%% manipulate time
time test=duration(date time string2);
elap time test=time test-time test(1);
neg=elap time test<0;</pre>
elap time test(neg)=elap time test(neg)+hours(12);
elap mins=minutes (elap time test);
time w=elap mins;
%% Calculate flux
%F]11X:
m perm=m perm-m beaker1;
%Check the units of time
if strcmp(unit time, 'min')
   time conv=60;
elseif strcmp(unit time,'sec')
   time conv=3600;
elseif strcmp(unit time, 'hour')
```

```
time conv=1;
else
    error('Time step is not written in a supported format')
end
flux=((m perm).*10^-3)./(((time w)/time conv)*A mem);
if isinf(flux(1))
    flux(1)=0;
    warning ('First data point has been replaced with 0 due to infinte value')
end
avg flux=mean(flux(floor((length(flux)*3/4)):end)); %avg flux for last 1/4 of experiment
m perm shift=[0;m perm(1:end-1)];
time shift=[0;time w(1:end-1)];
inst_flux=((m_perm-m_perm_shift).*10^-3)./(((time_w-time_shift)/time_conv)*A_mem);
avg inst flux=mean(inst flux(floor((length(inst flux)*3/4)):end)); %avg flux for last
1/4 of experiment
up bound=avg inst flux*1.1;
low bound=avg inst flux*.9;
up plot=ones(length(time w),1)*up bound;
low plot=ones(length(time w),1)*low bound;
avg_plot=ones(length(time_w),1)*avg_inst_flux;
duration=time w(end);
%% Write Conditioning Data to Excel File
good data=[time w, flux];
table label=[{strcat('Elapsed Time (',unit time,')')}, {'Flux (L/(m^2*hr))'}];
writematrix('Conditioning Raw Data',target file,'Sheet','Conditioning');
writecell(table_label,target_file,'Sheet','Conditioning','Range','A2');
writematrix(good data,target file,'Sheet','Conditioning','Range','A3');
writematrix('Avg Flux (last 1/4 of test)', 🖌
target file,'Sheet','Conditioning','Range','D4');
writematrix(avg flux,target file,'Sheet','Conditioning','Range','E4');
writematrix('L/(m^2*hr)',target file,'Sheet','Conditioning','Range','F4');
%% Create Plots
flux fig=figure;
plot(time w,flux,'LineWidth',1)
xlabel(strcat('Elapsed Time (',unit time,')'));
ylabel('Flux(L/(m^{2*hr}))');
title('DI Water Conditioning Flux vs. Time');
grid on;
% ylim([0 150])
hold on
plot(time w, inst flux, 'ro:', 'LineWidth', .75)
```

plot(time w,up plot,'r--')

plot(time_w,low_plot,'r--')
plot(time_w,avg_plot,'k--')
legend('Overall Flux','Instantaneous Flux','Location','Southeast')

```
clear;clc;clf;close all
%% MANUAL ENTRY:
% Insert File Names:
weight file=['C:\Users\jotom\Desktop\School\Research\SummerFall 2021 Research\Data\2.
Benchmark Testing Data\'...
   'Full test 96 weight.csv']; %file to pull weight data from
target file=['C:\Users\jotom\Desktop\School\Research\SummerFall 2021 Research\Data\2.
Benchmark Testing Data\'...
   'Full test 96 write 2.xlsx'] ;%target file to put new data
% Test parameters:
feed cond= 2.541; %conductivity of feed solution [mS/cm]
m beaker1= 66.2; %Mass of beaker 1 [g]
feed conc= 2; % concentration of feed solution [g/L]
P= 6.89476; %pressure [Bar]
% Constants:
timestep=1 ;
unit time='min';
feed cond=feed cond*10^3;
A mem=.000907 ;%Active membrane area [m^2]
spec flux low=49.3; %lmh
spec flux high=81.6; %lmh
spec P=7.6; %bar
%% Open files
%Weight Data time:
weight table=flip(table2cell(readtable(weight file)));
date time2=weight table(:,2);
date time string2=cellfun(@char,date time2,'UniformOutput',false);
time_test=duration(date_time_string2);
elap time test=time test-time test(1);
neg=elap time test<0;</pre>
elap time test(neg)=elap time test(neg)+hours(12);
elap mins=minutes(elap time test);
time w=elap mins;
%% manipulate time
m perm=cell2mat(weight table(:,4));
stability=weight table(:,8);
```

```
%% Calculate salt rejection and flux
```

```
%F]11X:
m perm=m perm-m beaker1;
if strcmp(unit time, 'min')
    time conv=60;
elseif strcmp(unit time,'sec')
    time conv=3600;
elseif strcmp(unit time, 'hour')
    time conv=1;
else
    error('Time step is not written in a supported format')
end
m perm shift=[0;m perm(1:end-1)];
time_shift=[0;time_w(1:end-1)];
inst flux=((m perm-m perm shift).*10^-3)./(((time w-time shift)/time conv)*A mem);
flux=((m perm).*10^-3)./(((time w)/time conv)*A mem);
if isinf(flux(1)) || isnan(flux(1))
    flux(1)=0;
    warning('First flux data point has been replaced with 0 due to infinite value')
end
%Takeaways:
avg_flux=mean(flux(floor((length(flux)*3/4)):end)); %avg flux for last 1/4 of experiment
avg inst flux=mean(inst flux(floor((length(inst flux)*3/4)):end)); %avg flux for last↓
1/4 of experiment
max flux=max(flux);
%% Useful data
data2=[time w flux];
table label=[{strcat('Elapsed Time (',unit time,')')},{'Flux (L/(m^2*hr))'},{'\
'},{strcat('Elapsed Time (',unit time,')')},{'Salt Rejection (%)'}];
writematrix('Test Raw Data',target file,'Sheet','Test Results');
writecell(table label,target file,'Sheet','Test Results','Range','A2');
writematrix(data2,target file,'Sheet','Test Results','Range','A3');
%Write relevant takeaways
writematrix('Avg Flux',target file,'Sheet','Test Results','Range','G4');
writematrix(avg flux,target file,'Sheet','Test Results','Range','H4');
writematrix('L/(m^2*hr)',target file,'Sheet','Test Results','Range','I4');
writematrix('Max Flux',target file,'Sheet','Test Results','Range','G5');
```

writematrix(max_flux,target_file,'Sheet','Test Results','Range','H5'); writematrix('L/(m^2*hr)',target file,'Sheet','Test Results','Range','I5');

```
%% Plot Things
```

```
flux_fig=figure;
plot(time_w,flux,'LineWidth',2)
hold on
plot(time_w,inst_flux,'ro:','LineWidth',.75)
xlabel(strcat('Elapsed Time (',unit_time,')'));
ylabel('Flux(L/(m^2*hr))');
title('Flux vs. Time');
% ylim([0 100]);
grid on;
legend('Overall Flux','Instantaneous Flux','Location','Southeast')
```

```
%Used to compile flux vs time data to analyze steady state regions and
%determine which tests are not stable
clear;clc;close all
%Enter files to pull data from (uncomment as needed)
%Full Data Sets:
   %tests=[40 41 42 45 49 79 80] %uncoated
   %tests=[65 67 68 81 82 85] %0.1% tests
    %tests=[[59 60 61] [69:1:78]] %0.3% tests
   %tests=[86 87 88 89 91 92] %0.5% tests
    %tests=[62 63 64 83 84 90] %1% tests
   %tests=[93 94 95] %3% tests
    %tests=[46 47 50 56 57] %5% tests, took out 48, 58
tests=[59 60 78];
%Selected Tests:
    %tests=[40 41 42] %uncoated
   %tests=[67 68 85] %0.1% tests
    %tests=[59 60 78] %0.3% tests
   %tests=[88 91 92] %0.5% tests
    %tests=[62 64 84] %1% tests
   %tests=[46 47 57] %5% tests
unit time='min';
for i=1:length(tests)
   spec file=num2str(tests(i));
   file=strcat('C:\Users\jotom\Desktop\School\Research\SummerFall 2021 Research\Data\2.1
Benchmark Testing Data\Full test ', spec file,' write 2.xlsx');
   conditioning=xlsread(file,'Conditioning');
   time=conditioning(:,1);
   flux cond=conditioning(:,2);
   label=strcat('Run ', spec file);
  plot(time,flux_cond,'DisplayName',label,'MarkerSize',16,'LineWidth',2)
  hold on
  xlabel(strcat('Elapsed Time (',unit time,')'));
  ylabel('Flux(L/(m^{2*hr}))');
   title('DI Water Conditioning Flux vs. Time');
  grid on;
   legend
00
     xlim([0 80])
end
flux fig=figure;
for j=1:length(tests)
   spec file2=num2str(tests(j));
   file=strcat('C:\Users\jotom\Desktop\School\Research\SummerFall 2021 Research\Data\2.4
Benchmark Testing Data\Full test ', spec file2,' write 2.xlsx');
   test data=xlsread(file,'Test Results');
   time f=test data(~isnan(test data(:,1)),1);
```

```
flux=test_data(~isnan(test_data(:,2)),2);
label=strcat('Run ',spec_file2);
%Create plot
figure(flux_fig)
plot(time_f,flux,'.:','DisplayName',label,'MarkerSize',16,'LineWidth',1)
hold on
xlabel(strcat('Elapsed Time (',unit_time,')'));
ylabel(strcat('Elapsed Time (',unit_time,')'));
title('Flux(L/(m^2*hr))');
title('Flux vs. Time');
grid on;
legend
```

end

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