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Stefan M. Schaepe
University of Nebraska-Lincoln, smschaepe13@gmail.com

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ENGINEERING GRAPHENE OXIDE MEMBRANES FOR CONTAMINANT REMOVAL AND BACTERIAL INACTIVATION

BY

Stefan Schaepe

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ENGINEERING GRAPHENE OXIDE MEMBRANES FOR CONTAMINANT REMOVAL AND BACTERIAL INACTIVATION

Stefan Schaepe, M.S.

University of Nebraska, 2015

Advisors: Yusong Li and Xu Li

The need for improved water filtration technologies continues to grow on a global scale. Membrane filtration devices are increasing in use because they can remove a variety of contaminants efficiently. The major issue with membrane filters is biofouling. Coating membranes with nanoparticles such as graphene oxide (GO) can increase contaminant removal and decrease microbial growth.

This research characterizes the properties of the GO itself, two procedures for producing GO coated membranes, the properties of the created membranes and the contaminant removal and bactericidal efficiencies of the membranes. Pure water flux values for GO coated membranes prepared using a direct deposition method via vacuum filtration had flux values that ranged from 16 to 133 L m^{-2} $h^{-1}$$bar^{-1}$. The GO coated membranes had 92% and 72% of *E. coli* remaining 1 hour and 5 hours after the cells were deposited on the membrane surfaces, respectfully. Insignificant removal of salts or organic dyes was measured. The low contaminant removal properties are likely due to the swelling of GO flakes when in a hydrated state that cause the effective pore size to increase. The GO coated membranes prepared using a chemical layer-by-layer deposition method provided high flux values, but no observed contaminant removal or bactericidal properties. As revealed by the Scanning Electron Microscopy (SEM) and Fourier

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Transform Infrared Spectrometry (FTIR), the lack of sufficient GO coverage over the supporting membrane was the cause of the poor filtration properties.

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Chapter 1: Project Overview and Objectives

1.1 Project overview

The versatility of Graphene Oxide (GO) has recently begun to be explored in a variety of different fields including water treatment. Along with the recent studies on GO properties, membrane filtration is continuing to grow as a popular means of water purification. With the acceptance of membrane filtration increasing at the same time as GO is being further characterized and explored, it seems to be the perfect opportunity to explore the potential synergy between the two technologies by coating GO onto membrane surfaces. Recent research suggesting that the structure of GO nanocapillaries is beneficial for water purification purposes (Joshi et al., 2014) has only scratched the surface of what is known about GO and its potential in the membrane field. Additional research needs to be completed in order to understand how GO coated membrane may be an effective and efficient tool for water treatment.

Membrane filtration provides many solutions to problems that can be present with more common filtration methods. Membranes provide the ability to be used as a standalone treatment system or in combination with conventional treatment systems (Madaeni, 1999). Standalone treatment systems are not the ideal case for membranes, as it can wear down the filter much quicker, but it provides a useful treatment process for places where a full treatment facility may not be available. Membranes also provide the advantage of not requiring any sort of chemicals to be used in order to purify water. Chemicals can be costly and also require constant monitoring of doses.

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The idea of fabricating GO membranes for the use of contaminant removal was most notably studied by Dr. Andre Geim who revealed GO membrane's ability to quickly pass water vapor through itself while being impermeable to liquids, vapors and gases, including helium, one of the most difficult elements in nature to contain (Nair et al., 2012). The research showed the ability of the fabricated membrane to pass water vapor through 10^{10} times faster than helium. Graphene oxide contains a unique structure of flakes that arrange themselves on top of each other in order to form pathways for exactly the space of one water molecule. A low friction flow of a monolayer of water is therefore possible through the two dimensional capillaries that are formed in the GO membrane. While this study was groundbreaking to the field of GO, it is not practical to be used in full-scale water treatment. Using membranes similar to that described above, liquid water has been tested by passing through the GO capillaries in order to understand if the process is still effective for real world applications where liquid water is used along with positive pressure. In a more recent study by Dr. Andre Geim's group they found that the GO membranes exhibited extraordinary separation properties while also suggesting that with modifications it may be possible to produce a GO membrane in which the smallest of salts would be able to be rejected (Joshi et al., 2014).

The efficiency of a membrane filtration process needs to be assessed based on two criteria. The first criterion is how effective is the membrane at removing contaminants. The pores of GO membranes are comparable to those of nanofiltration membranes. Nanofiltration membranes are expected to remove dissolved contaminants such as salts, organic materials, viruses, and multivalent ions such as hardness in water that ultrafiltration devices cannot. The second criterion is how efficient can water pass

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through the membrane. In treatment processes there are desired flow rates that must be met. Membranes need to be able to efficiently pass water in order to uphold the flow requirements. Finding a balance between removing desired contaminants as well as providing efficient flow is crucial to the success of membrane filtration. Reverse osmosis (RO) systems boast the best removal of contaminants, but also require a great deal of energy in order to pass water through. Membranes containing GO have shown the potential to be nearly as effective at removing contaminants while also being energy efficient.

In addition to the two aforementioned criteria, other properties of a membrane should be considered for its potential in water treatment. Membranes should be able to withstand a certain amount of pressure without being damaged. Damaged membranes lead to preferential flow, resulting in the passing through of much or all of the contaminants. Membranes should not be highly susceptible to fouling. Fouling occurs when the pores of a membrane become covered by contaminants which reduce the flow through the membrane. Bacteria that are present in water can result in the formation of biofilms on membrane surfaces. The formation of biofilms on membranes is a major concern because they act as a catalyst for fouling. Fouling occurs regardless of the membrane in use, but certain membranes may experience fouling at a much quicker rate. Certain procedures can be done in order to make a membrane better suited to handle fouling. There are several cleaning processes that can be done in order to increase the flux of an existing membrane. There are also preemptive measures such as anti-bacterial coatings that can slow the process of fouling. However, all membranes will reach a point where they are no longer practical to be used due to such a low efficiency. Therefore, the

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longevity of a membrane is an important parameter that must be taken into account when determining what type of filter is best suited for practical applications. Membranes should also be stable under a wide range of pH values. The wider range of pH values that a membrane can withstand increases the applicability of the specific type of membrane. Lastly cost can be an important factor in determining how useful a membrane can be. Membranes have been found to be effective while using only tens of nanometers of GO in thickness (Han et al., 2013), making them a potentially inexpensive additive for membrane filtration.

Membranes comprised of GO can come in multiple forms. They can either come as stand-alone membranes, or the GO can be used as a coating on an existing membrane. Stand-alone GO membranes are not as practical for water filtration, primarily because GO membranes can be very fragile. Only a few layers of GO are needed in order to create a successful membrane therefore such a thin membrane could be easily fractured. A more practical approach for water filtration membranes is to coat a layer of GO on an already fabricated membrane. A study of that nature reported significant contaminant removal values attributed to the GO surface on a supporting membrane (Hu & Mi, 2013). The GO surface acts as its own membrane and is given the stability of the supporting membrane. The experiments conducted in this study focus on GO coatings that are supported on a base membrane.

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1.2 Objectives

The purpose of this study is to create GO membranes using multiple methods in order to determine their potential for contaminant removal and bacterial inactivation. The goal of the study was centered on 3 primary objectives.

1. Fabricate and characterize GO membranes that are suitable for water purification.

2. Assess the GO membrane's ability to remove chemical constituents that are common to drinking water.

3. Assess the GO membrane's antibacterial properties.

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Chapter 2: Background

2.1 Membrane filtration

In recent years, membranes have been used more often in the water treatment processes because of their ability to handle a wider range of contaminants when compared with typical disinfection systems. Common disinfection system, such as: chlorination, ultraviolet disinfection and thermal treatment, cannot treat every contaminant efficiently, thus leaving room for new technologies, such as membrane filtration. Chlorination systems are widely used throughout the United States, but large dosages are required to remove microbial communities such as viruses and bacteria. A large dose of chlorine can cause issues with disinfection byproducts, which create an additional problem in water supply. Ultraviolet disinfection can be useful for removing microbial communities, but requires a long contact time and does not remove suspended solids that can still be in the water. Thermal treatment can effectively treat bacteria and viruses in water, but the application is limited due to the large energy needed in order to heat the water. Thermal treatment cannot remove any remaining suspended solids left in the water. With all of these treatment systems posing shortfalls for treating contaminated water, membranes look to be a viable alternative or a powerful supplement.

Various sorts of membranes exist and specific membranes are chosen depending on the types of contaminants that are going to be filtered. Membranes can be categorized into four different categories: microfiltration, ultrafiltration, nanofiltration and reverse osmosis. Microfiltration membranes have the largest pore size, followed by ultrafiltration, nanofiltration and reverse osmosis. Microfiltration membranes are often used because their larger pore size allows for the quicker passage of water. Typical pore

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sizes for microfiltration membranes are between 0.1µm and 0.4µm (Francy et al., 2012). In some instances a smaller pore size is needed to ensure that even smaller contaminants, such as viruses, are not allowed to pass through the membrane. For such cases ultrafiltration membranes can be used. Pore sizes for ultrafiltration membranes range from 0.02 µm to 0.1µm (Francy et al., 2012). Nanofiltration and Reverse Osmosis membranes can also be used, but have a larger tradeoff because of their smaller pore sizes. Smaller pore sizes result in the slower passage of water. Figure 1 shows typical pore sizes for membranes. Membranes can be used as purchased from the manufacturer, or they can be modified in order to obtain a newly desired characteristic.

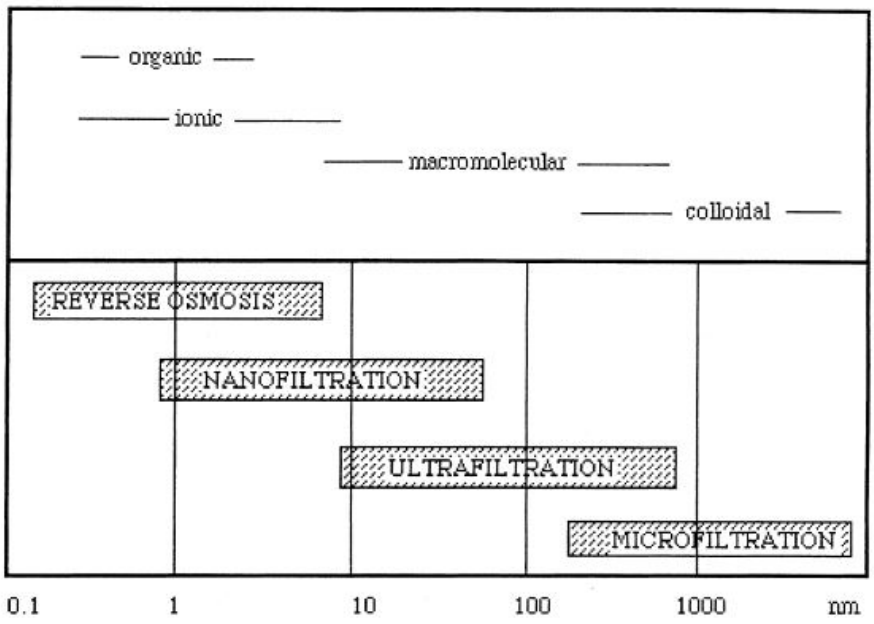

Figure 1: Membrane pore sizes (Madaeni, 1998)

Compared with typical treatment technologies, membranes do not require thermal inputs or the injection of chemicals. Retention rates can be nearly one hundred percent using membrane filtration, but a bigger problem exists with biofilms. Biofilms are a

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result of bacteria being retained on membranes and multiplying in order to form a bacterial surface that can greatly reduce the filtration efficiency. Biofilms can also render a membrane useless by blocking all of its pores. Understanding the characteristics of both bacteria and membranes as well as how they interact with each other will give a better idea about how membranes can be used to combat bacteria in the future.

Bacteria contribute to various waterborne diseases. In the United States cryptosporidium is known to be the most significant cause of waterborne diseases. In 1993 "the largest U.S. outbreak occurred in Milwaukee, WI" (Lovins et al., 2002). In this instance 450,000 people became ill and 144 people died as a result of cryptosporidium. While waterborne diseases have not been seen in this magnitude after many years within the United States, it is a common occurrence in developing countries. Membranes have been widely used in the United States and worldwide to prevent bacterial related diseases.

Two commonly studied bacteria include Escherichia coli K12 (*E. coli*) and clostridium perfringens. Bacterial cells generally have a range of 0.5 µm to 3.0µm (Francy et al., 2012). *E. coli* have an average cell size of 2µm. *E. coli* are gram negative bacteria, which means that they have a thinner cell wall, and an external lipid membrane. Sources of *E. coli* can vary, but often times they can be traced to animal waste. The bacteria are most likely to come in contact with an individual through contaminated food (foodborneillness.com). Clostridium perfringens have a cell size between 1 and 5µm (Lovins et al., 2002). Clostridium perfringens are gram positive bacteria which mean that they have a thicker wall, but do not have an external lipid membrane. Clostridium perfringens can be found in a multitude of places within the environment. Outbreaks of such bacteria can be associated with undercooked meat, which results in food poisoning

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(foodborneillness.com). Often times bacteria are better removed and inactivated if their charge is opposite of the membrane being used. For instance a negatively charged graphene oxide (GO) membrane would be more effective at inactivating gram positive bacteria.

In addition to bacteria, viruses, protozoa and parasites can be present in water. Viruses can range anywhere from 0.02 µm to 0.08µm in size (Francy et al., 2012) and require a membrane with a smaller pore size for filtration. Protozoa and parasites can also cause significant health issues if not treated. Protozoa and parasites can range anywhere from 4 µm to 15µm in size (Francy et al., 2012). Protozoa are generally smaller than parasites. Protozoa and parasite can be easily filtered using membranes because of their large particle size.

Now that the characteristics of both membranes and the bacteria have been discussed it is possible to look at the interaction between the two. The primary goal of bacterial filtration is to remove bacteria so that there isn't any in the effluent. The movement of bacteria through membranes can be driven by "either size exclusion or diffusion controlled mechanisms" (Lovins et al., 2002). Usually size exclusion is the primary factor that drives the removal of bacteria; however diffusion can be a factor if concentration differences between the influent and effluent streams become very high. For this reason it is important to not retain large numbers of bacteria on the surface of a membrane. Size exclusion bacterial transport is only dependent on the incoming stream concentrations. If concentration gradients are high, diffusion can result in the transport of bacteria through membranes.

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Lovins et al. sought to analyze the rejection of bacteria by using a multitude of smaller membrane types. The smaller membranes were used because they also wanted to test the rejection of viruses along with the bacteria. Three different types of nanofiltration membranes were used as well as one ultrafiltration membrane and one microfiltration membrane. The study was conducted using samples from a water treatment plant in East St. Louis, Illinois in 2002. In order to test whether size exclusion or diffusion controlled the removal mechanism, flux and concentrations were varied in order to monitor a change in removal trends. Since neither affected removal efficiency, it was determined that size exclusion was the primary removal mechanism. The removal results of the study can be found in Figure 2.

Table 2. Approximate organism diameter, log diameter, and log rejection value (LRV) for membrane challenges conducted at East St. Louis, IL.

	Approximate diameter μ	*Log diameter*	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*
NF1	0.03	−1.60	∞3.2	5.4	∞6	6.8	∞6.2	∞5.8	∞0.6	
	0.10	−1.00	∞3	5.7	∞6.5	6.2	∞6.4	∞6.1		
	1.50	0.18	∞2.6	5.7	5.4	6.1	∞5.4	∞5.4	∞3.7	
	4.00	0.60		∞4.2					∞3.8	
	10.00	1.00								
NF2	0.03	−1.60	2.1	1.4	2.6	2.1	4.3	4.6	∞0.6	
	0.10	−1.00	∞3	0.8	1.7	1.6	5.6	4		
	1.50	0.18	2.1	1.8	1.8	1.8	∞4.4	4.4	∞3.7	
	4.00	0.60		1.6					1.5	
	10.00	1.00								
NF3	0.03	−1.60	∞3.2	4.5	5.5	6				
	0.10	−1.00	∞3	6.1	∞6.5	6.5				
	1.50	0.18	∞2.4	5.3	∞6.4	6.1				
	4.00	0.60		∞4.1						
	10.00	1.00								
UF	0.03	−1.60				7		∞6.5		
	0.10	−1.00				∞7.9		∞6.4		
	1.50	0.18				7		∞6		
	4.00	0.60				∞4.8				
	10.00	1.00				∞4.7				
MF	0.03	−1.60								2.5
	0.10	−1.00								3.5
	1.50	0.18								6.2
	4.00	0.60								
	10.00	1.00								

∞EX = Infinite rejection given X log challenge.

Figure 2: Membrane rejection values (Lovins et al., 2002)

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The NF1, NF2 and NF3 are all similar nanofiltration membranes from different manufacturers. All of the nanofiltration membranes as well as the ultrafiltration membrane showed an infinite or nearly infinite removal of bacteria. A similar result was found for viruses as well. For the instance when microfiltration membranes were tested, high removal was shown for bacteria. However, lower values were shown for the removal of viruses. Inconsistent results were also reported for the microfiltration membranes, which was attributed to the local defects on membranes. Even the lowest reported values in this study were considered by the authors as far greater than regulatory requirements (Lovins et al., 2002), which demonstrates the effectiveness of membranes for bacteria removal.

2.2 Membrane surface coatings

Along with bacteria removal, preventing the formation of biofilms on the surface of a membrane is important. Biofilms form when bacteria stay active on a surface and continue to grow, which can inhibit water from passing through the membrane. To combat biofilms, membranes are typically chemically washed or thermally treated. By modifying the surface of membranes, bacterial growth can be inhibited due to the inactivation of cells.

Modifying membranes with nanoparticles is a way to slow the formation of biofilms. Nanoparticles used for inactivation of bacteria include: Carbon Nanotubes (CNTs), Graphene Oxide (GO), Iron Oxide (FeO), Titanium Dioxide (TiO_2), Zinc Oxide (ZnO) and silver nanoparticles. Membranes modified with antimicrobial surfaces “have the potential to replace or enhance conventional disinfection systems” (Li et al., 2008). It

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is great to envision modified membrane surfaces as a stand-alone treatment system, but as of now it looks to serve as an enhancement to current treatment processes.

In a 2008 study, Karnik et al. compared mortality rates of *E. coli* between uncoated ceramic membranes, ozonation, ozonation combined with membrane filtration and lastly ozonation combined with a FeO-coated membrane. The FeO was used because of its oxidative properties. Metal oxide nanoparticles have been used to inactivate bacteria, because they can cause cellular damage and eventually death to the cells. The oxidative stress interferes with the bacterial metabolic activity which ultimately prevents the bacteria from growing. The results of the study can be found in Figure 3.

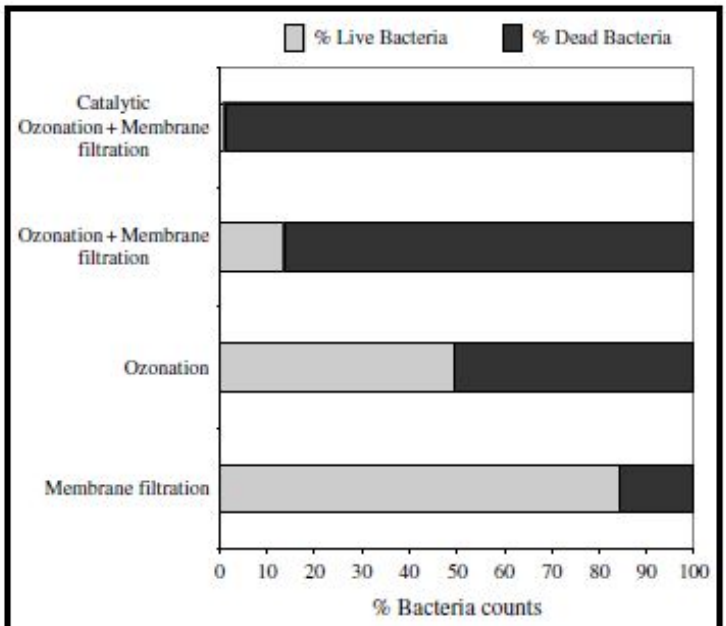

FIGURE 3. Percent of live dead bacteria in the permeate after different treatments. Experimental setup: see Figure 1 Operating Conditions: see Table 2. Membrane Size: 5 kDa, Gaseous ozone concentration 2.5 g/m^3, catalyst-coated membrane: coated 40 times with iron oxide nanoparticles, and then sintered in air at 900°C. The results were determined using fluorescence spectroscopy after staining with molecular probes. All values are the average of triplicates within experiments.

Figure 3: Bacterial inactivation results (Karnik et al., 2008)

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The combination of ozonation and the FeO-coated membrane achieved the highest death rate of *E. coli*. It is interesting to point out that the percent of dead bacteria was nearly 100% for this instance. No information was reported for FeO-coated membranes without ozonation, therefore it is difficult to decipher whether the ozonation or the iron oxide is playing the greater role in the inactivation of cells. Regardless, the research provides for a great insight into how oxidative nanoparticles can help retard the formation of biofilms.

Along with FeO, membranes modified with other nanoparticles have also shown great potential for bacterial inactivation. Single-walled carbon nanotubes reportedly had 79% inactivation of *E. coli* cells (Brady-Estévez et al., 2008). Single-walled carbon nanotubes force the flattening of *E. coli* which significantly alters the size and of the cell causing it to be inactive. Silver nanoparticles have also been used to coat membranes, and led to an inactivation of over 90% for *E. coli* (Zodrow et al., 2009). When using silver nanoparticles, Ag^{+} ions are released from the membrane which inhibits the ability of the bacteria to grow. Another method that has shown some potential is using charged membranes. Membranes with a highly negative charge that interacts with positively charged bacteria can cause rupture to the intracellular components, thus inactivating it. Often times, membranes that have nanoparticles deposited onto them have a given natural charge which can further enhance the inactivation process.

2.3 GO coated membranes

Currently GO is a popular research topic in membrane filtration because of its inherent flexibility and stability (Han et al., 2013). There are several methods for

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depositing GO onto various surfaces. While there are many different methods for creating GO coated membranes, the overall findings conclude that GO is a strong candidate to lead the way for coating membrane surfaces.

When GO is created using the Hummers method or some variation of the method, achieving pure graphene oxide solutions can be difficult (Rourke et al., 2011). Often times oxidative debris results on the surface of the GO following its fabrication. In 2011 Rourke et al. showed that oxidative debris can be bound strongly to the produced GO. In order to strip the GO of the debris a process of heating the GO in a water suspension with a small addition of Sodium Hydroxide (NaOH) to reflux for one hour can be done. It was also found that adding high concentrations of NaOH can have the same effect over a timespan of a few hours. Following either procedure, the GO suspension can be centrifuged in order to thoroughly wash the GO. The final result is a more pure GO suspension.

The procedure for stripping oxidative debris was done prior to the fabrication of GO membranes in a study conducted by Han et al. in 2013. Following the removal of oxidative debris the GO suspension was vacuum filtrated onto a membrane in order to completely cover the supporting membrane. Various microfiltration supports were used with an estimated pore size of 0.2 µm. The removal rates of both organic dye and various salts across the GO membrane were measured. The salt rejection and dye rejection results can be found in Figures 4 and 5 respectively. Rejection rates as high as sixty percent for some salts as well as the nearly complete rejection of dissolved organic dyes displays the strong removal properties possessed by the GO coated on the membrane.

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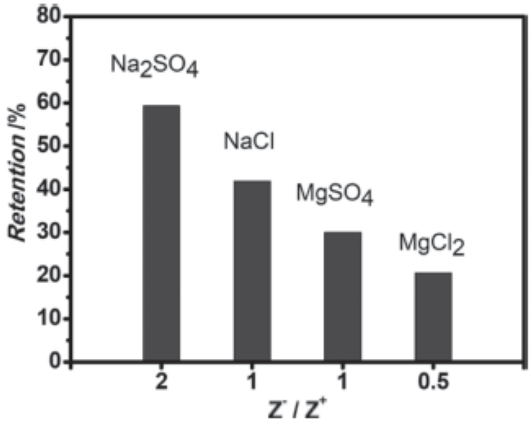

Figure 4: Salt rejection results (Han et al., 2013)

GO loading	Retention [%]	
[mg/m^2]	Methyl Blue	Direct Red 81
14.1	99.2	99.9
17.0	99.7	99.8
21.2	99.7	99.9
28.3	99.6	99.9
34.0	99.8	99.9

Figure 5: Organic dye rejection results (Han et al., 2013)

Paired with the strong removal capabilities of GO coated membranes are the bactericidal capabilities. In a 2014 study, Musico et al. oxidized GO nanoparticles and analyzed them for bacterial inactivation. Graphene oxide was studied individually as well as against graphene (G), poly(N-vinylcarbazole) (PVK) and a combination of the two (PVK-G). Graphene oxide was also paired with PVK (PVK-GO). All nanomaterials were deposited onto a cellulose nitrate membrane with a pore size of 8.0µm. The large pore size in this instance ensures that all of the removal and inactivation properties discovered

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can be attributed to the specific surface coated on the membrane. The results of the study can be found in Figure 6.

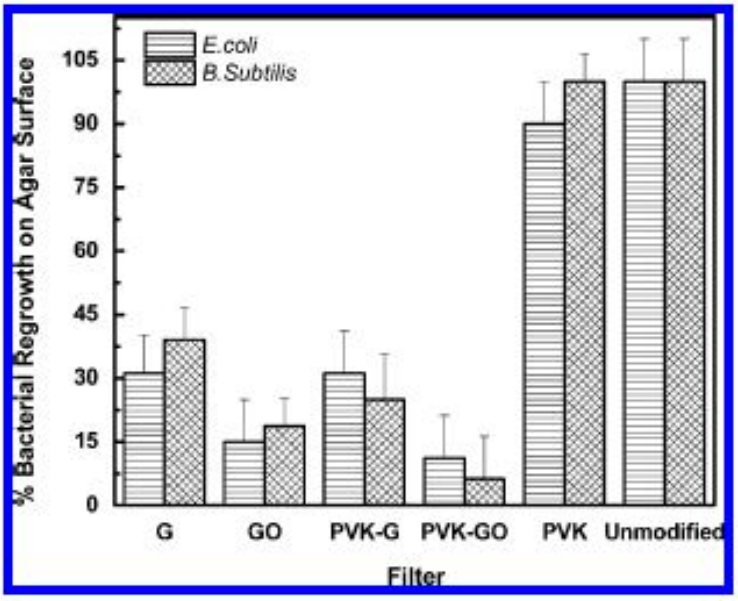

Figure 6: Inactivation results (Musico et al., 2014)

The highest inactivation of bacteria was found when pairing the GO with the PVK. While GO produced slightly higher inactivation than just graphene, it is important to point out that the graphene still reported high inactivation results. This means that the oxidative properties of the GO may only be contributing to a portion of the inactivation process. Graphene itself does have bactericidal properties of its own. The addition of PVK increased the antimicrobial properties of both the graphene and the GO. This is attributed to the "better dispersion of G and GO in the presence of PVK through π-π stacking interactions between the carbazole group of PVK and the aromatic groups present in the carbon nanomaterials" (Musico et al., 2014). Similarly, successful results

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for the biocidal property of GO were reported by Perreault et al. in 2013. The results of the study can be found in Figure 7.

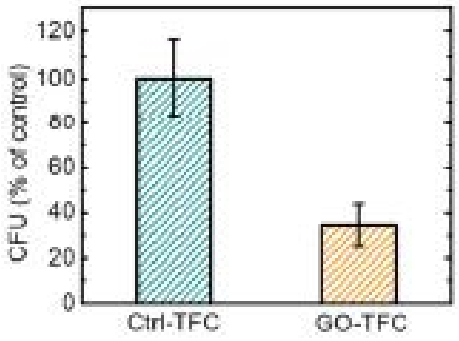

Figure 7: Inactivation Results (Perreault et al., 2013)

An inactivation value of 59% was recorded when compared with the control membrane containing no GO coating. In summary, multiple studies suggest that GO membranes have the potential to be successful at significantly retarding the growth of biofilms.

Pairing the GO with another substance has become a common practice in order to space the GO sheets further apart to increase flux values. In a study conducted by Hu and Mi in 2013, GO was interlinked with 1,3,5-benzenetricarbonyl trichloride (TMC). By linking the two together it "fine-tuned the charges, functionality and spacing of the GO nanosheets" (Hu & Mi, 2013). While the pairing increased the rate at which water was able to pass through the membrane, there was a reduction in contaminant rejection when compared with the results from Han et al.'s study. The results of the study can be found in Figure 8.

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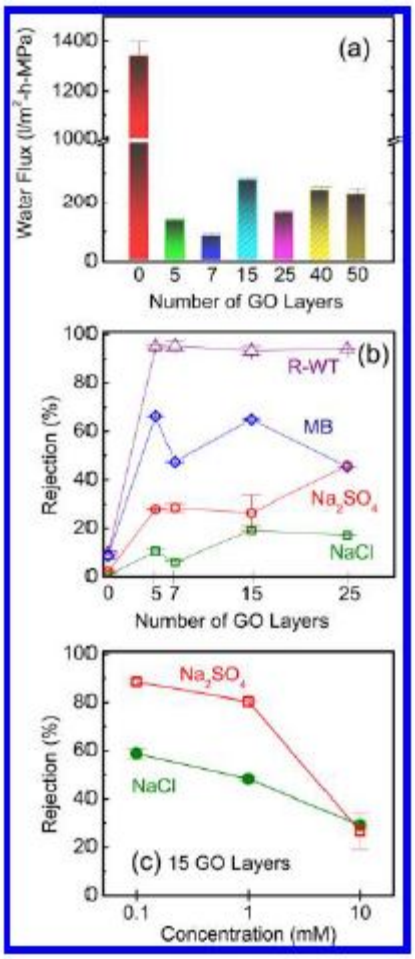

Figure 8: Flux and Rejection Results (Hu & Mi, 2013)

A rejection rate of 6-46% was reported for divalent salts. Rejection rates for organic dye Methyl Blue and Rhodamine-WT were 46-66% and 93-95% respectively. Depending on the specific application for which a membrane is to be used, cross-linking GO with another substance is a possible route to increase crossflow rates while still providing reasonable rejection values. Interestingly, water flux value remained relatively constant when the amount of GO on the membrane increased. The finding suggests that the thickness of the GO coating may not necessarily affect the flow properties. Another

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important finding suggests that even as few as five GO layers can greatly enhance the rejection properties of the supporting membrane.

There are many different options for preparing GO membranes, each with their own set of advantages. Increasing the purity of the GO can increase the potential for both contaminant rejection as well as bacterial inactivation. Cross-linking the GO with another substance can both increase the inactivation properties (Musico et al., 2014) and the flux (Hu & Mi et al., 2014). The drawback with cross-linking is that the potential for contaminant rejection is not as high. Membranes coated with GO can be created in a variety of different ways for a multitude of applications.

One concern with using nanoparticles as coating is the potential of those nanoparticles ending up in the effluent stream. Trace amounts of silver nanoparticles were reported to be present in the effluent from the membrane (Zodrow et al., 2008); therefore it is necessary to understand the potential risks associated with them. It is also necessary to propose a possible solution to the problem before any nanoparticles can be used on a large scale. Until now, no study reported any issue with GO ending up in the effluent. Generally GO is stable in the environment. If GO was to be released into the environment it can travel quickly into lakes and streams, which could potentially result in negative environmental impacts (Nealon, 2014). Another issue associated with modifying membranes is that the effective pore size is greatly reduced to approximately 1 to 2nm (Han et al., 2013). By studying the flux values of modified membranes we can better understand the energy required in order to run water through the fabricated membranes. Flux is equally as important as the inactivation and removal properties and should be considered in all studies in order to ensure that large energy inputs are not required to

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pass water through the system. Typical flux values for modified membranes fell in the nanofiltration range (20-50 L m^{-2} h^{-1} bar^{-1}) which could still be a viable option depending on the specific application in question.

Membrane filters look promising for the future, and hopefully with continued research efforts they will one day serve as stand-alone treatment systems in places where they are needed most. Membranes have proven to be effective at removing bacteria, viruses and many other contaminants from water sources. Size exclusion is the primary mechanism that membranes use in order to filter contaminants which makes selecting the right type of membrane straightforward, as long as the contaminants in the feed water are well characterized. A wide variety of membrane materials and pore sizes are available to be selected for site specific applications. For these reasons membranes have a distinct advantage over other disinfection systems such as chlorination, ultraviolet disinfection and thermal treatment. The formation of biofilms on membranes has shown to be the greatest drawback because it hinders the efficiency as well as the longevity of the membrane. However, recent studies have shown that coating membranes with nanoparticles can retard biofilm growth to increase filtration performance. It is not farfetched to suggest that antimicrobial coatings will be the new standard in membrane filtration. It is likely that current facilities not already using membrane filtration devices will turn to them in the future, either as the primary filtration process or in conjunction with current disinfection devices, in order to enhance bacterial removal and inactivation.

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Chapter 3: Materials and Methods

3.1 Introduction

One of the objectives of this research was to develop a method for fabricating graphene oxide based membranes that can be used in water filtration. The equipment used is important for creating reliable data and consistent results. The materials and processes used for creating graphene oxide (GO) coated membranes are outlined in this chapter. Both the procedures to create the membranes and the methods to characterize the membranes are described.

3.2 Materials

Single layered graphene oxide was purchased from ACS materials for all of the experiments conducted. The purchased GO was prepared using the modified Hummer's method (acsmaterial.com). The GO is in flake form and has a reported thickness of 0.8-1.2nm and a reported purity of 99%. The carbon to oxygen ratio is reportedly 1.67, but can vary depending on the manufacturing process. An image of the purchased GO can be seen in Figure 9.

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Figure 9: Purchased single layered graphene oxide

A polyethersulfone membrane was used as a base membrane to support the GO coating. The membrane serves as a support for the GO layered structure while having negligible influence on the removal efficiencies of contaminants. The membranes used were noted for their individual characterization properties and removal efficiencies in order to distinguish between the effects of the base support and that of the GO coating. The polyethersulfone membranes were purchased from Millipore. The filters are 47 mm in diameter, 150 µm thick, with a porosity of 79 percent. They have a pore size of 0.45µm which is significantly larger than that of the graphene oxide to be placed on the membrane. The filters are composed of mixed cellulose esters and are hydrophilic in nature. The reported water flow rate is 40mL/min-cm^2. The filters are white, flexible and can operate at a maximum temperature of 75^{o}C.

Another base support used was the Whatman Anodisc inorganic filter membrane. The membranes were purchased from Sigma Aldrich. The 47mm discs have a pore size

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of 0.2µm. The membranes provided for a smaller pore size than the polyethersulfone membranes, and were very fragile.

The virtually transparent membranes are composed of a high purity alumina matrix that is manufactured electrochemically. The structures of the pores are very precise allowing for a narrow pore size distribution. While the filters themselves are better structured, the GO that was placed on the Whatman Anodisc was not able to remain attached. The membranes would be more desirable in an instance where GO coatings were to be used as stand-alone membranes. For this reason the Anodisc membrane was not used in any of the contaminant rejection or bacterial inactivation tests. An image of both the polyethersulfone membrane and the Anodisc membrane can be seen in Figure 10.

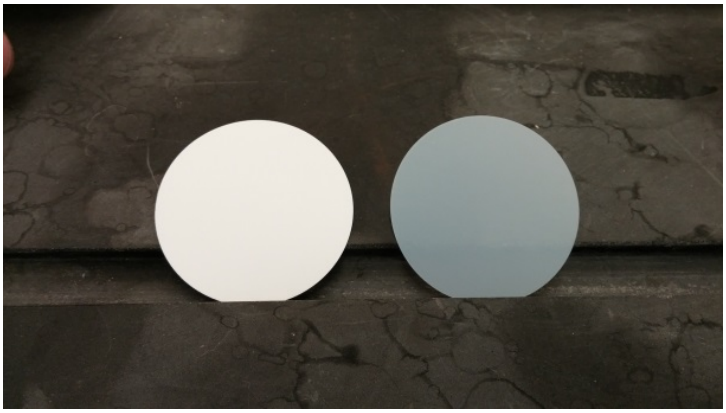

Figure 10: Polyethersulfone (left) and Anodisc (right) membranes

3.3 Methods to fabricate GO membranes

Two methods were used to create the GO coated membranes. The methods used were compared against each other in order to better understand what processes provided

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beneficial results in the membrane fabrication process. The procedures for both methods are described in the following sections.

3.3.1 Method 1

The method for this GO coated filter is based off of a previous study (Han et al., 2013). The GO coating was supported on both a polyethersulfone membranes as well as Whatman Anodisc membranes; however the GO was not able to remain attached to the Anodisc membranes. Specific amounts of purchased GO nanosheets were weighed on weighing paper with a scale having an accuracy of +/- 0.01mg. To start, 50mg of GO was weighed out and placed in 50mL of ultrapure water. The resulting starting concentration of the GO in water was approximately 1mg GO/mL of water.

The GO suspension was then sonicated to break large GO flakes into smaller and more stable particles. The sonication step helped create a stable suspension of GO in water. The bath sonicator that was used was purchased from Fisher Scientific and is a model Fs60 (Figure 11).

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Figure 11: Ultrasonication bath

The model has 130 watts of ultra-sonic power, 205 watts of heater power and 335 watts of total power. The beaker containing the GO suspension was covered with parafilm to prevent water loss or foreign particle's entrance into the suspension during sonication. The suspension was then placed in the sonicator bath, with the water level in the sonicator raising approximately one inch above the GO suspension in the beaker. The GO was sonicated for 15 minutes. An image of the GO suspension in water following the sonication process can be seen in Figure 12.

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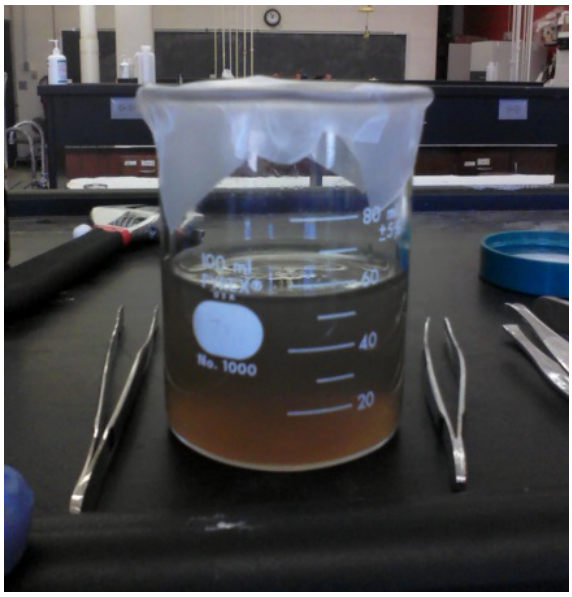

Figure 12: GO suspension following sonication

After the 15 minute sonication period the GO suspension was placed in a 50mL centrifuge tube. The tube was placed in the centrifuge and counterbalanced with a centrifuge tube filled with water to the 50mL mark. The centrifuge was a type 5804 R centrifuge from Eppendorf (Figure 13).

Figure 13: Centrifuge device

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The maximum rotations per minute (rpm) for the particular model using a 50mL tube were 11,000rpm. The GO suspension was centrifuged at 10,000 rpm at 25^{o}C for fifteen minutes. Temperature does not have a large effecst on the GO suspension and therefore the default temperature on the centrifuge was used. The rotational speed and time amount allowed the GO flakes to separate from the water and settle at the bottom of the centrifuge tube (Figure 14). The supernatant was disposed and the GO flakes were re-dispersed in 50 mL of ultrapure water.

Figure 14: GO following centrifuge process

The tube was shaken using a vortex mixer in order to thoroughly disperse the GO. The mixer was purchased from Fisher Scientific. The vortex mixer can be seen in Figure 15.

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Figure 15: Vortex mixer

The centrifuge tube was then placed in a beaker filled with water, and both the beaker and tube were placed in the sonication bath. The GO suspension was sonicated for fifteen more minutes, and then washed by centrifuging and re-suspending. The process of sonicating and washing the sample was repeated four times for a total of five times in order to clean the GO by stripping it of oxidative debris (Rourke et al., 2011). The final result of this process was a stable brown suspension of GO in water similar to that seen in Figure 12.

Following the washing of the GO, a low concentration of sodium hydroxide (NaOH) was added to the GO suspension to coat the GO flakes and prevent oxidative debris from forming on the surface of the GO (Rourke et al., 2011). Twenty milligrams of NaOH was added to the sample. In order to add 20mg of NaOH the mass of a solid single

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pellet of NaOH was measured, recorded and then dispersed in 1mL of ultrapure water. Once the NaOH had completely dissolved in the water, the known concentration was used to determine the exact volume of solution needed to be added to the GO suspension. The amount calculated was then pipetted into the GO suspension.

Following the addition of NaOH, the GO suspension was immediately put under nitrogen flow for 30 minutes. The GO suspension was placed in a 500mL Schlenk flask and connected to a nitrogen tank and a reflux condenser tube. The Schlenk flask contained two openings. The primary opening connected the flask to the reflux condenser tubing while the second one was plugged using a rubber stopper. To connect the nitrogen to the flask, tubing was connected to the tank, with a needle connected to the end of the tubing. The needle was placed through the rubber stopper in the Schlenk flask. The nitrogen flow was increased enough so that the GO suspension was noticeably being stirred by the flow of nitrogen coming from the needle. This was done so that the nitrogen could come in contact with the entire suspension. The suspension was stirred under the nitrogen flow for 30 minutes for sufficient contact with nitrogen and complete deprivation of oxygen. The depravation of oxygen caused the GO suspension to quickly change from light brown to black. While the nitrogen was beneficial for removing oxygen, it could also covalently bond with the surface of the GO to form hydrazones, amines, aziridines and other similar structures which can result in impurities in the structure of the GO (Dreyer et al., 2009).

Following the nitrogen purge, chilled water flow was turned on to allow it to run around the outer tubing of the reflux condenser tube. The reflux condenser tubing was made of glass and was composed of a long outer cylindrical tube, with spiral inner

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tubing. The outer tubing was connected to a chilled water line, allowing cold water to run from the bottom of the tubing to the top. The heated GO suspension evaporated into the inner tubing, and then the surrounding cold water caused the vapor to condense and drip back into the suspension. The flask sat on a heating blanket to hold it steady as well as to provide the heat. The heating blanket that surrounded the Schlenk flask was turned on to 120 volts at about 75% power. The power was adjusted so that the suspension just reached its boiling point. The suspension was heated to reflux for one hour. The heat acts as a catalyst in order to speed up the reaction between the GO and the NaOH. Using a higher concentration of NaOH has been found to have the same effect as using a small concentration and heating to reflux (Rourke et al., 2011). In this study, only the heat to reflux procedure was used for the NaOH and GO interaction. Following the hour of heating to reflux, the black suspension was allowed to cool to room temperature. An image of the heating to reflux apparatus can be seen in Figure 16.

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Figure 16: Heating to reflux apparatus

After the GO modification process, the GO suspension was washed again to remove any impurities that may have resulted from the process. The GO suspension was placed in a 50 mL centrifuge tube and centrifuged at a speed of 11,000 rpm at 25^{o}C for ninety minutes. The centrifuge was counterbalanced as before with a centrifuge tube filled with water. The maximum speed for the centrifuge was used in order to reach sufficient separation of GO and water. Another study reported using a higher speed of

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17,900 rpm for sixty minutes (Han et al., 2013), but the limits on the centrifuge device used did not allow such high rotational speeds. The resulting sediment was a black pasty substance (Figure 17), while the supernatant was nearly clear with a black tint.

Figure 17: Paste-like GO sediment

The supernatant was discarded and the pasty sediment was re-dispersed in 50 mL of ultrapure water as before. The new dispersion was shaken using the vortex mixer to create a uniform dispersion. The new suspension was then placed back in the centrifuge for 15 minutes at 25^{o}C and 10,000 rpm. The washing step was repeated two more times to fully clean the GO. After the final washing, the supernatant was almost completely clear indicating a clean and stable modified GO paste. Modified GO paste was re-suspended in water, vortex mixed and transferred into a beaker. The resulting modified GO suspension could remain stable for multiple months (Figure 18).

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Figure 18: Stable GO suspension following Method 1

The actual concentration of GO in the water was measured, because the GO initially added to water might be lost during the centrifuge processes as well as heating to reflux. The weight of a tin cup was recorded as the initial weight and then three milliliters of GO suspension was pipetted out of the sample and into the cup. The tin cup was then placed in a 105^{o}C oven for 24 hours in order to remove all of the water from the sample. The final weight was recorded and the GO concentration of the suspension was calculated using the known volume and the difference in the beginning and final weights of the tin cup. The process was done for 3 samples and the recorded concentration was the average of the three. Three milliliters was used because it contained enough GO to be accurately measured. The three samples that were averaged in order to determine the concentration of the suspension were consistently similar in value giving a high level of confidence in the final concentration found. However, the final concentrations varied from batch to batch and ranged from 0.313-0.628 mg GO/mL water. The wide range of

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final values from batch to batch could be caused by the inherent complexities of the GO that can cause it to vary from sample to sample.

Based on the measured concentration of the GO suspension, small amounts of the suspension were pipetted into 50 mL of ultrapure water to create the target concentration for making GO membranes. The target concentration varied depending on the loading rate that was desired. Diluted GO solutions were covered with parafilm and sonicated for 15 minutes in order to thoroughly mix the GO in the ultrapure water. The concentrations of the diluted GO solutions ranged from 0.3-6.3 µg/mL depending on the desired thickness of the GO layer on the membrane. A support membrane was placed on a vacuum filtration funnel device and the vacuum was turned on. The 50mL of diluted GO solution was then poured into the funnel in order to disperse the GO onto the support membrane while the water from the sample was pulled into the beaker supporting the funnel. The result was a dark circle of GO deposited onto the filter. The denser the solution poured into the funnel the darker the GO deposit was. An image of GO coated on a polyethersulfone membrane following the vacuum filtration process can be seen in Figure 19.

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Figure 19: Membrane coated with GO following Method 1

The vacuum was then turned off and the membrane was removed from the funnel support and placed in a closed container to dry overnight and to prevent particles in the air from settling on the membrane. A summary of Method 1 can be found in Figure 20.

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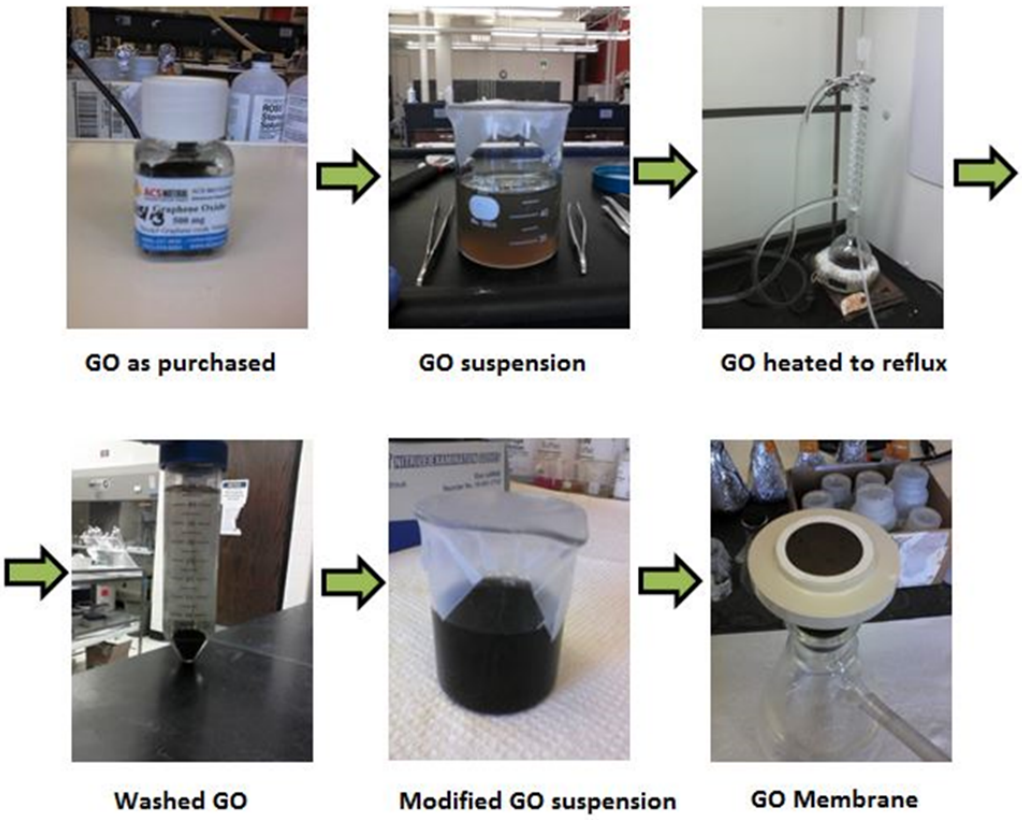

Figure 20: Method 1 procedures summary

3.3.2 Method 2

The protocol for Method 2 was based off of a previous study (Hu & Mi, 2013). The method was explored to create a GO layer used on a polyethersulfone membrane. The support was intended to pair GO with 1,3,5-benzenetricarbonyl trichloride (TMC) in order to space the sheets of GO further apart to allow for a higher water flux. First, GO flakes were crushed into a more powder like substance in order to reach a more homogeneous dispersion in Isopar G oil. Isopar G is a solvent produced by ExxonMobil

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Chemical. Approximately 20mg of crushed GO was added to 300mL of Isopar. An image of the crushed GO can be seen in Figure 21.

Figure 21: Crushed GO flakes

Once the GO was crushed into a fine powder, 20mg was added to the Isopar in a glass container. Isopar is a clear, fabricated solvent that is commonly used for coating materials. Isopar has a low acute and chronic toxicity. Isopar can potentially dissolve some plastics; therefore, plastic containers were not used in any part of the procedure. Glass was also used because it is better at transferring energy during the sonication step.

The GO-Isopar solution was sonicated for twenty hours. It was important to keep the sonicator bath cool because the Isopar has a low flash point at ninety five degrees Fahrenheit. Ice was added to the sonicator and the suspension was mixed by swirling the

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container every hour in order to keep it cool and provide an even temperature throughout the suspension. GO flakes often did not completely disperse in Isopar. Due to the hydrophilic nature, it requires much more energy to create a stable GO suspension in an oily substance like Isopar as compared to water. An image of the GO suspended in Isopar can be found in Figure 22. It is clear in this instance that not all of the GO was able to be dispersed.

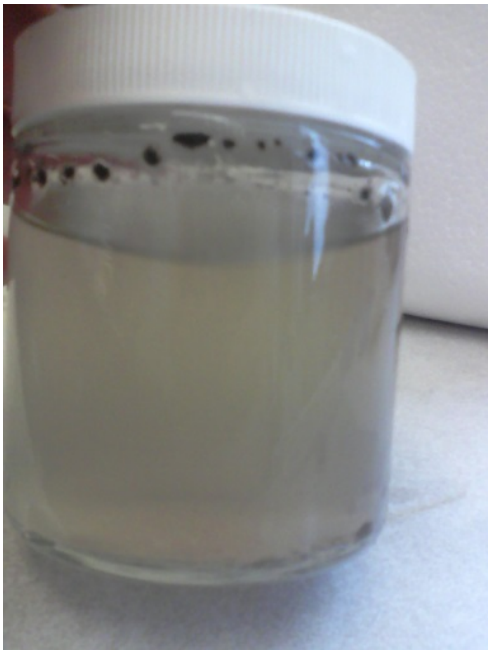

Figure 22: Suspension of GO in Isopar

Along with the GO suspension it was also necessary to create a suspension of TMC and Isopar. A TMC-Isopar solution was created by adding TMC (0.15% by weight) to the Isopar and placing a magnetic stirrer in the solution and stirring for at least 6 hours to completely dissolve the TMC. Following the stirring, the magnetic stirrer was removed from the solution and it was ready to be used in the coating stage. No visual change was noticed following the addition of TMC to the Isopar, and the solution remained clear.

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In order to prepare the base membrane for the GO and TMC coating, the base membrane was first coated with dopamine. Dopamine is often used to coat membrane surfaces in order to reduce the effects of fouling by creating a smoother membrane surface (Kasemset et al., 2012). A solution of 2mg of dopamine per 1mL of Tris Buffer was created. The dopamine was added to the buffer and swirled to create a uniform solution. Once the dopamine was completely dissolved the polyethersulfone membrane was immediately placed in the solution. The polymerization process starts occurring immediately after the buffer comes in contact with the dopamine so it is important to add the filter to the solution right away. The solution with the polyethersulfone membrane was placed on a mixer for one hour to create an even dopamine coating. After the hour the membrane was removed from the suspension and dried in a 65^{o}C oven for 24 hours.

Finally the coating of the membrane can be completed once the GO suspension, TMC solution and base polyethersulfone membrane have been prepared. Approximately 50mL of Isopar was added to a new beaker. 10mL of the GO suspension and 10mL of the TMC suspension were also placed in separate beakers. The dried polyethersulfone membrane coated with dopamine was placed in the 10mL of TMC suspension for fifteen minutes to form approximately a single layer of TMC. The membrane was then transferred to the beaker with the 50mL of Isopar and swirled to remove any excessive TMC. The membrane was subsequently placed in the GO suspension for 15 minutes to coat the surface with a single layer of GO (Hu & Mi, 2013). While the membrane was soaked in the GO suspension the beakers with the isopar and TMC solution were discarded and a new 50mL and 10mL were placed in the respective beakers. After the membrane had soaked for fifteen minutes in the GO suspension it was estimated that one

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layer of TMC and GO had been deposited onto the support. The membrane was once again rinsed in a clean 50mL of Isopar. The used GO suspension was discarded and replaced with a new 10mL of suspension. The process was repeated in order to achieve the desired number of GO and TMC coatings on the membrane. For the purposes of this study ten coatings were added to the membrane surface. Once the final TMC and GO coating had been deposited onto the membrane the filter was placed into a 95^{o}C water bath for two hours in order to remove any excessive Isopar on the membrane surface. The membrane was then allowed to dry at room temperature for at least 12 hours before use. An image of a final membrane following this procedure can be seen in Figure 23. It is clear that there is a much more limited amount of GO deposited on the surface when compared with method 1.

Figure 23: Membrane with TMC and GO coated surface following Method 2

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3.4 Characterizing GO membranes

3.4.1 Pure water flux measurements

Pure water flux measurements are important to compare the rate at which water can pass through a specific membrane. Flux measurements determine the rate at which water is passing through a certain membrane area. Pure water flux measurements were conducted using a nitrogen tank for feed pressure, a pressure vessel, a stirred cell membrane holder and a digital scale.

The one gallon pressure vessel was purchased from EMD Millipore. It is made of stainless steel and is approximately nine inches tall. The maximum inlet pressure for the vessel is 100 psi. An Amicon 8010 stirred cell was used to hold the fabricated membranes. It was purchased from EMD Millipore as well and can hold 10 mL of solution. A magnetic stirrer inside the cell can mix the solution before it passes through the membrane. The maximum pressure allowed in the cell is 75 psi, and has an effective filter area of 4.1cm^2. With the filtration area being smaller than that of the support membranes, the produced GO membranes needed to be cut in order to be able to fit into the stirred cell. The filters were cut down to a size of 25mm in diameter from the total 47mm diameter. A circle cutter was used to carefully complete this step and not damage the membrane. An image of a membrane that was cut down to size as well as the cutting tool is shown in Figure 24.

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Figure 24: Membrane coated with GO cut to 25mm

Polypropylene tubing was used to connect the nitrogen feed tank to the pressure and then to the stirred cell. Tubing was 1/4" in diameter and male pipe adapter 1/4" x 1/8" and 1/4" union elbows were purchased from Sigma Aldrich. The union elbows were used to connect the tubing to the pressure tank, while the pipe adapter was used to connect the tubing to the nitrogen tank. The stirred cell came with its own adapter to connect the tubing to the cell. An image of the entire pure water flux set up can be seen in Figure 25. The nitrogen tank was connected to the pressure vessel using the clear tubing. The pressure vessel was then in turn connected to the stirred cell which held the membrane and sat on top of a magnetic stirring plate. The effluent flows out of the small tube exiting the bottom of the stirred cell. Not pictured in the figure is the container sitting on top of a digital scale in order to catch and measure the flow rate.

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Figure 25: Pure water flux measurement set up

To start the procedure ultrapure water was poured into the pressure vessel to fill it and the lid was closed and air tight. Tubing and adapters were used in order to connect the nitrogen tank to the pressure vessel and then the pressure vessel to the stirred cell. The stirred cell was elevated on a stand in order to allow the effluent water to pour into a bucket placed on the scale.

Once the GO membrane was cut down to size, the stirred cell was disassembled and the membrane was placed on the filter holder and held in place by a rubber O-ring (Figure 26).

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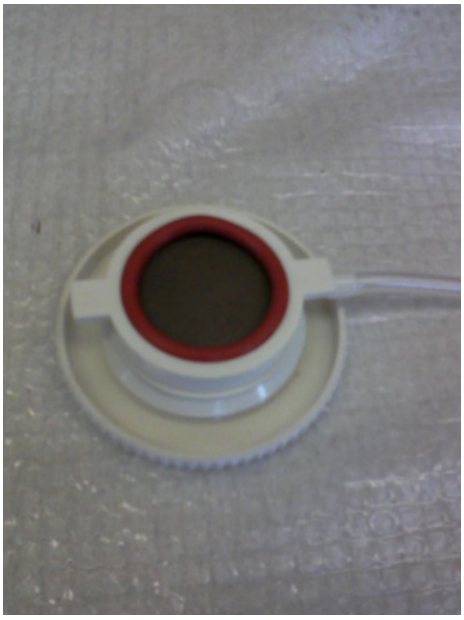

Figure 26: Resized GO coated membrane in stirred cell

The stirred cell was then reassembled and stationed on the stand above the bucket where the effluent was to be captured. The scale was set to zero with the bucket on top of it in order to only account for the weight of water that was to enter.

To start the flux tests, the nitrogen valve and the valve opening to the system were opened to increase pressure. Once the first drop of water came out of the effluent tube a timer was started. The valve was continued to be opened until the desired pressure inside the pressure vessel was reached according to the gauge attached to the pressure vessel. The weight of the scale was recorded every two minutes for a period of three hours in order to fully encapsulate the trend of the pure water flux. The pressure usually remained steady throughout the experiment.

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The density of water was assumed to be 1g/mL since the temperature was consistently close to 25°C and the system was open to air allowing for the pressure to equal 1atm.

Flux values were calculated using the following equation:

$$F = (V_2 - V_1)/(\Delta t_{min}/60_{min/hr})/A/P$$

The "V" values are the volume of water that has passed through the filter at a given time in Liters. The difference in sequential volume measurements is divided by the time interval in minutes, which is divided by 60 minutes per hour. The value is then divided by the effective area of 0.00041m^2 for the filter, and then the pressure that is applied to the system in bars. The final result is a unit of $\frac{Liters}{m^2 * hour * bar}$ which is a typical unit for flux measurements.

3.4.2 SEM imaging

Scanning Electron Microscopy (SEM) images were taken on a LEOL JSM-6360 SEM device to show the surface of the GO coatings as well as the surfaces of the supporting membranes. The Biomechanics, Biomaterials and Biomedicine Instrumentation Facility at the University of Nebraska-Lincoln produced the SEM images.

SEM images of GO coated membranes using Method 1 and Method 2 were obtained. A small piece of the produced membrane was cut and placed on a stand. The GO is not highly conductive and can turn out transparent on SEM images; therefore the GO membrane surfaces were sputter coated with gold to form a conductive surface.

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Images were also taken of the polyethersulfone membrane. SEM images allowed for the determination as to how well and how evenly coated the base membranes were with GO.

3.4.3 AFM imaging

Atomic Force Microscopy (AFM) images were taken using a Brucker Dimension ICON SPM to better understand the properties of individual GO flakes deposited onto the support filters. The Central Facility for Scanning Probe and Materials Characterization at the University of Nebraska-Lincoln conducted the AFM analysis.

One hundred microliters of the dark, stock GO solution prepared using Method 1 was added to fifty milliliters of ultrapure water. The diluted suspension was sonicated for ten minutes to fully disperse the GO. After sonication, three drops of the suspension was dropped onto a small silicon wafer. Silicon wafers were used because of their smooth surface. The wafer was then placed in a closed container to prevent dust particles in the air from settling on the wafer. The drops were allowed to dry overnight before AFM images were taken.

The silicon wafer with the dried GO suspension was then stationed under the AFM device. Pictures of the surface were taken on a scale of 5-15µm in order to view the size of individual GO flakes. The AFM was also used to measure the height of the GO flakes.

3.4.4 FTIR measurements

Fourier Transform Infrared Spectrometry (FTIR) measurements were conducted on a Bruker Tensor 37 FTIR to identify the functional groups on the GO surface. The

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Department of Chemistry at the University of Nebraska-Lincoln acquired the FTIR measurements.

Measurements for FTIR were conducted for the GO membranes created using Method 1 and Method 2 as well as for base polyethersulfone membranes. For Method 1, membranes having a thickness of 50mg/m^2 and 150mg/m^2 were analyzed. Small pieces of the individual membranes were placed under the tip of the FTIR probe during measurements. The FTIR measurements were all compared against each other in order to understand how each fabrication process affected the chemistry of the membranes.

3.4.5 Zeta potential and particle sizing measurements

The relationship between pH and the properties of the GO was characterized to determine what values of pH the membranes produced would be able to withstand. The pH of GO suspensions created using Method 1 was measured and recorded. Particle sizing and zeta potential measurements were also done for the batch solution. Often times the batch solution needed to be diluted with ultrapure water further in order to receive accurate results during the particle sizing and zeta potential measurements.

To adjust the pH, sodium hydroxide and hydrochloric acid were added to the GO suspension. The natural pH of the batch GO suspension was about 8.5. The pH was initially increased to 9.0 and 10.0 by adding sodium hydroxide or decreased to 8.0, 7.0, 6.0, 5.0, 4.0 and 3.0 by adding hydrochloric acid. The zeta potential and particle size were measured for each pH value. The pH was measured by using an Orion 4 Star Benchtop pH/Conductivity Meter from Thermo Scientific (Figure 27).

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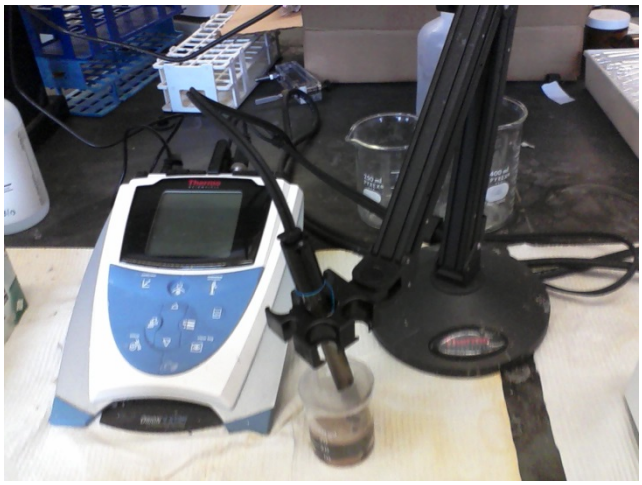

Figure 27: pH meter

In order to measure particle size, approximately three milliliters of the suspension was added into a cuvette. A lid was placed on the cuvette and it was slid into the particle sizing/zeta potential machine. Particle sizing software was run. Parameters that were entered for the suspension were pH, temperature and dust cutoff. The pH and temperature were measured and entered, while the dust cut off value was left at the default value of 30. For samples with very high or very low concentration the dust cutoff could be adjusted accordingly, but was not necessary for the GO samples. Once all of the parameters were entered, three runs at three minutes each were completed. The average of the effective diameters from the three runs was taken to be the particle size for that batch.

Zeta potential measurements were done in a similar fashion as the particle sizing. For this measurement a small probe was inserted into the cuvette with the suspension and was plugged into the machine while the cuvette was still in the holder. The zeta potential is a measurement of the surface charge of the GO surface. Higher zeta potential values

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indicate a more stable suspension. Zeta pals software was run to measure zeta potential. The parameters for the software were set to three runs at thirty cycles. The average zeta potential value of the three runs was considered the zeta potential for that batch. Once the software completed its measurement the probe was rinsed with ultrapure water to remove any GO that might have attached to the probe. The process for particle sizing and zeta potential was completed for each pH value tested. Both particle sizing and zeta potential measurements were completed using a 90Plus Particle Size Analyzer (Brookhaven Instruments Corporation, Holtsville, NY). An image of the device can be seen in Figure 28.

Figure 28: Particle size analyzer

3.4.6 Contact angle

Water droplet contact angle measurements were conducted in order to determine the nature of the fabricated GO membranes. A ramé-hart contact angle goniometer/tensiometer was used to conduct these measurements. A higher contact angle

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is indicative of a more hydrophobic membrane, while a lower contact angle represents a more hydrophilic membrane.

3.5 Methods to measure contaminant removal

3.5.1 Introduction

The potential of GO coated membranes to remove contaminants was tested. Both salts as well as organic dyes were used to test the efficiency of the produced membranes. Membranes created from Method 1 and Method 2 were tested for their removal efficiencies of salts and organic dyes. Two different salts as well as two different organic dyes were used for removal efficiency tests.

3.5.2 Rejection tests

Salt rejection tests were conducted by measuring the conductivity of a solution before and after passing through the GO membrane. Sodium hydroxide (NaCl) and sodium sulfate (Na_2SO_4) were used in this study. A solution of 0.1mM batch solution was created for both salts. The conductivity reading for the NaCl and Na_2SO_4 batch solutions was about 1.40µs/cm and 2.70µs/cm respectively. The conductivity was found by soaking the conductivity probe in the unfiltered or filtered salt solutions for about a minute and then measuring. The same procedure for measuring conductivity was done at ten minute time intervals after the solution was being pushed through a GO membrane using the same procedure for the pure water flux tests. The first test was done after 10 minutes to allow for enough filtered water to be available for a measurement. A portable Hach HQ14d conductivity meter was used for the measurement of all salt rejection tests. An image of the conductivity meter can be found in Figure 29.

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Figure 29: Conductivity meter

Organic dye rejection tests were completed in order to measure how well the GO membranes were able to remove organic materials. A UV-Vis spectrophotometer was used in order to measure the absorbance of dye in water. A Thermo Scientific NanoDrop 2000C spectrophotometer was used for all dye rejection tests. An image of the device can be seen in Figure 30.

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Figure 30: Spectrophotometer

The spectrophotometer was connected to a computer containing the appropriate software. The NanoDrop2000 software was able to calculate the absorbance of a solution based on a given wavelength. The wavelengths provided by the manufacturer were 555nm for Rhhodamine and 605nm from Methyl Blue. Rhodamine WT and Methylene blue dye were purchased from Fisher Scientific and Sigma-Aldrich respectively. Initially a set of ultrapure water samples had known concentrations of 50µL of Rhodamine or Methylene blue dye per liter of water. The absorbance of these samples was used to establish a standard curve between absorbance and concentration.

Unfiltered solution was made by adding 50µL of dye into one liter of ultrapure water. The dye was mixed in the container in order to create a homogenous solution. Approximately three milliliters of the solution was added into a cuvette. The same amount of pure water was also added into a cuvette. The cuvette with pure water was

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added into the NanoDrop spectrophotometer and the NanoDrop software was loaded on the computer. The absorbance wavelength was set at 555nm for Rhodamine WT. The pure water was used to blank the spectrophotometer. The absorbance measurement was consistently equal to or near zero for the clean water. The average of three measurements of absorbance was made for each sample.

Once the absorbance of the dye had been measured the remaining dye water was placed in the pressure vessel. The dye solution was filtered using the same method that was done to measure the pure water fluxes. Flux was still recorded for dye solution to compare against pure water fluxes. Once the dye solution had been filtered, the absorbance of the filtrate was measured again using the spectrophotometer. The average value found was then plotted on the absorbance versus concentration plot in order to estimate the final concentration. The removal rate of dye was calculated as the difference in the influent and effluent dye concentrations.

3.6 Methods to test bacterial inactivation

3.6.1 Introduction

The bactericidal property of the GO membranes was tested. When biofilms form on membranes it leads to a higher rate of fouling. The inherent oxidative properties of GO make it a possible candidate for inactivating microbes. Coating membranes with substances that can slow the formation of biofilms ultimately increases the life expectancy of filters and makes them a more cost effective treatment process.

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3.6.2 Bacterial inactivation tests

E. coli was used in the inactivation tests. Lysogeny broth (LB) medium were inoculated with bacterial stock solutions. The LB medium was formed by combining 1L of ultrapure water, 10g of tryptone, 5g of yeast and 10g of NaCl. The mixture was stirred and subsequently autoclaved. A LB agar medium was created in the same way as the LB medium except 15g of agar was added to the solution prior to autoclaving. The LB agar medium was poured into petri dishes.

The plates were then placed in a refrigerator upside down until use. The agar plates were used as a surface for the *E. coli* to grow. A 0.9% saline solution was created by adding 9g of NaCl into1L of ultrapure water and then autoclaved.

After the solutions had been created and the plates were solidified, 100uL of thawed *E. coli* stock solution was transferred to 100mL of LB medium using an autoclaved pipette. The solution was placed in an Erlenmeyer flask covered with a cotton ball that had been previously autoclaved, and placed in an incubator at 37^{o}C on a mixer at 90rpm for six hours to reach a cell density of 10^{8} colony forming unites per milliliter (CFU/mL).

Upon harvest the *E. coli* solution was measured using the bacterial cell count tool on the UV-Vis spectrophotometer. A sample of LB medium was used to blank the spectrophotometer. Following calibration, the OD600 value of the bacterial solution was measured three times and the average value was recorded. The value was converted to CFU/mL by using a previously created conversion curve for OD600 to CFU/mL. The initial concentration was usually in the range of 10^{8} CFU/mL.

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Following the determination of the bacterial solution's concentration, 20mL of the solution was centrifuged at 9000g for 12 minutes at 4^{o}C in order to wash the bacteria. Following the centrifuge the supernatant was discarded and 10mL of the saline solution was added into the centrifuge tube with the bacteria. The bacteria and saline were then mixed in a vortex mixer until the bacteria was completely dispersed in the saline. The solution was then washed 3 more times using the same procedure. Following the final centrifuge step the supernatant was discarded and 20mL of saline was added to the bacteria prior to vortex mixing. By adding 20mL after the final wash the concentration of the solution was expected to be the same as the initial solution. The concentration was again measured using the UV-Vis spectrophotometer. Once the concentration was determined the solution was diluted to $1*10^5$ CFU/mL using the saline solution.

In each inactivation test, six membranes were tested: three membranes with a GO coating produced using either Method 1 or Method 2, and three polyethersulfone membranes as a control. The membrane was placed on a vacuum filtration stand which had been previously autoclaved. Using an autoclaved pipette tip 1mL of bacterial suspension was added onto the surface of the membrane. Approximately 1.5mL of saline solution was added on top of the membrane as well in order to better spread the bacteria around the entire surface of the membrane. The vacuum was then turned on to pull the solution through the membrane while *E. coli* remained on the membrane surface. The membrane was then placed in a petri dish and 2mL of saline solution was placed on top of the membrane surface to keep it moist. The membrane is kept moist in order to ensure that the death of the bacterial cells is due to the membrane surface and not the drying of the membrane. The start time was marked on the petri dish for when the E.coli was

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placed on the membrane. One GO coated membrane and one blank membrane was tested for 1 hour, 3 hours and 6 hours, thus resulting in six total membranes.

After the allotted time had passed for a specific membrane the membrane was rinsed by dipping the membrane vertically in a centrifuge tube filled with saline. A second rinse was done in a second tube filled with saline. Finally 25mL of saline was added to a centrifuge tube and the membrane was placed in the solution. The solution with the membrane was placed in a sonicator bath for 7 minutes to exfoliate the active cells from the membrane. The tube was then vortex mixed for ten seconds to create an even suspension of the bacteria. The membrane was then removed from the tube and discarded.

Once the final bacterial suspension following the contact with the membrane surface was produced it could be spread on the agar plates created previously. The agar plates provide a medium for the remaining living cells to grow. From the tube, 100µL of the bacterial suspension was added to an agar plate and spread evenly over the plate. The process was repeated for two more plates for a total of 3 plates per membrane. A 10-fold dilution was created as well by adding 100µL of bacterial solution to 900µL of saline. The suspension was vortex mixed and 100µL of the created dilution was pipetted onto an agar plate and spread. Again, the process was repeated two more times for a total of three plates. The plates were labeled and then placed upside down in an incubator at 37^{o}C for 24-48 hours in order to allow the colonies of *E. coli* to fully grow. Once the necessary time had passed the cells were counted using a standard plate count method. Plates with colonies between the count of 30 and 300 were considered valid.

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The values of the GO coated membranes were compared against the control membranes. The bacteria on the membranes were also compared for the different time intervals to see if longer contact times with the membranes increased the inactivation of the cells.

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Chapter 4: Results

4.1 GO Membrane Characterization

4.1.1 Characterization of GO suspensions

4.1.1.1 AFM imaging

The properties of graphene oxide (GO) flakes in the suspension were characterized using Atomic Force Microscopy (AFM). A 15µm by 15µm AFM image was taken with a side by side comparison of the height profile and surface roughness (Figure 31). In the height profile image on the left of Figure 31, particles that are higher are displayed as a lighter color while lower surfaces are darker. In this instance the dark red is the silicon base and the white surface is an individual GO flake. The surface roughness on the right side of the image more clearly reveals a rough GO surface. A more detailed depiction of the height profiles is provided in Figure 32. The upper left of the image shows the graphical representation of the difference in height from the silicon (red triangle on the right) to the GO flake (red triangle on the left). The difference is represented as the "Vert distance" on the right side of the image. The height of this particular GO flake is 1.189nm. Multiple flakes were measured for their height profiles. Values ranged from 1.0 to 1.2nm.

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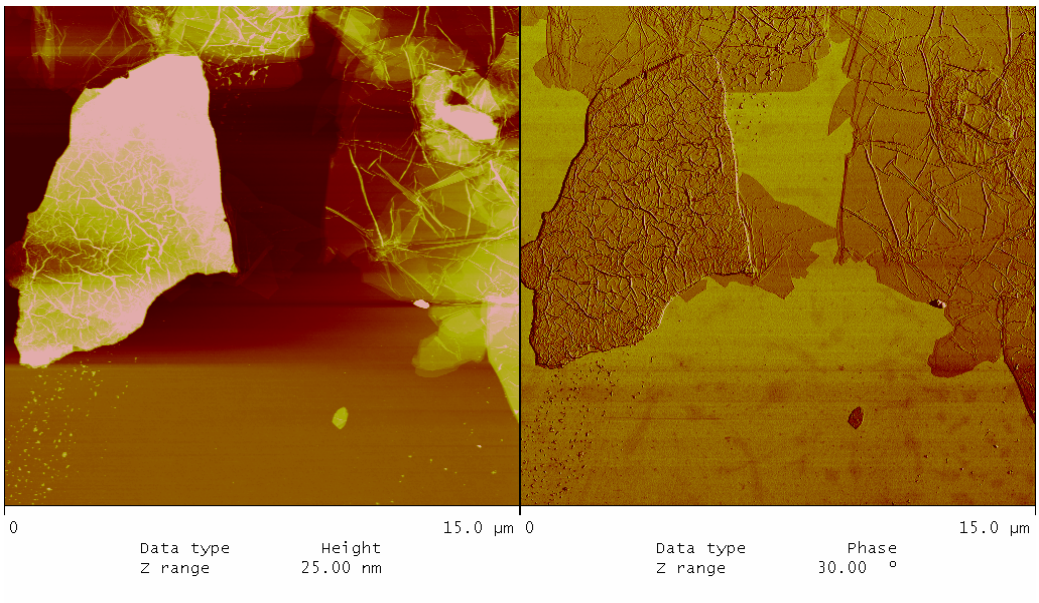

Figure 31: AFM image of GO flake height profile (left) and surface roughness (right)

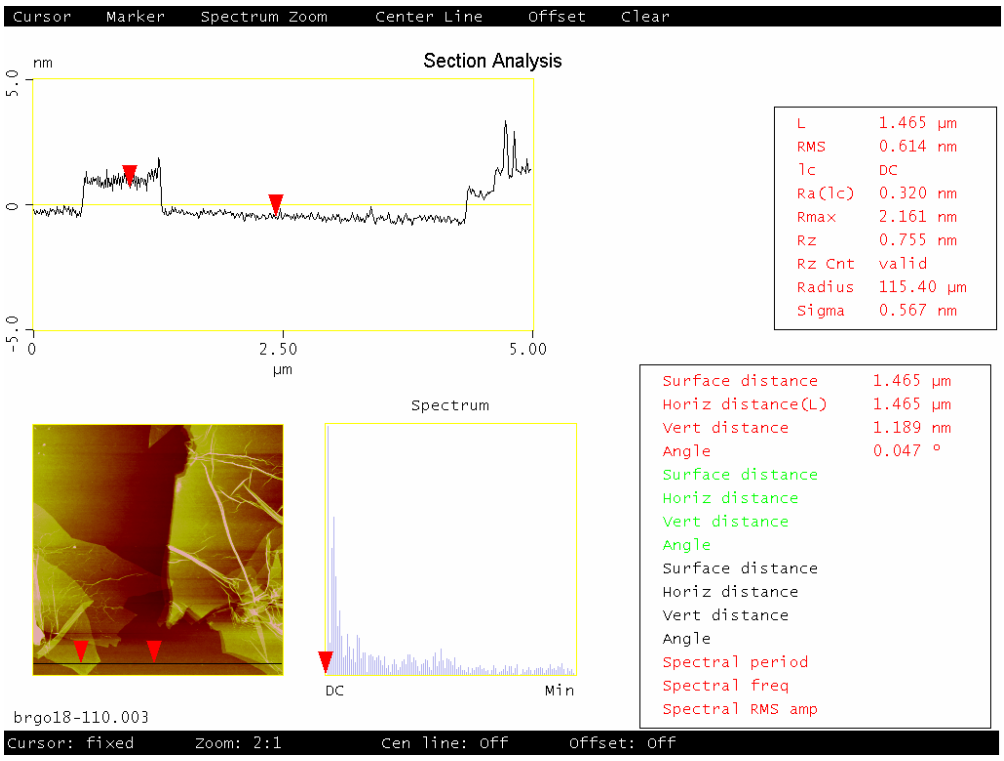

Figure 32: AFM height profile of GO flakes

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4.1.1.2 Zeta potential and particle sizing measurements

In order to better understand the stability of the GO coated membranes the zeta potential and particle size distribution of the GO flakes in the suspensions were measured over varying pH values. A portion of the black stock GO suspension created using Method 1 was used. Figure 33 displays the particle size measurements that were conducted for four different suspensions of modified GO that were created. The four suspensions were taken from four different batches of modified GO that were created. The pH measurements ranged from 4.0-10.0 for the particle sizing. Readings outside of this pH range were inaccurate. Inaccuracies can be attributed to the natural variations in GO flake size, how well mixed the suspension is and the geometry of the flakes. The natural variations in GO flake sizes is apparent as the average batch size ranged anywhere from about one micron to almost five microns in size with the average value being near 2.5 microns. Following the sonication of the GO flakes, size distribution can vary greatly from one flake to another. The larger flakes tend to settle faster in suspension, therefore mixing the sample prior to measurements was important. Even with mixing it can be difficult to obtain a representative sample for the entire batch. Measurements conducted on a non-representative sample of the entire suspension are a likely source of error. The shape of the flakes plays a large part in the error associated with the particle size measurements as well. Particle size measurements are based on the principle of dynamic light scattering. For this process the flakes are considered spherical, therefore the size measured is an equivalent spherical particle. While the specific measurements for particle size are estimated, there is still information and trends that are useful for characterizing the GO flakes.

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Samples 1 and 2 provided for the most consistent particle size values across varying pH values, while the particle sizes of samples 3 and 4 were less consistent. The inconsistencies can be attributed to the inherent variations in flake size with GO as no trend was found when compared with the pH values. Larger GO flakes may be more difficult to break during the sonication stages, therefore the final particle size measurements is highly dependent on the initial size of the flakes used in Method 1's procedure. The size variations within an individual sample are likely due to the small sample size taken from the larger suspension to be used for the measurement. The particles size measurements coincide well with the AFM images which revealed flakes over 6.0µm in effective diameter. Smaller flakes had a diameter less than 0.5µm in diameter. A While it is difficult to predict the size of GO flakes that will be present in the final suspension, the size is not likely to have a major effect on the contaminant removal or bactericidal properties of the GO.

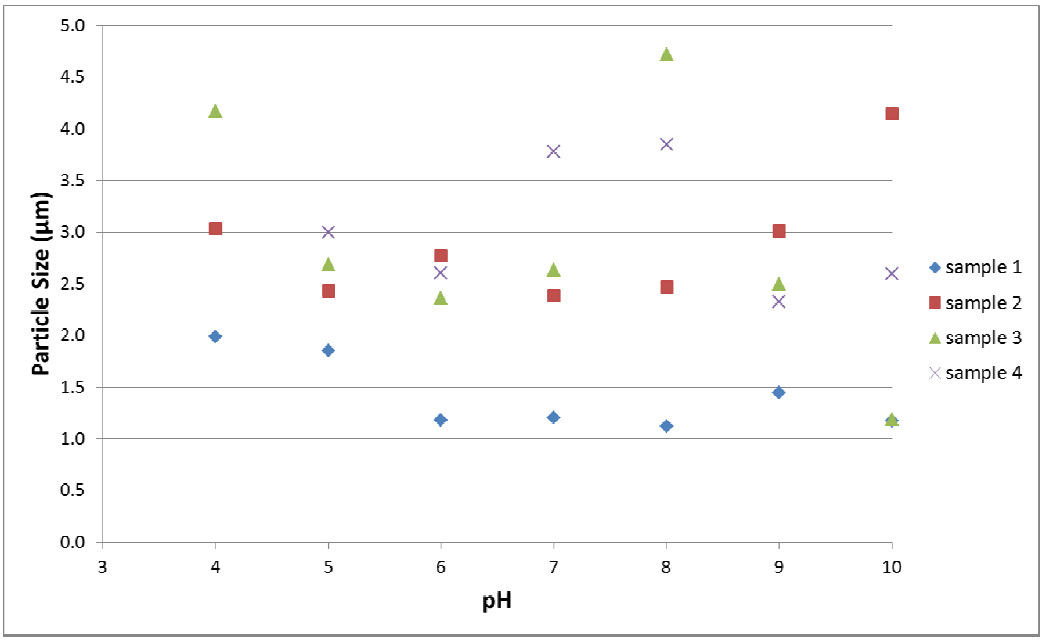

Figure 33: Particle size of GO flakes vs pH

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Along with the particle size measurements zeta potential was conducted in a similar manner to further understand the stability of the GO flakes in suspension. Zeta potential was measured in millivolts. The results of the zeta potential measurements can be found in Figure 34. Zeta potential values were measured for pH values ranging from 3.0-10.0. The average value for zeta potential was measured at -38.5mV representing a stable suspension. Higher pH values resulted in a slightly less stable GO suspension, but even the most dramatic drop to -31mV is still representative of a high surface charge. In general GO has a highly negatively charged surface, it does not appear that varying pH values has any significant effect on the stability of the GO suspension. The zeta potential of the GO suspension was measured after a one month period as well as a two month period in order to determine if there were any changes over time. Zeta potential values remained near the average -38.5mV for both time periods indicating that the temporal dimension had even less effect than the varying pH values. Having a stable GO suspension allows for the suspension to be used for a longer time period, and indicates that GO coated membranes could be effective at treating water with varying pH values.

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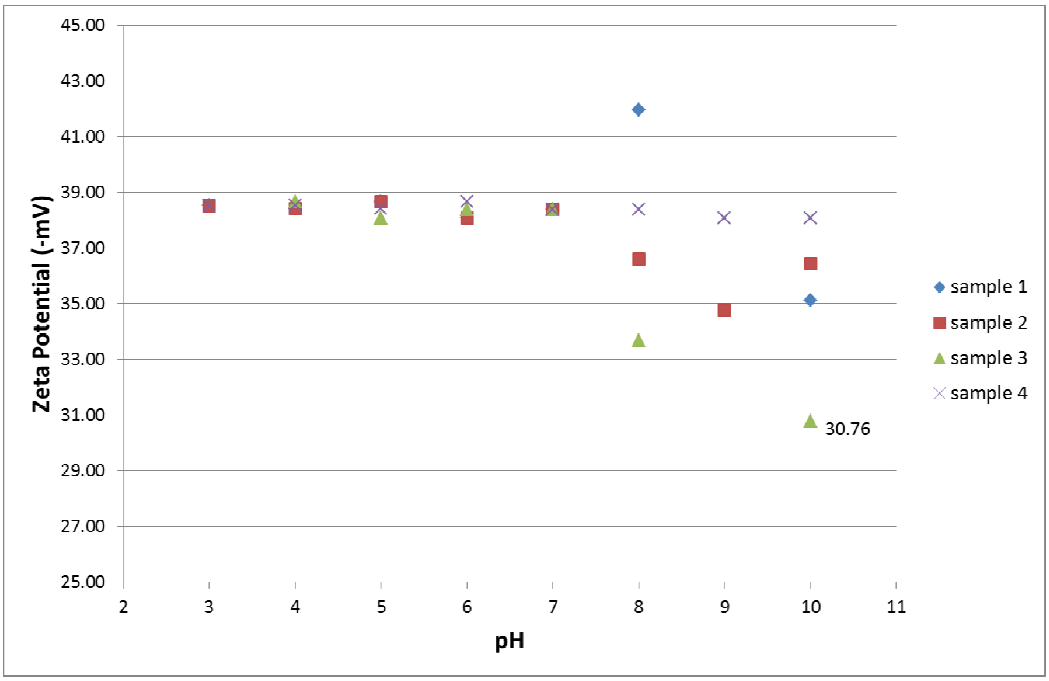

Figure 34: Zeta potential of GO flakes vs pH

4.1.2 Characterization of GO Membrane

4.1.2.1 Pure water flux

Pure water flux measurements were conducted for membranes created using Method 1. Flux measurements were completed for membranes containing various thicknesses of GO coatings. The thickness of a GO layer is measured as milligrams of GO per square meter of membrane (mg/m^2) and is referred to as the loading rate. Five loading rates between the range of $50mg/m^2$ and $300mg/m^2$ were recorded for their pure water flux values. Figure 35 shows data collected from typical pure water flux measurement experiments.

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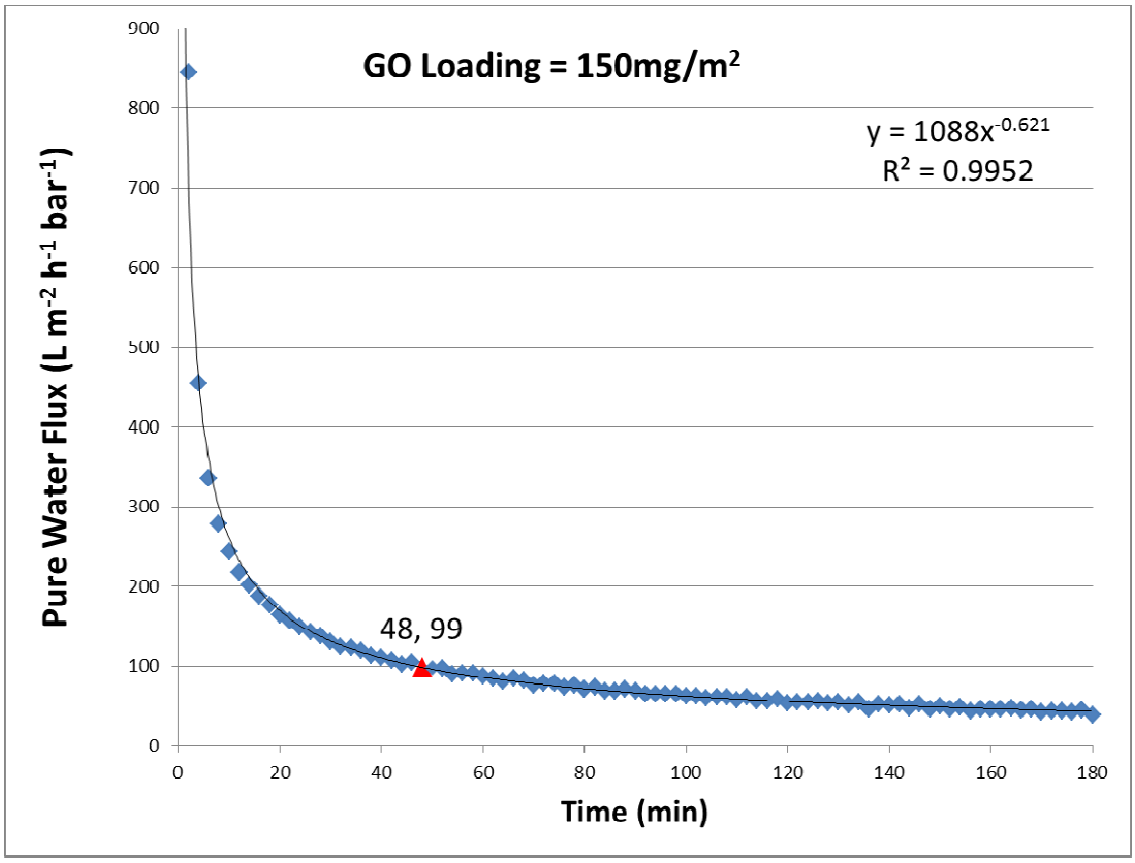

Figure 35: Typical pure water flux measurement

The pure water flux measurement was recorded over a three hour period for this particular example. The flux values for the individual membrane drop dramatically in the first twenty minutes. The reported flux was measured at the point where the value has become stable. The point of stability was determined by fitting a curve to the data, and finding the point at which the second derivative was equal to one. The point on the curve is highlighted with a red triangle and labeled with the appropriate time and flux value. For the example shown in Figure 35, a time of 48 minutes was recorded as the point of stable flux and the corresponding flux was 99 L m^{-2} h^{-1} bar^{-1}. It is important to note that the point of stable approach mentioned above is different from previous studies (Han et

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al., 2013, Hu & Mi, 2014) that quantified water flux by recording the flux after a given time increment. We found that the time needed to approach a stable flux can vary from membrane to membrane depending on how fast the flux values stable out, hence why the second derivative of the curve was considered to be more reasonable. From the figure, the corresponding equation for the curve can be found along with the R^2 value. The R^2 value over 0.99 was found in almost all pure water flux measurements which provide a high confidence level in the individual tests.

Pure water flux tests were run for various membranes containing the same GO loading rate. Multiple water flux tests (at least 3) were run for each GO loading rate, and the combined flux values were averaged and reported as the flux value for the specific loading rate. The flux values for various loading rates can be found in Figure 36. The amount of membranes tested is shown in parenthesis for each loading rate.

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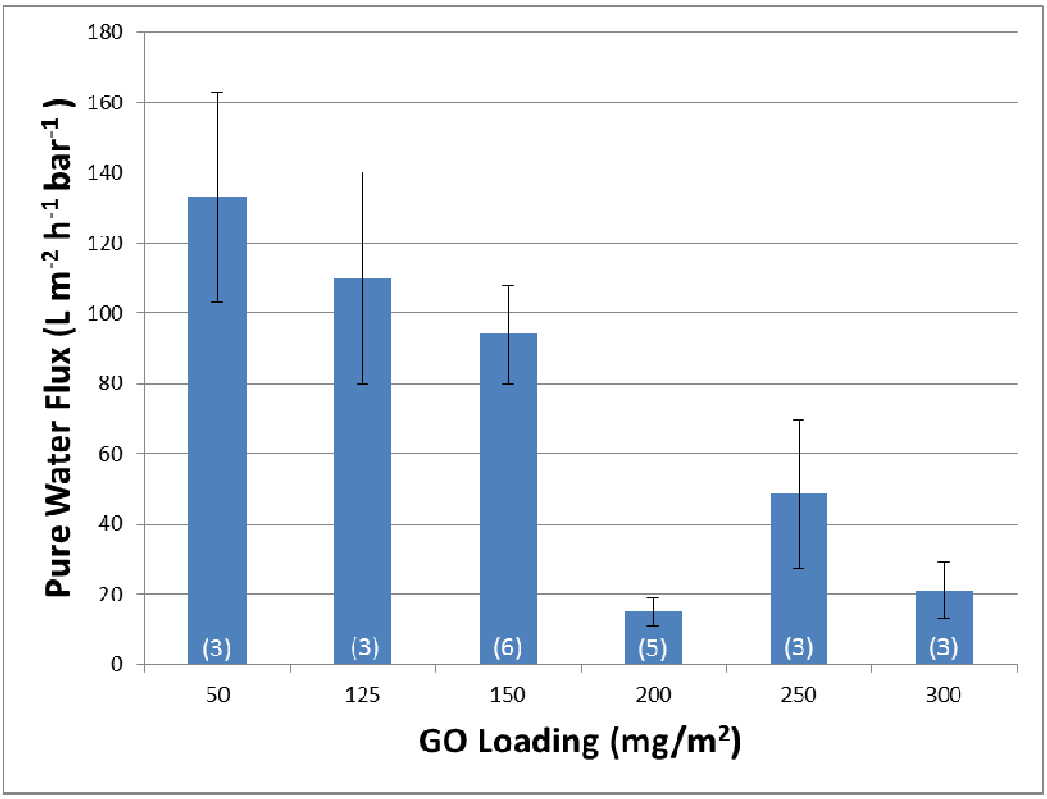

Figure 36: Pure water flux values for various GO loading rates

The figure reveals an overall trend in decreasing flux values with an increase in GO thickness. The only outlier lies with the loading rate of 200 mg/m^2 which had an unexpectedly low flux value. This instance, as well as the error bars at a maximum of 30 L m^{-2} h^{-1} bar^{-1} can be attributed to the variations in individual GO coated membranes. Instances where more membranes were tested resulted in a decrease in the error bar range. It is expected that with an increased number of pure water flux trials for membranes at every loading rate tested a linear trend will continue to be better developed.

Values for flux ranged anywhere from 16 to 133 L m^{-2} h^{-1} bar^{-1} for the GO coated membranes created using Method 1 on a polyethersulfone membrane. Compared with a polyethersulfone membrane with no coating of GO the pure water flux significantly has a

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reported pure water flux value as high as 12,000 L m^{-2} h^{-1} bar^{-1} (emdmillipore.com). The GO coating results in a dramatic drop in the flux values therefore it is evident that the coating has a significant impact in reducing the pure water flux rate. Typical values for nanofiltration devices range anywhere from 20-50 L m^{-2} h^{-1} bar^{-1}, while ultrafiltration devices range anywhere from 30-150 L m^{-2} h^{-1} bar^{-1} (Benjamin & Lawler, 2013). The values for the GO coated membranes at higher loading rates fall within the typical nanofiltration range while the lower loading rates reach the higher end of the typical ultrafiltration devices. The pure water flux values discovered reveal an appropriate value for the use in water purification systems.

Pure water flux values were measured for membranes created using Method 2 as well; however, the values were too high to gather accurate readings.

4.1.2.2 SEM imaging

Scanning Electron Microscopy (SEM) images were taken for membranes created using Method 1 and Method 2 as well as polyethersulfone membranes with no GO coating. All images were taken at the same magnitude of zoom except for instances where close up visuals were needed to enhance a particular feature. A scale is located at the bottom right of every SEM image. Images that were zoomed in further were done so at a 10x zoom when compared with the other images. The scans are approximately 30µm by 30µm except for the close up images. The image of the polyethersulfone membrane (Figure 37) displays the woven structure of the membrane. The membrane has an effective pore size of 0.45µm, but from the SEM image it is clear that the individual pore's range in size. The range should not have any significant effect on the results from

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the membranes coated with GO. Images from GO coated membranes following Method 1 can be found in Figures 38-40.

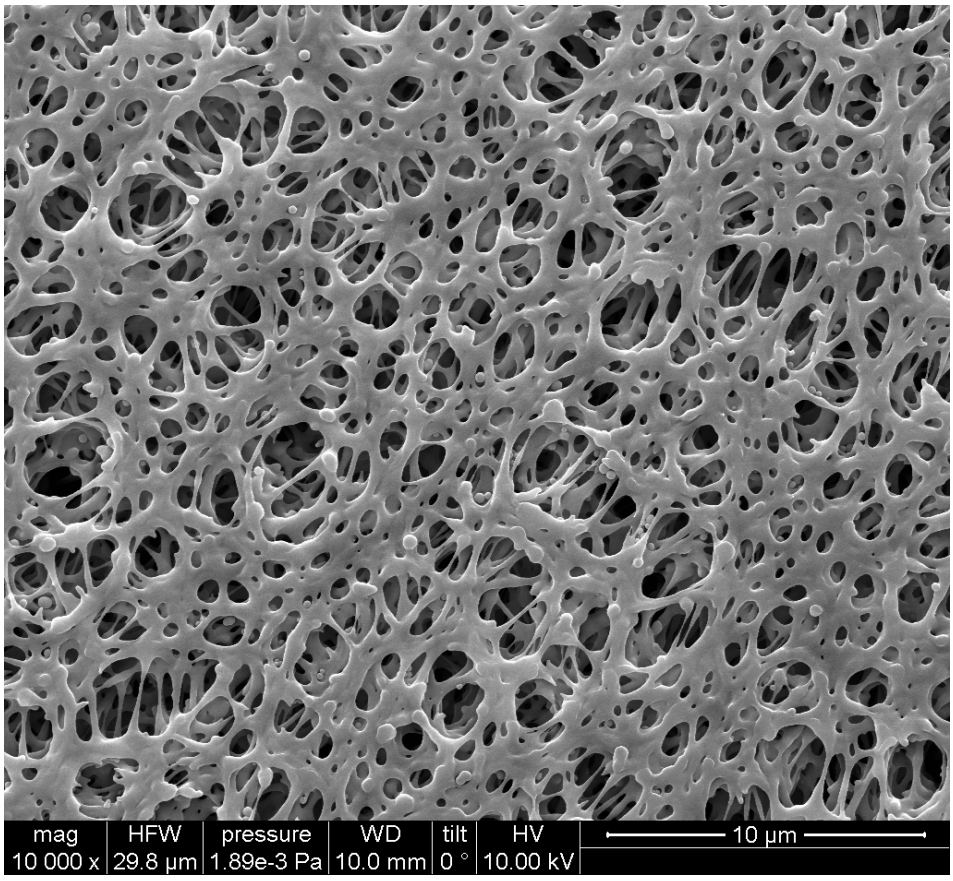

Figure 37: SEM image of polyethersulfone membrane

An SEM image was taken of the edge of a GO coated membrane where the polyethersulfone and GO coating met (Figure 38). While the surface of the membrane near the edge appears to be uneven it is clear that there is a significant GO deposit onto the polyethersulfone membrane. The coating is still somewhat transparent due to the low conductivity of the GO even following the sputter coating process. It is clear from the SEM image taken far away from the edge (Figure 39) that the GO exhibited full coverage

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over the polyethersulfone membrane. Multiple places amidst the membrane were scanned in order to ensure a complete coating of GO. The coatings for the images shown using Method 1 were taken of a GO membrane with a loading rate of 50mg/m^2 which is the thinnest membrane used in the study. While the support membrane is completely covered there appears to also be a crack in the GO surface. Cracks in the GO surface are a potential source of error in the pure water flux measurements that were completed. Membranes with a higher percentage of cracks could result in a higher pure water flux value. Along with cracks the images also reveal a wrinkled GO surface which coincides with the AFM images shown previously. A close up view of the surface can be seen in Figure 40. Distinct wrinkles are formed as the GO sheets stack on top of one another (Rourke et al., 2011).

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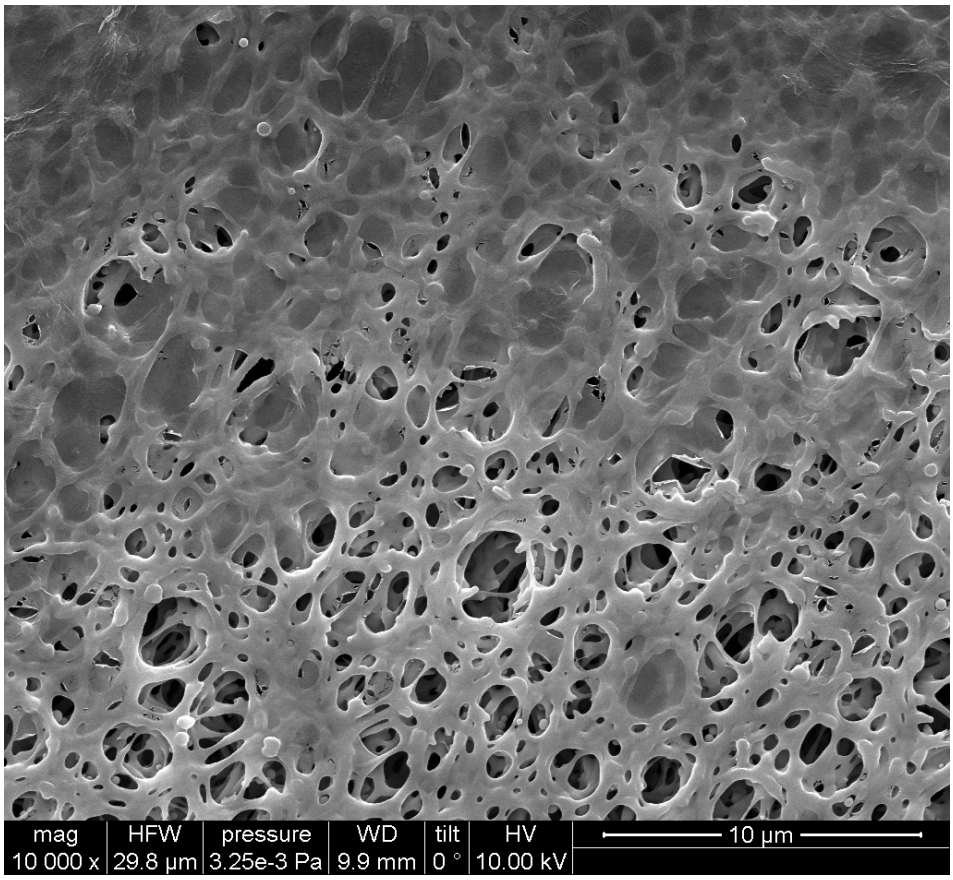

Figure 38: SEM image of polyethersulfone membrane at the edge of a GO coating

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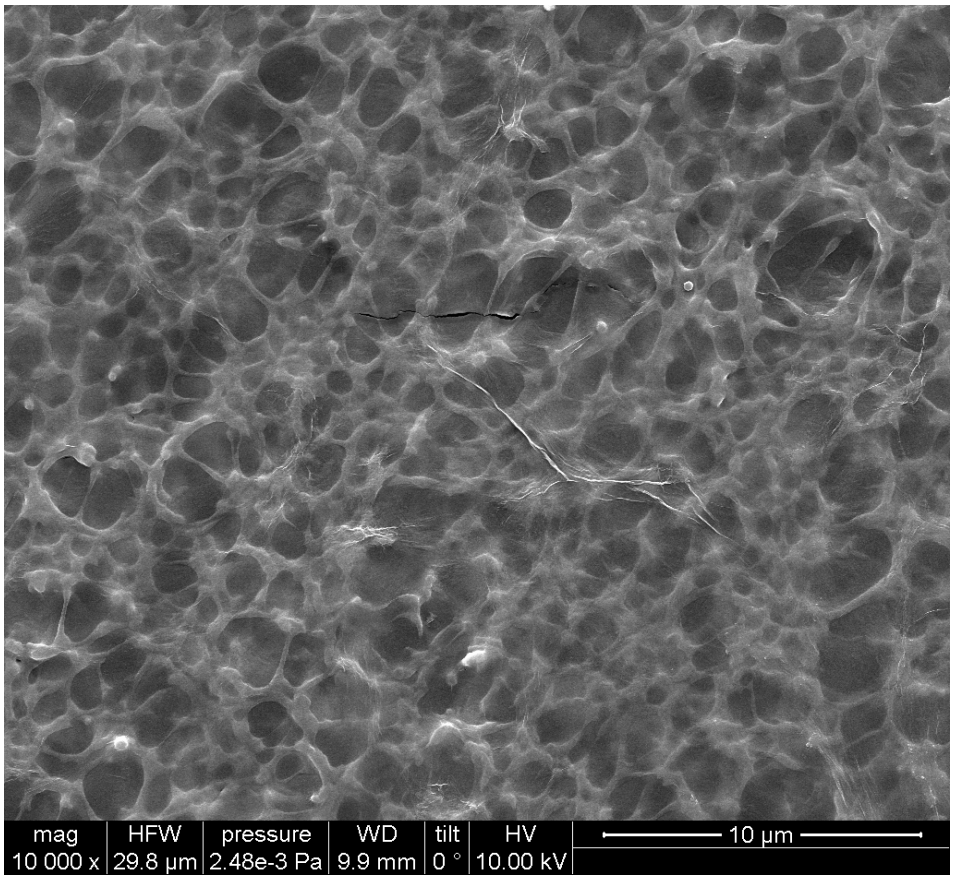

Figure 39: SEM image of polyethersulfone membrane with GO coating

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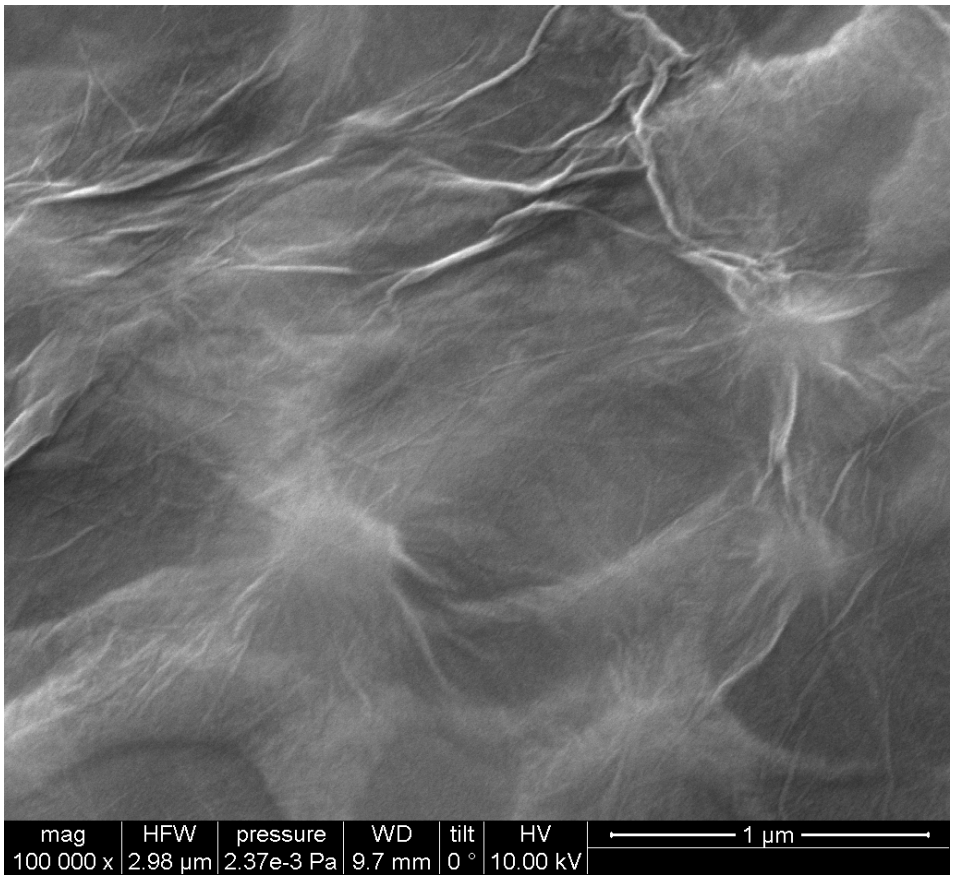

Figure 40: SEM image of polyethersulfone membrane with GO coating (close up)

The SEM images of the membranes using Method 2 can be found in Figures 41-43. Figure 41 represents the polyethersulfone membrane following the dopamine process as well as the addition of a coating of TMC. The image reveals a lack of TMC coverage. The lack of TMC cover is likely due to the difficulty of dissolving the TMC in the Isopar substance. The dopamine deposition is not visible on the SEM image, but is apparent by the darkened color of the polyethersulfone membrane following the process. An image following the deposition of GO on top of the TMC and dopamine (Figure 42) reveals a lack of coverage of GO. The wrinkled flakes on the membrane reveal some deposition of GO, but there is not complete coverage over the entire surface. The challenges of

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dissolving the GO in Isopar resulted in a suspension with a low concentration of GO which in turn resulted in a limited coverage of GO on the polyethersulfone membrane. A close up view of the coated membrane in Figure 43 represents a cluster of TMC that was unable to be dismembered during the mixing step. The limited coverage of GO as well as TMC resulted in high pure water flux values and is likely to cause limitations in contaminant removal and bacterial inactivation.

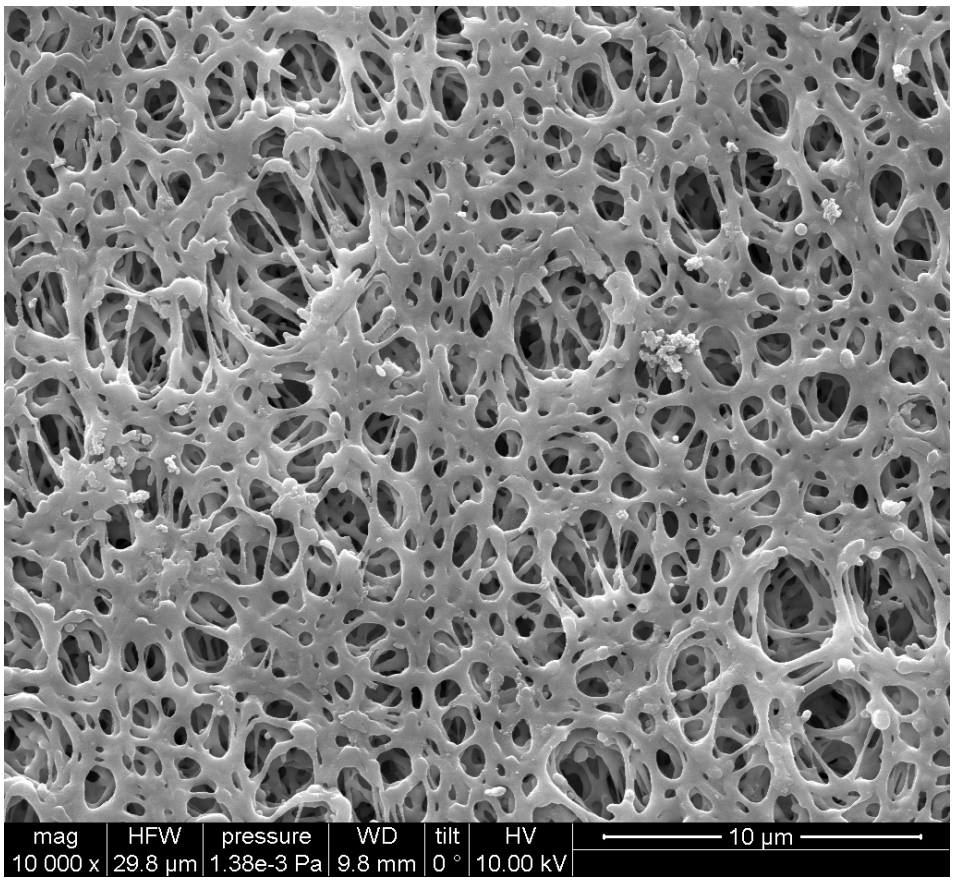

Figure 41: SEM image of polyethersulfone membrane with dopamine and TMC coating

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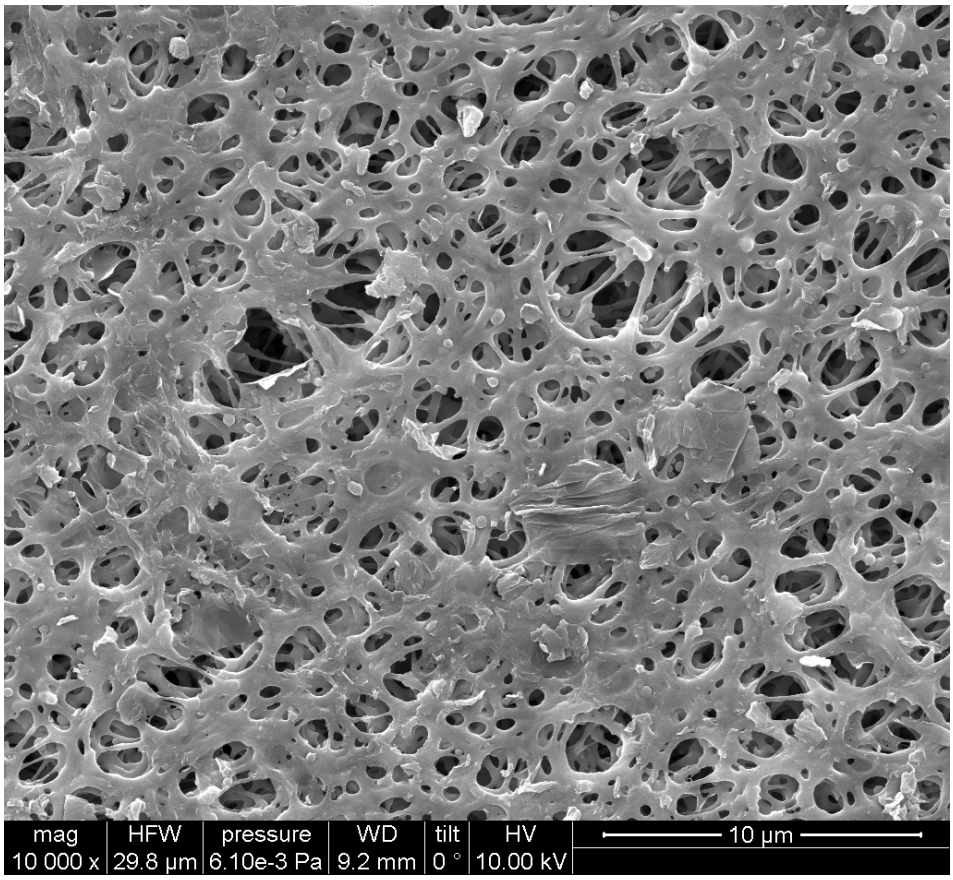

Figure 42: SEM image of polyethersulfone membrane with dopamine, TMC and GO coating

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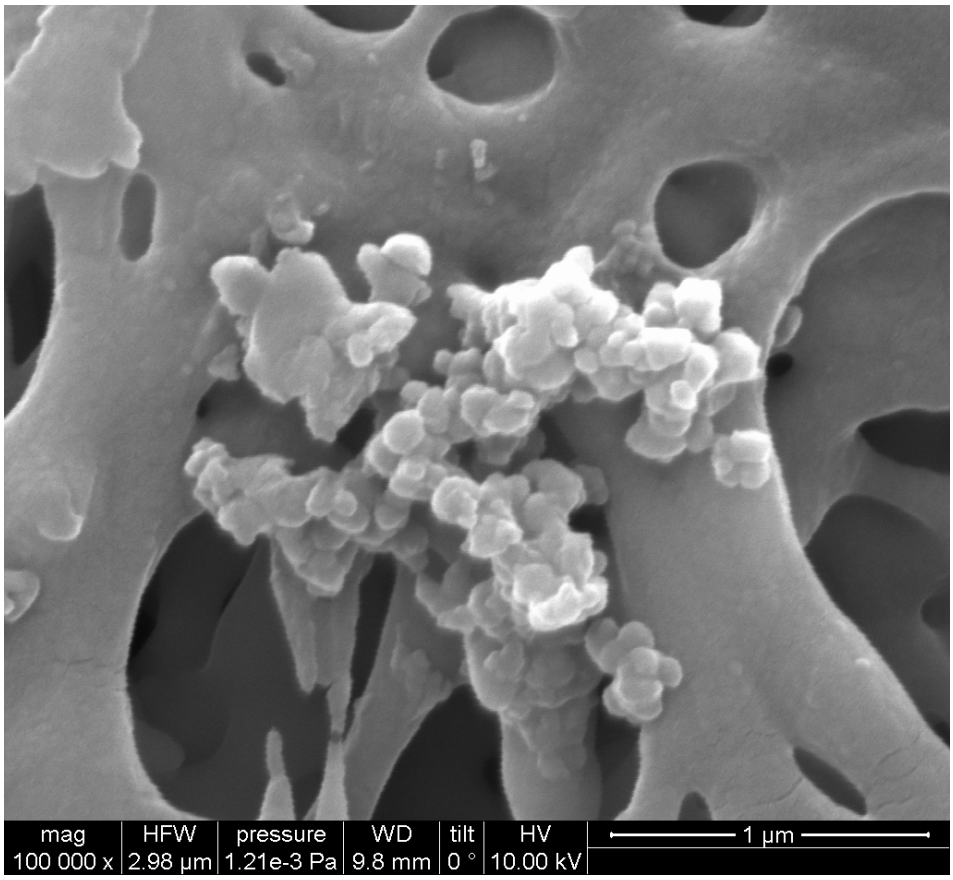

Figure 43: SEM image of polyethersulfone membrane with dopamine, TMC and GO coating (close up)

4.1.2.3 FTIR measurements

Fourier Transform Infrared Spectrometry (FTIR) measurements were conducted in order to better compare the functional groups within the membranes created. An image of the FTIR measurement taken in order to compare membranes from Method 1 is shown in Figure 44. The peaks in the figure represent various chemical bonds taking place within the membranes. Measurements were taken for a polyethersulfone membrane, and two membranes of varying GO thickness developed using Method 1. There are no major differences in the locations of the peaks between the three membranes which is expected

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since the only difference between the three is the amount of GO being used. There are two major takeaways from the FTIR results. First the peak on the left hand side of the figure reveals the presence of water within the sample. The membrane with no GO coating has no peak and therefore no water in the sample. The membrane consisting of the GO loading of 50mg/m^2 contained a small amount of water while the thicker 150mg/m^2 GO coated membrane revealed an even higher amount of water. The same volume of water is used in the vacuum filtration process during Method 1 which is where the polyethersulfone membrane is introduced to the GO suspension; therefore the extra content of water found in the FTIR measurement is likely contributed by excess water contained within the GO sheets. Secondly the variations in the percent transmittance are an indicator of the thickness of the GO coating. The polyethersulfone membrane stays consistently around the 100% transmittance. Similarly the thinner GO coated membrane also stays around the 100% transmittance mark which reveals that there is only a thin coating of GO present on the surface. The drop in transmittance for the thicker GO coated membrane ensures what was also confirmed with the SEM images that full coverage is in fact present on the polyethersulfone filter. The loading rate of 50mg/m^2 was the lowest amount that provided complete coverage of GO over the polyethersulfone membrane (revealed by the SEM images). FTIR measurements were also conducted for membranes created using Method 2. The results were similar to that of the polyethersulfone filter which coincides with the SEM results that there was not complete coverage of TMC and GO across the polyethersulfone filter.

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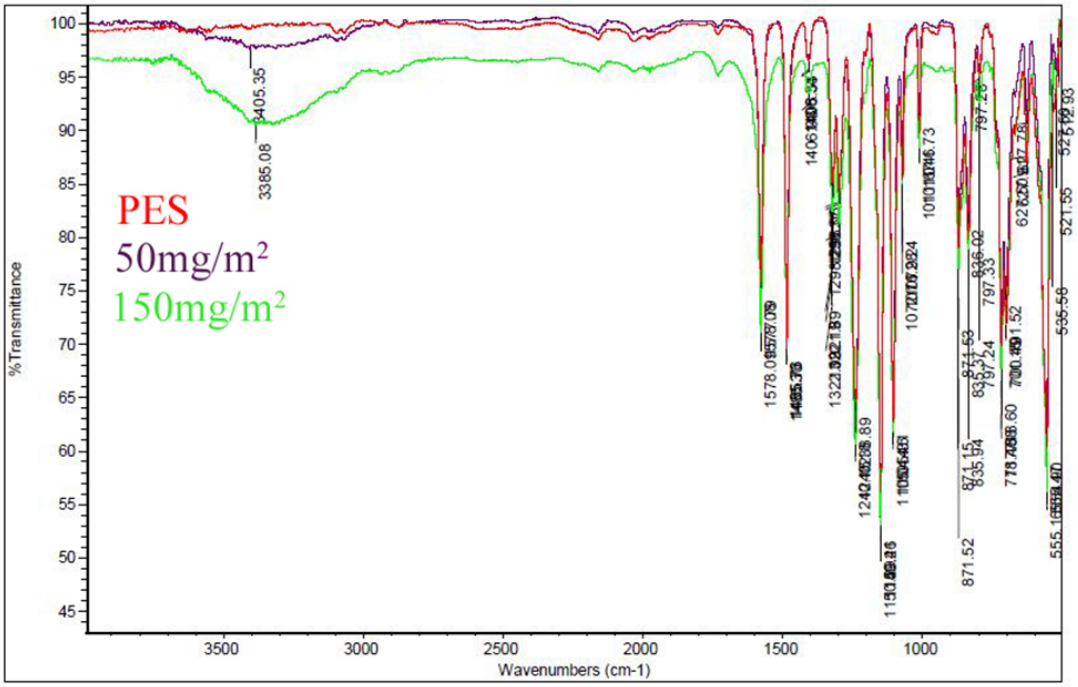

Figure 44: FTIR measurements

4.1.2.4 Contact angle

Contact angle measurements were conducted in order to better understand the hydrophobicity of the GO membranes. The contact angle for a membrane created using Method 1 (Figure 45) was compared against a membrane that was created using GO that was not modified (Figure 46). Contact angle measurements were not able to be conducted for the membranes created using Method 2 because the surface was not able to support a water droplet. The membrane created using Method 1 displayed a much higher water contact angle of 59 degrees when compared with the unmodified GO membrane which resulted in a contact angle of 28 degrees. The increase in the hydrophobicity can be attributed to the addition of NaOH, when modifying GO, which decreases the polar functionality of the membrane (Dreyer et al., 2009). The increase in the contact angle

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suggests that the modified membrane is likely to be able to have a higher water flux value than that of the more hydrophilic membrane that was created without the modification of the GO.

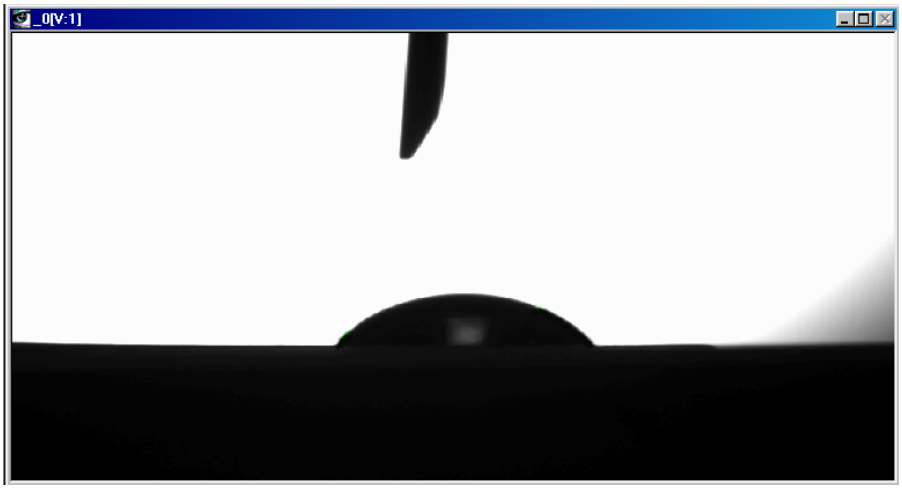

Figure 45: Contact angle for Method 1 membrane (59^{o})

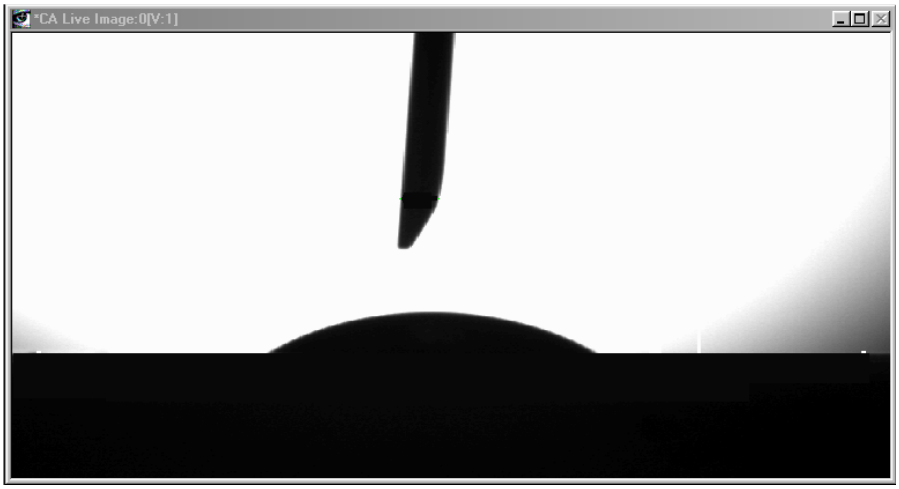

Figure 46: Contact angle for unmodified GO coated membrane (28^{o})

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4.2 Contaminant removal

The following section contains information on the contaminant removal capabilities of the GO coated membranes created using Method 1 and Method 2.

4.2.1 Salt rejection

In order to test the ability of GO membranes to remove dissolved salts from water 0.1mM NaCl and 0.1mM Na_2SO_4 solutions were used. The concentration of salt allowed for a high enough conductivity reading so that any reduction in concentration that occurred after passing through the GO would be significant enough to provide accurate results.

For membranes formed using Method 1 as well as Method 2 insignificant salt rejection was observed. A maximum rejection of 4% and 2% of Na_2SO_4 and NaCl respectfully was observed for membranes formed using Method 1. For Method 2 no rejection values were higher than 1% for either of the salts. The small differences in conductivity values were likely contributed to the sensitivity of the conductivity meter. In most instances the effluent conductivity was close or equal to the influent conductivity, for both types of GO coated membranes, indicating no salt rejection. Various loading rates of GO were tested, but no trend was found indicating that the thickness of the GO coating improved the salt rejection values.

The limited salt rejection for GO membranes created using Method 2 is due to the inability to obtain complete GO coverage on the support membrane. For the membranes created using the Method 1, one possible explanation for the poor salt rejection could be that there is swelling present between the GO sheets. The FTIR measurements indicated a

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significant amount of water present in the GO which could be causing the spacing between the GO surfaces to expand allowing for a larger effective pore size. Reducing the spacing between the GO sheets would likely result in more appealing salt rejection values. Another reason for the poor salt rejection values could also be due to the way the rejection was measured. The GO flakes are negatively charged and are more likely to reject only the anionic species of the salts. Therefore, conductivity may not be the best method to measure the rejection of salts. Another method in order to test salt rejection values could be to measure the pH value of the salt solution in order to give a better idea if cations are more easily being passed through the GO coated membranes.

A 2014 study by Joshi et al. found that smaller ions were able to permeate through GO coated membranes thousands of times quicker than was expected. They attributed the behavior to nanocapillaries that open up when in a hydrated state. Method 1 for producing GO coated membranes was based off of a study by Han et al. in 2013. The GO coated membranes from their study were also run under a hydrated state, but produced salt rejection as high as 60% as seen previously in Figure 4. The same method was attempted to be duplicated by another study group (Hu & Mi), which found that the vacuum filtration process resulted in a pasty GO coating that was unusable for filtration purposes. The varying results from the method are likely linked to how the GO was produced. For our study the purchased GO was produced using the modified Hummer's method. While the same method was reportedly used for both other studies, slight modifications in the preparation of the GO could contribute to the varying results from each of the studies.

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4.2.2 Organic dye rejection

Both Methyl Blue and Rhodamine-WT organic dyes were used in order to measure how well the membranes were able to reject dissolved organic contaminants. The 50µL of dye per 1L of ultrapure water used as the starting concentration allowed for a high enough concentration in order to accurately measure influent and effluent values. A relationship between measured UV-Vis absorbance and concentration was developed as standard curve to estimate concentration as shown in Figure 47. From 10µL to 60µL of dye an accurate linear relationship formed shown by the R^2 value near one. Concentrations that were higher than 60µL per liter of water strayed from the linear relationship of absorbance.

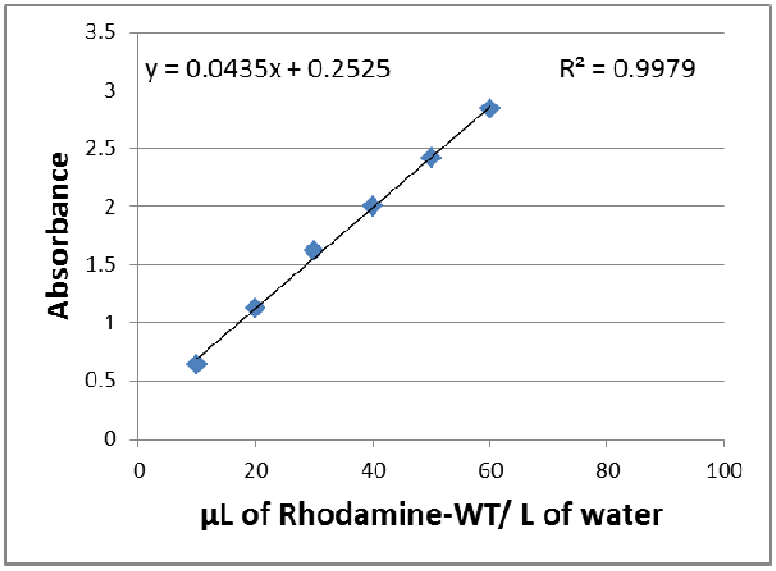

Figure 47: Relationship for Absorbance versus concentration for Rhodamine-WT dye

A limited amount of organic dye rejection was observed for membranes formed using Method 1 and Method 2. A maximum of 1% rejection of Rhodamine-WT dye was observed for membranes created using both methods, and is likely due to experimental

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errors rather than rejection by the membrane. For the Methyl Blue dye limited rejection was also observed. Influent and effluent absorbance values of Methyl Blue dye were compared against one another. There was no significant change in absorbance; therefore there is no evidence that suggests that the GO coated membranes created using either method were able to retain the Methyl Blue dye. Another possible explanation for the limited dye rejection could likely be due to the properties of the GO purchased. While the GO is reported as being produced using the modified Hummer's method, variations in the process compared to that of other studies is unknown. The 2013 study by Han et al. reported using a modified Hummer's method as well, yet produced over 99% rejection of similar dyes. It is expected that some rejection due to sorption would be accounted for in the rejection tests. Since no rejection was measured it is likely that some properties of the GO itself may not be comparable to the produced GO in Han et al.'s study. Producing GO as opposed to purchasing could result in more favorable rejection values.

4.3 Bacterial inactivation

Bacterial inactivation tests were conducted for the membranes formed from Method 1. The GO coated membranes were compared against the base polyethersulfone membranes for all of the tests, and it was assumed that no inactivation of bacteria took place on the polyethersulfone membranes.

Results from the bacterial inactivation experiment are shown in Figure 48. There were 92% of cells remaining after the 1 hour contact time and 72% remaining after the 5 hour period. The percentage of cells that remained alive after 3 hour of contact time was similar to that after 1 hour of contact time.

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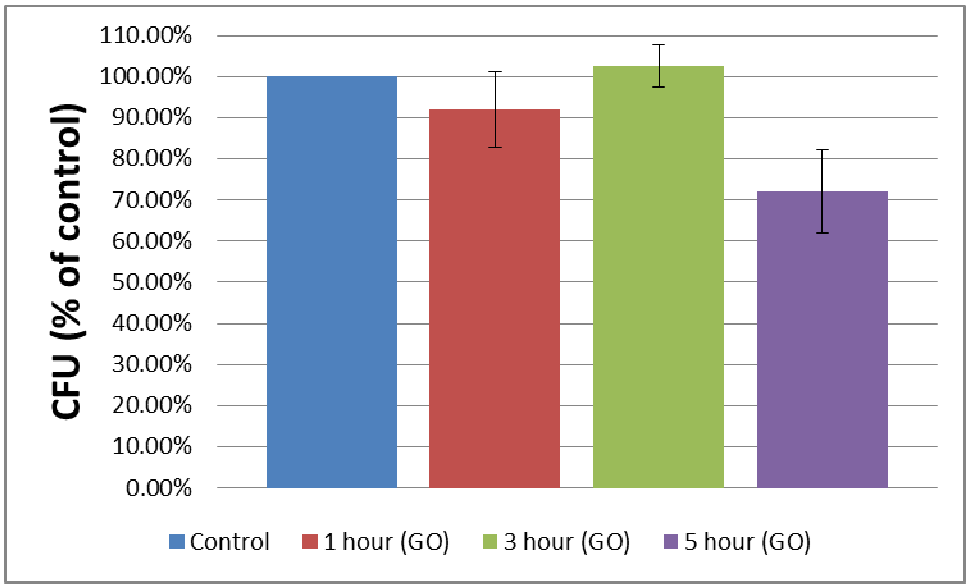

Figure 48: Bacterial inactivation resutls

The GO coated membranes created using Method 1 showed increased inactivation properties when compared with the polyethersulfone membranes besides for a few exceptions. For Method 1 a trend was shown in a few trials that revealed that contact time with the GO membrane increased the percentage of inactivated cells. Further trials are needed before a definitive conclusion can be drawn as to whether or not increased contact time improves bacterial inactivation for GO membranes created using Method 1.

Bacterial inactivation tests were conducted for membranes created using Method 2, but no inactivation was measured. The lack of bactericidal properties using Method 2 is due to the lack of coverage of GO on the polyethersulfone membrane support.

A study conducted using similar GO coated membranes reported 41% of *E. coli* cells remaining after a 1 hour contact time (Perreault et al., 2013). They also stated that increased contact time increased the inactivation of cells. Trials from the study also revealed increased inactivation after increased contact times. While our studies revealed

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inconsistent results, the overall trend revealed the possibility of achieving similar inactivation results. An increased number of trials likely will result in similar results as the study by Perreault et al. in their 2013 study.

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Chapter 5: Conclusions

5.1 Overview

The focus of the study was to develop a graphene oxide (GO) coated membrane, and test its applicability for water filtration. Two methods were used to produce the GO coated membranes. Method 1 was based on direct deposition via vacuum filtration of GO, and Method 2 was based on a chemical layer-by-layer deposition. The surface charge and particle size of the individual flakes were measured using a zeta potential and particle sizing analyzer. Images of the membranes were taken using Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). The functional groups of GO were measured using Fourier Transform Infrared Spectrometry (FTIR). Water contact angles on the GO membranes were also measured. Pure water flux values of the GO membranes were measured using a pressure driven dead end filtration system.

Contaminant removal tests were conducted using two salts: Na_2SO_4 and NaCl and two organic dyes: Methyl Blue and Rhodamine-WT. The test for salt removal was completed using a dead end filtration system and a conductivity probe. Organic dye removal was conducted using a spectrophotometer along with the dead end filtration system.

Bacterial inactivation tests for the GO coated membranes were completed using *E. coli*. The inactivation of cells was measured over various time periods and was compared against a polyethersulfone membrane with no GO coating.

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5.2 Conclusions

1. Pure water flux measurements revealed that increasing the loading rate of the GO coating on the polyethersulfone following Method 1 decreased the pure water flux. Pure water flux measurements ranged from 16 to 133 L m^{-2} h^{-1} bar^{-1}. Pure water flux values in this range suggest that GO coated membranes can efficiently pass water.
2. The SEM images and FTIR measurements revealed complete coverage of GO on the polyethersulfone membrane following Method 1 and a lack of coverage when using Method 2. The SEM and AFM images revealed a wrinkled GO structure as well as some cracks in the surface. The cracks in the GO surface could cause inconsistencies in pure water flux and contaminant removal values.
3. Zeta potential measurements revealed a surface charge around -38.5mV for individual GO flakes. Adjusting pH values had a minimal effect on the zeta potential values. The steady zeta potential values suggest that GO coated membranes are likely to be stable under varying pH values.
4. Water contact angles for unmodified GO surfaces had a contact angle of 28^{o} while the modified GO surface following Method 1 had a contact angle of 59^{o}. The increased contact angle suggests that the GO membranes modified with NaOH can more quickly pass water than an unmodified GO membrane. The membranes from Method 2 were not able to support a water droplet which supports the SEM images and FTIR measurements that reveal a limited coverage of GO on the polyethersulfone membrane support.

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5. Method 1 is a practical method for creating GO coated membranes because it allows the ability to easily create multiple membranes following the creation of the batch GO suspension. The difficulties of suspending GO and 1,3,5-benzenetricarbonyl trichloride (TMC) in Isopar as well as the inability to easily create various GO coated membranes at once make Method 2 a less practical method.
6. Limited salt and organic dye rejection was measured for GO membranes created using Method 1 and Method 2. The limited rejection in Method 1 membranes is likely due to swelling between individual GO flakes that occurred when submerged in water. The Method 2 membrane's lack of rejection values is due to the limited GO coverage on the base membrane. The results suggest that the two methods created as reported are not effective for water purification purposes.
7. Bacterial inactivation tests revealed that GO coated membranes using Method 1 had some bactericidal properties. Increased trials are likely to reveal higher inactivation rates for longer contact times. Coating membranes with GO is likely to reduce the formation of biofilms and decrease fouling. By decreasing fouling, GO coatings have the potential to increase the life of a membrane.
8. Purchased GO may contain slightly different properties that effect the contaminant removal and inactivation properties of the GO coated membranes. By creating GO as opposed to purchasing it, the methods used to coat the polyethersulfone membrane with GO may provide improved contaminant rejection and bactericidal properties.

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5.3 Future suggestions

1. Method 1 should be modified to reduce the water located in the GO coating revealed by the FTIR measurements that could be causing the swelling of the spacing between flakes.
2. Continued pure water flux measurements for varying GO loading rates should continue to be conducted to better define the relationship between GO thickness and flux.
3. Additional bacterial inactivation tests should be conducted to increase the accuracy of the results. A longer time increment should also be used to check if the contact time greatly increases the inactivation.
4. SEM images of bacteria before and after inactivation should be taken in order to visually show the effect that the GO has on the geometry of the bacterial cells.
5. Another method or continued modification of Method 2 would help compare results with Method 1 and give insight into the properties that are beneficial for flux values, contaminant removal and bacterial inactivation.
6. Repeat Method 1 and Method 2 using GO produced in the laboratory using a modified Hummers' Method as opposed to purchasing it.

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