

5-1-2017

## Crosslinking Graphene Oxide and Chitosan to Form Scalable Water Treatment Membranes

Jose Mattei Sosa

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Crosslinking graphene oxide and chitosan to form scalable water treatment membranes

By

Jose Mattei Sosa

A Thesis  
Submitted to the Faculty of  
Mississippi State University  
in Partial Fulfillment of the Requirements  
for the Degree of Master of Science  
in Civil and Environmental Engineering  
in the Department of Civil and Environmental Engineering

Mississippi State, Mississippi

May 2017

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2017

Crosslinking graphene oxide and chitosan to form scalable water treatment membranes

By

Jose Mattei Sosa

Approved:

---

Veera Gnaneswar Gude  
(Major Professor)

---

Dennis D. Truax  
(Committee Member)

---

James L. Martin  
(Committee Member)

---

John J. Ramirez-Avila  
(Committee Member)

---

Christopher Griggs  
(Committee Member)

---

Jason M. Keith  
Dean  
Bagley College of Engineering

Name: Jose Mattei Sosa

Date of Degree: May 5, 2017

Institution: Mississippi State University

Major Field: Civil and Environmental Engineering

Major Professor: Veera Gnanaswar Gude

Title of Study: Crosslinking graphene oxide and chitosan to form scalable water treatment membranes

Pages in Study: 58

Candidate for Degree of Master of Science

Graphene Oxide (GO) has emerged within the last decade as a next generation material for water treatment. Fabrication of graphene oxide membranes has been limited in scale and application due to repulsive hydration forces causing GO layers to electrostatically separate. In this study, chitosan is utilized to increase GO stability in the wet state through interactions with the negatively charged GO sheets (CSGO). This simple aqueous self-assembly allows scalable fabrication and enhanced stability for membrane applications in cross-flow. The CSGO membrane's performance was tested in a cross-flow reactor and challenged with methylene blue at concentrations ranging from 1 to 100 ppm at 345 kPa with fluxes ranging from 1 to 4.5 L/(m<sup>2</sup> hr) with 100% removal by physical rejection. This work demonstrates that the CSGO composite matrix is a potential alternative to traditional polymeric membranes for water treatment using a renewable biopolymer and minimal chemical input.

## ACKNOWLEDGEMENTS

I would like to thank all who contributed to the work conducted for this thesis. First and foremost, I thank my academic advisor, Dr. Veera Gude, for his guidance during the course of this project. Additionally, I would like to thank my committee members Drs. James Martin, Jonathon Ramirez-Avila, and Dennis Traex for their interest in my work.

I am very grateful to Drs. Victor Medina and Chris Griggs (ERDC) for their mentorship during this process and for providing a cooperative atmosphere, useful feedback, and insightful comments on my work. I would also like to thank various members of the Environmental Engineering Branch for their assistance in reviewing this document.

Finally, I would like to acknowledge friends and family who supported me during this time. I would like to thank my wife, Regina Mattei, for her constant love and support.

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## CHAPTER I

### BACKGROUND

Membrane filtration systems are widely used as a means to separate dissolved contaminants from water. While the effluent produced by these systems is of high quality, they suffer from a variety of issues which include high capital and operating costs, large quantities of wastewater/concentrate end products, and fouling. New membrane materials are sought to reduce these problems while also minimizing operation costs.

Graphene Oxide (GO) has progressively been studied using computational models and also at laboratory studies (Cohen-Tanugi & Grossman, 2015). The studies focused on the preparation of laboratory-scale GO membranes. These studies have been successful in creating pristine, composite, and coated membranes. These have been tested solely in dead end flow systems (Huang et al., 2014; Lim, Huang, & Loo, 2012; J. Shen et al., 2014; Y. Shen, Wang, Liu, & Zhang, 2015; Wang et al., 2015; Zhao, Xu, Chen, & Yang, 2013).

While these GO membranes have been successful at separating organic compounds at varying fluxes, most studies have centered on making GO membranes via vacuum assisted self-assembly (VASA) (M. Hu & Mi, 2013; Perreault, Fonseca de Faria, & Elimelech, 2015a). The membranes made by VASA tend to be smaller in shape since

they are restricted in size by the funnel and filter support size. Hence, they cannot be used on large cross-flow reactors.

To overcome the size limitations of VASA, solution casting was used to create GO/chitosan composite membrane (CSGO) membranes for cross-flow (I prefer cross-flow, because they both refer to a flow.) filtration. By using this method a membrane of any size could be manufactured.

Graphene oxide materials and composites have been produced using vacuum filtration but the scalability factor of these materials has been an ongoing challenge. The purpose of this study is to demonstrate that graphene oxide/chitosan composite membranes can be manufactured, scaled efficiently, and used as a membrane in a cross-flow reactor.

## CHAPTER II

### LITERATURE REVIEW

#### 2.1 Graphene Oxide and Its Potential Uses in Water Separation

Graphene oxide is a pseudo two-dimensional solid that contains hydroxyl, epoxide and carboxyl functional groups throughout its surface and outer edges. These functional groups allow GO to bind with other monomers to form strong lamellar structures. These groups also allow GO to adsorb contaminants such as dissolved metals and organic dyes (Fan et al., 2012; Gao et al., 2011; Hadi Najafabadi, Irani, Roshanfekar Rad, Heydari Haratameh, & Haririan, 2015; Jiao et al., 2015; Liu et al., 2012). Some researchers have created a magnetic form of GO for adsorbent recovery (Li, Luo, Li, Duan, & Wang, 2014). However, this has not been tested in *in situ* applications.

Computational and laboratory studies have determined that GO can also act as a molecular sieve with high flux properties for water. When formed into a flat membrane, GO could remove small particles via size exclusion while allowing water to pass through at a high rate (Perreault et al., 2015a). Modeling results have suggested that GO membranes can achieve fluxes of 400 to 4000 L m<sup>-2</sup> bar<sup>-1</sup> while still rejecting salts and with performance increases of 2 to 3 orders of magnitude higher than reverse osmosis (Cohen-Tanugi & Grossman, 2012).

While computational studies have demonstrated that this is possible, laboratory studies have encountered many challenges trying to achieve this. The main problem was

the dissociation of graphene oxide over time when submerged in water unless a crosslinking agent is added to stabilize the membrane. In Yeh, Raidongia, Shao, Yang, & Huang (2015) reported that the use of an anopore disk in a vacuum apparatus stopped dissociation of GO membranes in water. It was discovered that aluminum from the anopore disk leached into the graphene oxide solution and incorporated itself into the membrane strengthening its bonds. This allowed the resulting membrane to be tested in water-based solutions. Although this issue has been resolved, it is unclear if these membranes are feasible for commercial use.

GO composites and crosslinking materials still need further investigation to resolve stability and scalability issues.

## **2.2 Chitosan**

Chitosan is a readily available and inexpensive chemical that comes from the waste products of the shrimping and crab industry. Chitin which is the major constituent of these exoskeletons is deacetylated to form chitosan. Chitosan exhibits resistance to most organic solvents and has been studied as membrane material.

Chitosan consists of amine and hydroxyl functional groups along a “backbone” that makes up the chitosan polysaccharide. The amine groups are responsible for the complexation of the chitosan material, but the group as a whole adds hydrophilicity to the material which can make it a problem for water filtration. A chitosan membrane can lose its structural integrity as the material swells when hydrated which would make it a poor candidate for water filtration. Although swelling is an issue for water treatment, it is an advantage for other applications such as tissue engineering, controlled release of fertilizers, and drug delivery (Xu et al., 2013).

### 2.3 Chitosan and Graphene Oxide Materials

Chitosan and graphene oxide materials haven't been thoroughly studied as a membrane material. There have been studies in which a chitosan/graphene oxide composite has been tested for mechanical properties, antimicrobial properties, and the absorbance of heavy metals (W. Hu et al., 2010; Perreault, Fonseca de Faria, & Elimelech, 2015b; Xi et al., 2016). It was found that the Young's Modulus increased 4.6 fold and the tensile strength increased by 2.5 fold when compared with a pristine chitosan membrane (Dharupaneedi, Anjanapura, Han, & Aminabhavi, 2014). However, the absorbance for Au(III) and Pd(II) were 1076.649 mg/g and 21.920 mg/g, respectively (Liu et al., 2012). Though these initial studies show this composite's promise more studies are needed to understand its capabilities at various loading ratios.

The characteristics for chitosan/graphene oxide materials are summarized in Table 2.1. Chitosan and graphene oxide on their own are unsuitable for membrane filtration as they are prone to swell, adsorb methylene blue, and/or disintegrate. However, the combination of these materials minimize or completely eliminate these characteristics. This is beneficial as the inability to adsorb MB indicates that CSGO can act as a membrane rather than a sorbent.



Table 2.1 Desired Properties for Competent Membrane

| Material                  | Methylene Blue Sorption Capacity (200mg/L)    | Aqueous Stability  |
|---------------------------|---|--|
| Graphene Oxide            | 46% Reduction<br>Q <sub>e</sub> (139.29 mg/g) | Negatively Charged upon hydration causes layer separation and disintegration |
| Chitosan                  | 0% Reduction                                  | Swells and degradation 14.6 ± 1.4 MPa in wet state                           |
| Chitosan & Graphene Oxide | 17% Reduction<br>Q <sub>e</sub> (46 mg/g)     | Stable in wet state at 43.4±1.8 MPa  |

Table 2.2 Literature Review Table

| Paper   | Authors                  | Year | Journal  | Premise  | Difference in CSGO work  |
|---|--------------------------|------|--|--|--|
| Graphene-based antibacterial paper  | Hu, Wenbing et al        | 2010 | ACS nano   | Vacuum Assembled GO paper for inhibition of E. Coli  | Chitosan/ GO solution wet cast and evaporated  |
| Hydrogen bond networks in graphene oxide composite paper: structure and mechanical properties.  | Medhekar, Nikhil V et al | 2010 | ACS nano   | Theoretical simulation of hydrogen bonding of water and GO   | Experimental studies of water permeation in CSGO   |
| Well-Dispersed Chitosan/Graphene Oxide Nanocomposites   | Yang, Xiaoming et al     | 2010 | ACS applied Material and interfaces                | Enhanced mechanical strength of chitosan with added GO   | Stability of CSGO in the wet state for pressure driven water treatment   |
| Engineered Graphite Oxide Materials for Application in Water Purification   | Gao, Wei                 | 2011 | ACS applied Material and interfaces                | GO coated sand for lig and Dye sorption  | GO/ Biopolymer membrane for separations  |
| Adsorption of Lead(II) Ions from Aqueous Solution on Low-Temperature Exfoliated Graphene Nano sheets                                  | Huang, Zheng Hong        | 2011 | Langmuir   | Sorption of Pb by GO sheets  | Physical rejection of contaminants   |
| Green fabrication of chitosan films reinforced with parallel aligned graphene oxide   | Pan, Yongzheng           | 2011 | Carbohydrate Polymers                              | Mechanical strength of GO/ chitosan films  | Different application and wt.% of GO filler  |
| Fabrication of novel magnetic chitosan grafted with graphene oxide to enhance adsorption properties for methyl blue                   | Fan, Lulu                | 2012 | Journal of Hazardous Materials                     | Sorption of Pb by GO sheets  | No sorption of MB observed, membrane rejection of MB   |
| Preparation of novel magnetic chitosan/graphene oxide composite as effective adsorbents toward methylene blue                         | Fan, Lulu                | 2012 | Bioresourcse Technology                            | Sorption of MB dye   | No sorption of MB observed, membrane rejection of MB   |
| Facile preparation of graphene-based chitosan films: Enhanced thermal, mechanical and antibacterial properties                        | Lim, H.N.                | 2012 | Journal of Non-Crystalline Solids                  | Optimized production of GO for enhancement of CS   | Physical enhancement of CS thermal and mechanical properties in dry state, no discussion of aqueous stability                                      |
| Preparation and characterization of chitosan/graphene oxide composites for the adsorption of Au(III) and Pd(II)                       | Liu, Li                  | 2012 | Talanta  | Sorption of Pd (II) & Au (III)   | CSGO beads were produced for sorption system   |
| Unimpeded Permeation of Water Through Helium-Leak-Tight Graphene-Based Membranes  | Nair, R. R.              | 2012 | Science  | Evaporated water permeated GO faster than He and solvents  | Water permeation in a CSGO composite was evaluated in a pressure driven cross-flow system  |
| New Routes to Graphene, Graphene Oxide and Their Related Applications   | Zhu, Yu                  | 2012 | Advanced Materials                                 | Synthesis of graphene based materials by solution, vapor, and solids                                       | Composite membrane is predominantly chitosan   |
| Enabling Graphene Oxide Nano sheets as Water Separation Membranes   | Hu, Meng                 | 2013 | Environmental Science and Technology               | GO was placed on a polydopamine coated polysulfone support with 44-66% rejection of MB                     | CSGO composite membrane is freestanding with 100% rejection of MB  |
| Salt concentration, pH and pressure controlled separation of small molecules through lamellar graphene oxide membranes                | Huang, Hubiao            | 2013 | Chemical communications                            | Layered GO was prepared by vacuum filtration   | Chitosan/ GO solution wet cast and evaporated  |
| Graphene oxide cross-linked chitosan nanocomposite membrane   | Shao, Lu                 | 2013 | Applied Surface Science                            | 1% wt GO loading on chitosan makes chitosan 1.41% stronger in dry state                                    | Experiments carried out in wetted states to assess aqueous stability   |
| Nonionic polymer cross-linked chitosan hydrogel: preparation and bioevaluation  | Liangxin Xu,             | 2013 | Journal of biomaterials science. Polymer edition   | Chitosan-polyacrylamide hydrogels were produced for medical applications                                   | CSGO is derived from a renewable biopolymer not a synthetic petro-polymer  |
| Effect of graphene oxide concentration on the morphologies and antifouling properties of PVDF ultrafiltration membranes               | Zhao, Chuanqi            | 2013 | Journal of Environmental Chemical Engineering      | UF membranes were coated with a PVDF/GO and were tested for pure water flux                                | CSGO membranes are free standing and independent of other types of membranes.  |
| Fabrication of biocompatible and mechanically reinforced graphene oxide-chitosan nanocomposite films                                  | Zuo, Ping-ping           | 2013 | Chemistry Central Journal                          | Explores the mechanical properties over different wt. %  | Different percentages of GO to CS and not applied to water treatment   |
| Functionalized Graphene Sheets Embedded in Chitosan Nanocomposite Membranes for Ethanol and Isopropanol Dehydration via Pervaporation | Dhanupaneedi, Ushas P    | 2014 | Industrial & Engineering Chemistry Research        | Pervaporation for dehydration of ethanol and isopropanol   | Our work is concentrated on aqueous filtration vs organic solvents.  |
| A Graphene Oxide Membrane with Highly Selective Molecular Separation of Aqueous Organic Solution                                      | Huang, Kang              | 2014 | Angewandte Chemie - International Edition          | GO was supported on a ceramic hollow fiber membrane and tested for dimethyl carbonate (DMC)/water mixtures | CSGO membranes are freestanding and were not tested for organic solvents   |
| Precise and ultrafast molecular sieving through graphene oxide membranes  | Joshi, R. K.             | 2014 | Science  | Vacuum Assembled GO laminate diffusion of salts  | CSGO composite in a pressure driven system   |
| Preparation of magnetic ionic liquid/chitosan/graphene oxide composite and application for water treatment                            | Li, Lilei                | 2014 | International Journal of Biological Macromolecules | Using a Magnetic chitosan and graphene oxide-ionic liquid composites can be used as biosorbents of Cr(VI)  | CSGO membranes are not magnetic, are not used as a sorbent, and it does not use ionic liquids in it's formation.                                   |
| Theoretical and Experimental Approaches of Liquid Entry Pressure Determination in Membrane Distillation Processes                     | Gabor Rácz               | 2014 | Periodica Polytechnica. Chemical Engineering       | The paper is focused on membrane distillation  | Our approach differs in that we are not going membrane distillation but membrane filtration. They are also using commercially available membranes. |

Table 2.2 (Continued)

|  |      |                          |   |   |  |
|--|------|--------------------------|---|---|--|
| Membranes with Fast and Selective Gas-Transport Channels of Laminar Graphene Oxide for Efficient CO <sub>2</sub> Capture.  | 2014 | Shen, Jie                | Angewandte Chemie (International ed. in English)    | This paper examines the performance of CO <sub>2</sub> permeation of GO membrane  | Aqueous separations vs. gas phase CO <sub>2</sub> capture  |
| Poly(vinyl alcohol)-graphene oxide nanohybrid "pore-filling" membrane for pervaporation of toluene/n-heptane mixtures  | 2014 | Wang, Naisin             | Journal of Membrane Science                         | The paper examines a PVA/GO membrane composite for pervaporation of toluene/n-heptane mixtures  | While our membranes are made of CS/GO and are also not using organic solvents, mixes for filtration. I did try to make a PVA/GO membrane but it dissociate when in contact with water.             |
| Graphene Oxide Membranes for Ionic and Molecular Sieving   | 2014 | Mi, Boxia                | Science   | Perspective on the potential of Layered GO for water treatment  | Our work experimentally verifies cross-flow membrane application is possible   |
| Wetting of graphene oxide: a molecular dynamics study.   | 2014 | Wei, Ning                | Langmuir - the ACS Journal of surfaces and colloids | Uses computational molecular dynamics simulations to study GO's water contact angles and how this can be affected by it's hydrophilic regions.  | Our CS/GO studies are practical lab studies vs computational.  |
| Graphene oxide-embedded thin-film composite reverse osmosis membrane with high flux, anti-fouling, and chlorine resistance   | 2015 | Chae, Hee-Ro             | Journal of Membrane Science                         | a GO Thin-film composite (TFC) is used to enhance a traditional polyamide membrane for anti-fouling and chlorine resistance to the hydroxide law.   | CS/GO membranes are freestanding resulting in a greater thickness and lower flux.  |
| Nanoporous graphene as a reverse osmosis membrane: Recent insights from theory and simulation  | 2015 | David Cohen-Tanugi       | Desalination  | Review paper on computational models of GO  | Our CS/GO studies are practical lab studies vs computational.  |
| Removal of Cu <sup>2+</sup> , Pb <sup>2+</sup> and Cr <sup>6+</sup> from aqueous solutions using a chitosan/graphene oxide composite nanofibrous adsorbent                                   | 2015 | Hadi Najafabadi, Hossein | RSC Adv.  | Electrospun CS/GO fibers for sorption of Cu, Pb, and Cr   | Our CS/GO membranes are created using a solution casting method and also are used as a membrane filter vs an adsorbent as discussed in this paper.   |
| High-Efficiency Water-Transport Channels using the Synergistic Effect of a Hydrophilic Polymer and Graphene Oxide Laminates  | 2015 | Huang, Kang              | Advanced Functional Materials                       | Chitosan and GO is coated on a ceramic hollow fiber membrane  | CS/GO membranes are freestanding, flat sheet membrane  |
| Self-Assembly Reduced Graphene Oxide Nanosheet Hydrogel Fabrication by Anchorage of Chitosan/Silver and Its Potential Efficient Application toward Dye-Degradation for Wastewater Treatments | 2015 | Jiao, Tifeng             | ACS Sustainable Chemistry & Engineering             | Hydrogels made from CS, GO and Silver nanoparticles were formed by self-assembly and exhibited a pseudo-second order model  | CS/GO is not a hydrogel nor is it used as an adsorbent but it has been proven to remove methylene blue from solution by size exclusion.  |
| Fabrication of novel magnetic nanocomposite with a number of adsorption sites for the removal of dye   | 2015 | Li, Lilei                | International Journal of Biological Macromolecules  | An Fe <sub>3</sub> O <sub>4</sub> (chitosan)/GO material was synthesized and tested in batch adsorption tests of methylene blue. The equilibrium adsorption isotherms and had an adhered to Langmuir isotherms and had an adsorption capacity of 282 mg/g | No sorption of MB observed, membrane rejection of MB   |
| Preparation of poly(vinyl alcohol)/chitosan hydrogel compounded with graphene oxide to enhance the adsorption properties for Cu(II) in aqueous solution                                      | 2015 | Li, Luchong              | Journal of Polymer Research                         | PVA/CS/GO composite for Cu sorption   | This hydrogel was made for adsorption while our membranes were created as flat sheet membranes for size exclusion processes.   |
| Highly Porous Core-Shell Structured Graphene-Chitosan Beads  | 2015 | An-Ouyang                | ACS Applied Materials & Interfaces                  | Graphene Oxide/CS/GO beads were formed by coating GO cores with chitosan by a freeze-drying method. These were tested for the adsorption of Methyl orange.  | These beads were made for adsorption while our membranes were created as flat sheet membranes.   |
| Environmental applications of graphene-based nanomaterials   | 2015 | Perreault, François      | Chem. Soc. Rev.                                     | Review on potential applications for GO   | Experimental studies of water permeation in CS/GO  |
| A ZnO decorated chitosan-graphene oxide nanocomposite shows significantly enhanced antimicrobial activity with ROS generation  | 2015 | Jay Chowdhuri, Angshuman | RSC Adv.  | The membrane in the paper had ZnO added to it's CS/GO structure to generate Reactive Oxygen Species (ROS)   | Work on CS/GO is not focused on antibacterial properties or ROS  |
| Enhanced Performance of a Novel Poly(vinyl Amine)/Chitosan/Graphene Oxide Mixed Matrix Membrane for CO <sub>2</sub> Capture  | 2015 | Shen, Yijia              | ACS Sustainable Chemistry & Engineering             | PVA, CS, GO was later grafted onto a PS support. GO was later grafted onto the support with polyethylene. This material was tested against CO <sub>2</sub> /N <sub>2</sub> has separation tests to determine the permeance of CO <sub>2</sub> .           | Aqueous separations vs. gas phase CO <sub>2</sub> capture  |
| Polymer-Graphene Oxide Quad Layer Thin-Film Assemblies with Improved Gas Barrier   | 2015 | Tzeng, Ping              | Langmuir  | Hydrophobic oxygen barrier for gas purification   | CS/GO membranes are being used for hydrophilic water filtration not gas selectivity.   |
| O-(Carboxymethyl)-chitosan Nano filtration Membrane Surface Functionalized with Graphene Oxide Nano sheets for Enhanced Desalting Properties   | 2015 | Wang, Jiali              | ACS Applied Materials & Interfaces                  | NF membrane was coated with GO and the resulting material was characterized and was tested against salts.   | CS/GO is a free standing membrane and is not coated onto a commercial membrane.  |
| On the origin of the stability of graphene oxide membranes in water  | 2015 | Che-Ning Yen             | Nature Chemistry                                    | Dissolution of Al <sup>3+</sup> from the anopore disc crosslinks GO   | The positive charge on the amine of chitosan in acid interacts with the negative charges on GO   |
| High Performance of Alkaline Anion-Exchange Membranes Based on Chitosan/Poly(vinyl Alcohol) Doped with Graphene Oxide for the Electro oxidation of Primary Alcohols                          | 2016 | García-Cruz, Leticia     | Journal of Carbon Research                          | a 50/50 PVA/CS/GO composite was created then later doped with GO and formed into a membrane by solution casting. The resulting membrane had a reinforced structure and was a good physical barrier for alcohol permeability.                              | CS/GO membranes do not contain PVA. Though I had created PVA/CS/GO membranes in the past but dissociate when either submerged or used for water filtration.  |
| Declining flux and narrowing Nano-channels under wrinkles of compacted graphene oxide Nano filtration membranes  | 2016 | Wei, Yi                  | Carbon  | GO membranes were created by pressure-assisted self assembly. These membranes were tested for water flux which decreased over time. The wrinkles found in the membrane were discussed and discussed in the paper  | We use a different method and solution to form CS/GO membranes via solution casting vs vacuum filtration. Also this membrane is a thinner allowing higher over all fluxes.                         |
| Graphene Oxide Membranes with Strong Stability in Aqueous Solutions and Controllable Lamellar Spacing  | 2016 | Xi, Yue-Heng             | ACS Applied Materials & Interfaces                  | Reduced-GO can be used to bind GO lamellar plates to form water stable membranes for water filtration.  | We use chitosan as a binder to form CS/GO membranes via solution casting instead of mixing reduced GO into the pristine GO dispersion.   |
| High Flux MWCNTs-intertlinked GO hybrid membranes survived in cross-flow filtration for the treatment of strontium-containing wastewater   | 2016 | Zhang, Lin               | Journal of Hazardous Materials                      | MWCNT were used to increase the spacing between GO lamellar layers for increased flux. These were bound onto a PAN support by vacuum filtration. This material exhibited high fluxes at 4 Mpa   | CS/GO membranes do not use MWCNT and they are freestanding as opposed to being adhered to a PAN support. Our fluxes are also significantly lower than that of the material presented in the paper. |

## CHAPTER III

### HYPOTHESIS

Vacuum filtered graphene oxide membranes without a crosslinking agent tend to dissociate in water, and cannot be used for water filtration. We hypothesize that using chitosan as a crosslinking agent would allow for a chitosan-GO composite to form a scalable membrane that can be used for treatment of aqueous solutions in cross flow filtration.

CHAPTER IV  
MATERIALS AND METHODS

4.1 Materials

4.1.1 Graphene Oxide

Graphene oxide was obtained from Graphene Supermarket (graphene-supermarket.com, Calverton, NY) in three different forms. These include a dispersion at 6.2 g/L concentration, and two powders that were differentiated by their size and structure. One of the powders was called granular graphene which had a thickness of one atomic layer with a flake size of 0.3 to 0.07 microns. While the other powder was called nano graphene oxide which had a thickness of 1 nm and a diameter of 90 nm.

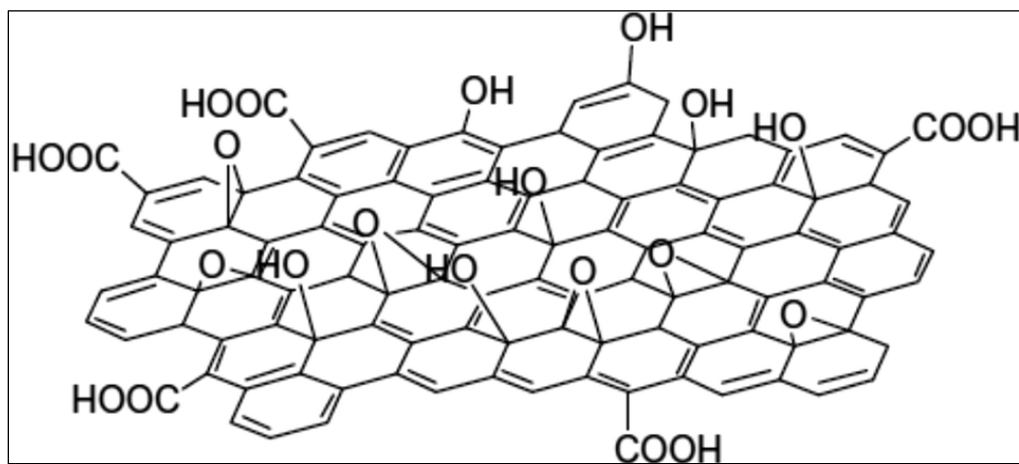


Figure 4.1 Chemical Structure of Graphene Oxide

(Nasrollahzadeh, Babaei, Fakhri, & Jaleh, 2015)

#### 4.1.2 Chitosan Solution

Chitosan material used during experimentation was obtained from Sigma Aldrich Company (medium molecular weight, Poly-D-glucosamine) 448877-50G. Acetic Acid was used as a solvent to dissolve chitosan in water (Sigma Aldrich A6283-2.5L ( $\geq 99\%$ )).

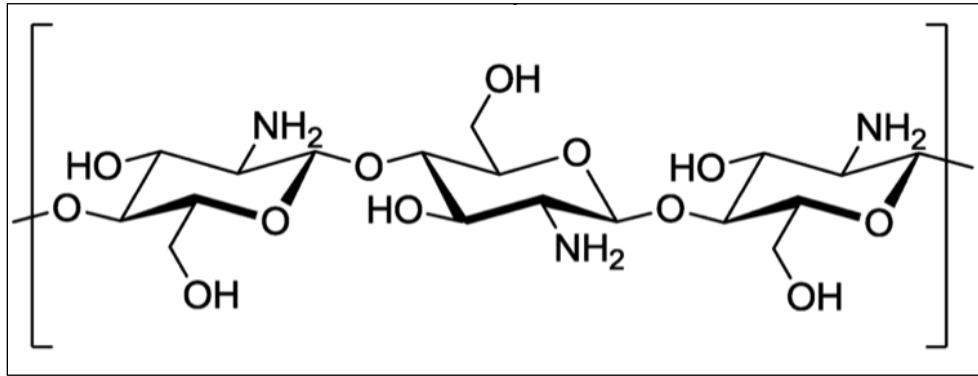


Figure 4.2 Chemical Structures of Chitosan

(Heckel, Dagmara Konieczna, & Wilhelm, 2013)

#### 4.1.3 Methylene Blue

Methylene blue (MB) was purchased from (Sigma Aldrich M9140-100G). The challenge solutions were made by mixing methylene blue and water to form solutions with concentrations ranging from 1, 10, 50, 100, and 130 mg/L. Methylene blue was used in this study as it is a cationic dye with medium molecular weight (319.85 g/mol) that can be visually and chemically quantified.

#### 4.1.4 Nitrocellulose Millipore Membrane

Nitrocellulose membrane rolls were obtained from Bio-Rad (bio-rad.com, Hercules, CA) (Roll, 0.45  $\mu\text{m}$ , 30 cm  $\times$  3.5 m, Cat #: 1620115).

## **4.2 Methods**

### **4.2.1 Chitosan Graphene Oxide (CSGO) Solutions**

CSGO solutions were made with Graphene Oxide powders. A dispersion of GO was also used to initially prototype CSGO materials. These solutions were cast into membranes which were challenged with methylene blue in a cross-flow reactor. Flux and removal efficiency of these membranes were calculated at a pre-determined time interval.

#### **4.2.1.1 Formulation of CSGO Solution**

Three hundred milligrams of GO and 100 mL of water were transferred into a 500 mL Nalgene Bottle and sonicated for 60 min. One and a half grams of medium molecular weight Chitosan (Sigma Aldrich) were then added to the solution along with 1 mL of 99% acetic acid. The solution was then stirred for 72 hours.

#### **4.2.1.2 Formulation of d-x-CSGO Solution**

Three hundred milligrams of GO and 150 mL of water were transferred into a 500 mL Nalgene Bottle and sonicated for 60 min, 1.5 grams of medium molecular weight Chitosan were then added to the solution along with approximately 1 mL of 99% acetic acid. The solution was then stirred at for 72 hours.

### **4.2.2 Evaporative Membrane Casting (EMC)**

CSGO solution was poured into a desired casting mold and left to dry in an incubator and in a bell jar. The drying time was 144 hours for the bell jar and 24 hours for the incubator. The incubator was subsequently used for drying all subsequent membranes.

### 4.2.3 Scaled Membrane (SM)

Seven hundred twenty milliliters of d-g-CSGO solution was used to cover an area of 1394 cm<sup>2</sup> at a loading rate of 2 mg/mL. The volume was poured into a 46 cm × 30 cm Plexiglas mold, and dried in a fume hood over a period of 72 hours at 25°C.

### 4.2.4 Cross-Flow Method (CFM)

CSGO membranes were created by pouring 50 mL of a d-x-CSGO solution in a 97-cm<sup>2</sup> mold. These were then, punched out, and placed on a cross-flow reactor. The membranes were tested in both a supported and an unsupported mode or configuration. Two cross-flow reactors (CFR) were obtained from Sterlitech. One of them was an Acrylic CF042A reactor, while the other was a stainless steel CF042SS. Most of the experiments were conducted using the acrylic reactor. These reactors were arranged in a continuous flow configuration with a recycling loop which allowed for extended run times over several days. The cross-flow reactor experiments were conducted at a flow rate of 10 mL/min with an operating pressure of 345 kPa, unless specified otherwise. Flux data, concentrate & permeate samples were taken and placed in scintillation vials every 24 hours.

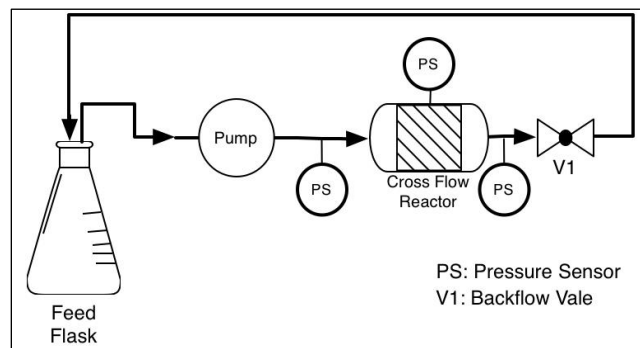


Figure 4.3 Block Flow Diagram of Experimental Setup for Cross-flow Reactor



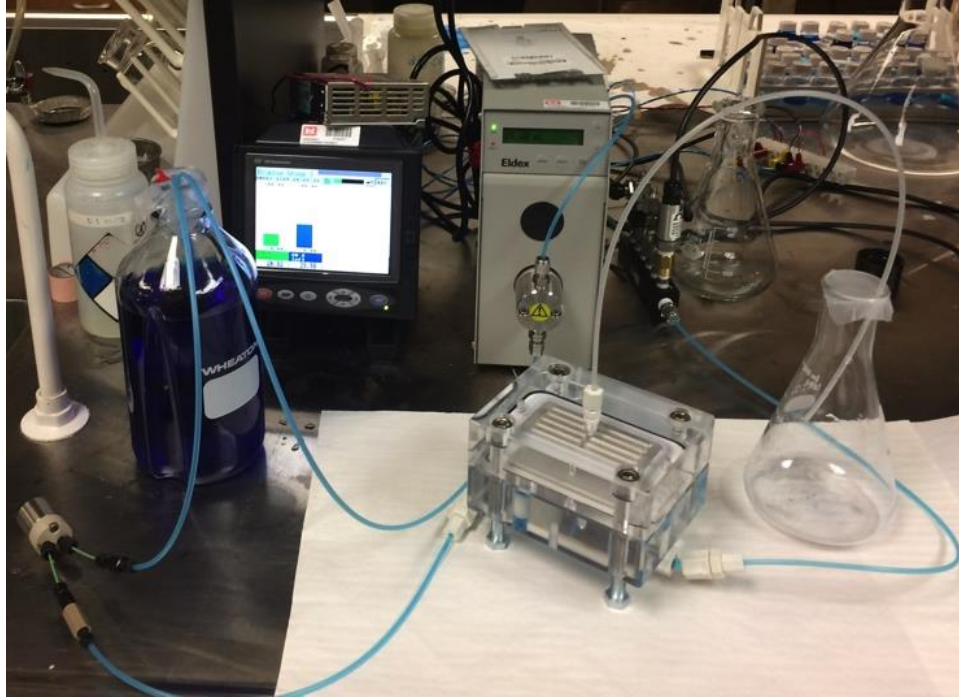


Figure 4.4 Cross-flow Membrane Experimental Setup for Acrylic Reactor



Figure 4.5 Sterlitech Membrane Die (12 cm × 6 cm)

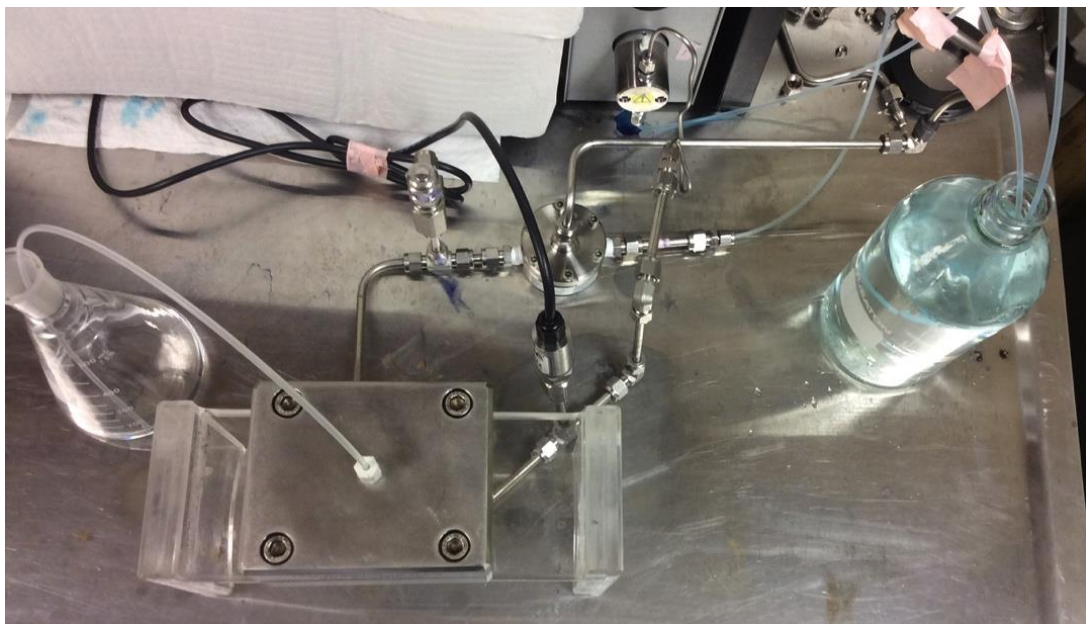


Figure 4.6 Cross-flow Membrane Experimental Setup for Stainless Steel Reactor

Methylene blue was used as the model contaminant in this study. Methylene blue has a molecular weight of 319.85 g/mol and a density of 1.77 g/mL. MB solution was prepared at different concentrations utilizing deionized water. Samples for the concentrate and permeate were taken and analyzed using an Agilent 8453 UV-visible Spectroscopy System and following ASTM E275. A 1:10 dilution was required for samples above 20 mg/L. All samples were analyzed at a fixed wavelength of 660 nm and concentrations were calculated based on the calibration curves below.

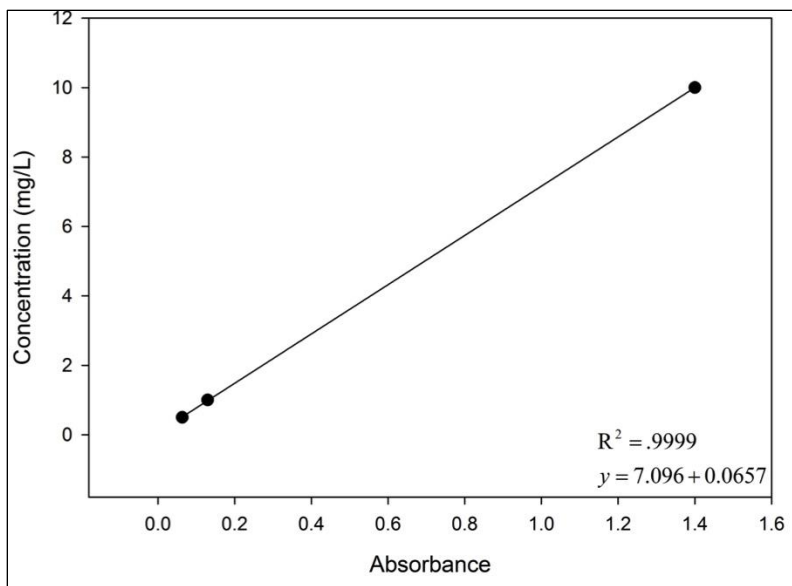


Figure 4.7 MB Calibration Curve at 660 nm

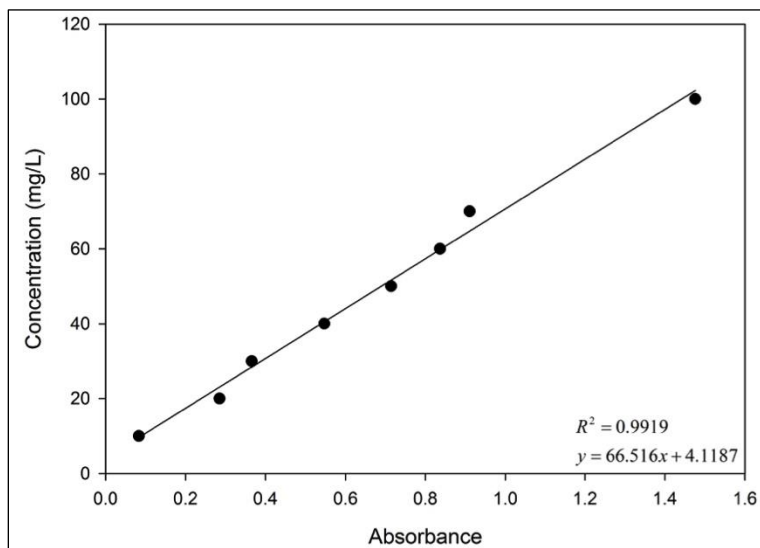


Figure 4.8 MB Calibration Curve at 660 nm

#### 4.2.5 Morphological and Chemical Analysis

The surface and cross-section morphologies for samples were studied by scanning electron microscopy (SEM, Nova nanolab 200, 15 kV). For the cross-section observation, liquid nitrogen was used to freeze the samples before cutting. The films were also coated with gold and then analyzed by SEM. ATR-Fourier Transfer Infrared (ATR-FTIR) spectrophotometer (Spectrum BX FTIR spectrometer equipped with Pike technology accessory) was used to study the molecular interaction between GO and CS. The spectra were used at 8 cm<sup>-1</sup> resolutions in the range of 4000 to 500 cm<sup>-1</sup>. X-ray photoelectron spectroscopy (XPS - PHI versaprobe 5000 with PHI MultiPack data analysis software) was used to evaluate the chemical composition of the films. Initial survey scans (0 – 1400 eV binding energy) were followed by detailed scans for carbon (275 to 295 eV) and nitrogen (390 to 410 eV). High resolution X-ray diffraction (Philips X'Pert- MRD diffractometer, Cu K radiation source) was used to determine the crystallinity of the samples. XRD patterns were taken within recorded region of 2θ from 5 to 35 with a scanning speed of 1 min<sup>-1</sup> at the voltage of 45.0 kV and a current of 40.0 mA.

#### 4.2.6 CSGO Membrane pH Compatibility

The 5.1 cm × 1 cm coupons of CSGO were prepared and placed in glass test tubes with 10 mL of water with pH values ranging from 1 to 12. Coupons were submerged for 24 hours before analysis.

#### **4.2.7 NaOH Treated CSGO Membranes**

The d-g-CSGO membranes were treated with a pH 14 solution of NaOH @ 1 M. The membranes were left in a glass container for a period of 24 hours. Afterward the membranes were dried with a paper towel and placed in a CFR for testing.

#### **4.2.8 Thermal Treated CSGO Membranes**

The d-g-CSGO membranes were placed in an oven at 105°C for a period of 24 hours before being placed in a CFR for testing.

## CHAPTER V

### RESULTS

#### 5.1 Manufacturing Scalable CSGO Membranes

##### 5.1.1 Evaporative Formation of CSGO

Two membranes were formed in a petri dish using the evaporative casting method (ECM). One was placed in an incubator, the other in a bell jar. The resulting membranes were 150  $\mu\text{m}$  thick with a strong, plastic-like texture. Upon removal from the petri dish, small holes were observed throughout the membrane but these did not appear to weaken the membrane.



Figure 5.1 CSGO Solution After Drying for 24 Hours (Left – CSGO Solution Dried in a Bell Jar; Right - CSGO Solution Dried in an Incubator)

During the membrane's formation an interesting characteristic was observed. Instead of the membrane congealing and drying uniformly, a nucleation site formed along a corner and radiated throughout the membrane during the drying process. The nucleation site can be seen on the left membrane in Figure 5.1. This behavior is characteristic of CSGO materials as it occurred while drying every sample.

A CSGO membrane capable of fitting a cross-flow reactor was desired. ECM was adjusted for a 200 mL solution and cast in an acrylic mold. The mold was then placed in an incubator for 48 hours. The resulting CSGO material had similar properties to past CSGO materials and was of sufficient size that it could be cut to fit a cross-flow reactor.

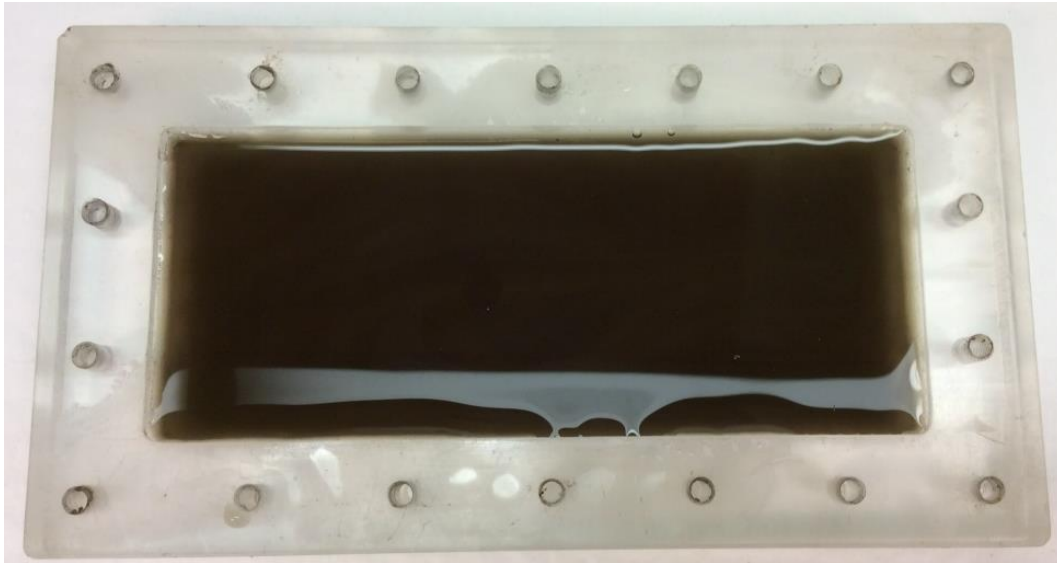


Figure 5.2 Mold with 200 mL of CSGO Dispersion Solution



Figure 5.3 Dried d-CSGO Membrane After 72 Hours of Incubation

### 5.1.2 CSGO Membranes in a Cross-flow Reactor

A CSGO membrane using d-GO was prepared using ECM and placed in a cross-flow reactor. The membrane was challenged against a solution of 10 mg/L MB using CFM. Initially, the membrane had a small amount of clear permeate accumulate in the permeate reservoir. But the membrane failed soon after causing methylene blue to accumulate in the permeate reservoir. This failure occurred because of chitosan's tendency to absorb water. Although some expansion was expected, the expansion observed was significantly greater than anticipated. The expansion led to the membrane thinning in areas, thus losing its structural stability and failing due to tangential forces acting upon the membrane causing it to tear.





Figure 5.4 d-CSGO Membrane on Cross-flow Reactor



Figure 5.5 Membrane Filtering Methylene Blue (10 mg/000



Figure 5.6 Top View of d-CSGO Membrane After Failure

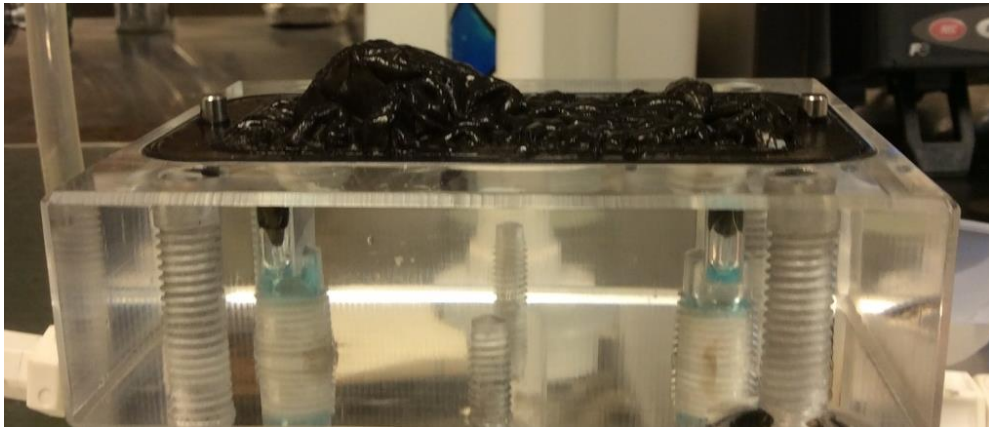


Figure 5.7 Side View of d-CSGO Membrane After Failure

A n-CSGO membrane was cast and tested using a CFR. This membrane was virtually impermeable after 6 hours on the cross-flow reactor at 344.74 kPa. When the CFR was opened it became obvious why there was no permeate. The membrane failed due to chitosan hydration, exponential expansion, and structural deformation.

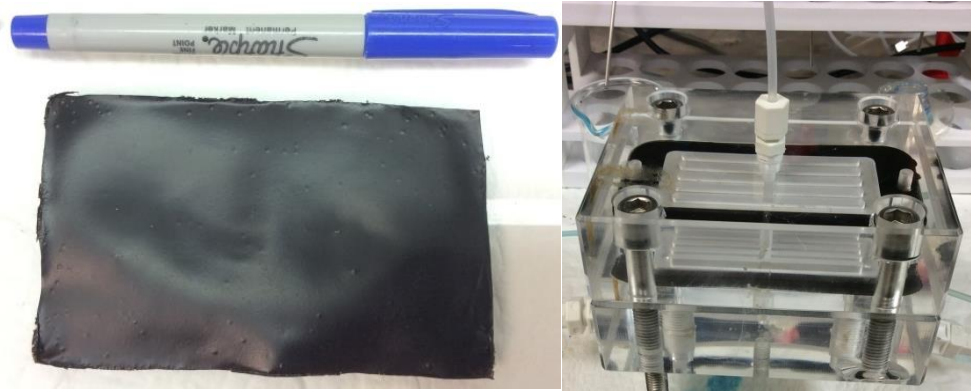


Figure 5.8 n-CSGO Membrane After Trimming and n-CSGO Membrane in Cross-flow Reactor



Figure 5.9 n-CSGO Membrane Failure After 6 Hours in a Cross-flow Reactor

This kind of behavior was not seen in dead end filtration as constant pressure throughout the membrane prevents swelling. While in cross-flow filtration forces exerted on a membrane are in tangential direction. CSGO membranes also swelled to several times their original thickness exacerbating the structural deformities. Thus, freestanding CSGO membranes cannot be used for cross-flow filtration without a support of some kind.

A method was developed to reduce the effects of CSGO membranes by adding structural support and diluting the CSGO solution by 50%. This allowed membrane to swell within the confines of the support, while still allowing the membrane to be used for cross-flow filtration.

### 5.1.3 Membrane Performance

The new membranes were designated d-x-CSGO, these were created and tested in a CFR. These membranes were permeable with low swelling that could be controlled by external supports. As such, d-g-CSGO membranes were challenged with methylene blue at 10 mg/L with a feed rate of 10 mL/min at 344.74 kPa over 72 hours. The resulting flux was 1.25 LMH.

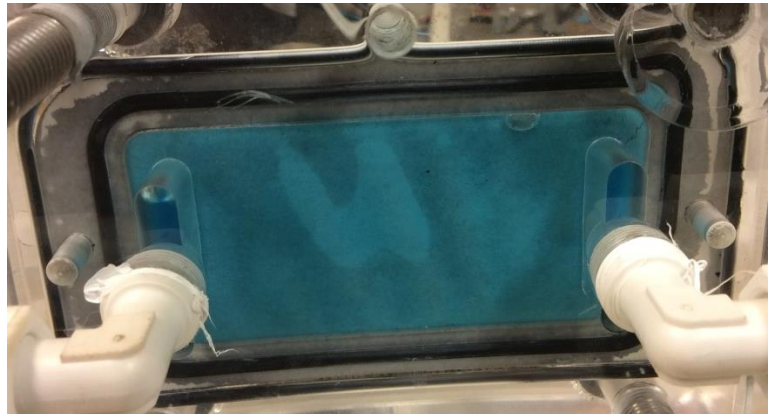


Figure 5.10 Bottom of the Cross-flow Reactor

Using the same membrane, a subsequent experiment was performed in which the membrane was challenged with a 20 mg/L solution of methylene blue for the same duration. The resulting flux was 1.68 LMH. In both flow through experiments, the feed solution was being concentrated with little breakthrough of methylene blue, suggesting that the mechanism of removal was size exclusion.

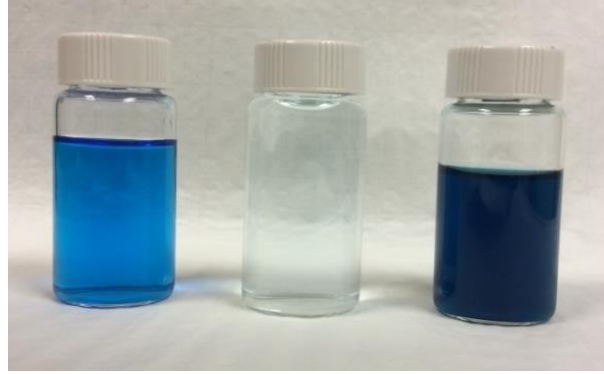


Figure 5.11 From Left to Right: 10 mg/L Methylene Feed, Membrane Permeate, Feed Concentrate

Samples were analyzed via UV-visible spectroscopy using ASTM E257, concentrations were calculated using the calibration curves found in Figures 4.7 and 4.8.

Table 5.1 d-g-CSGO Flux of Methylene Blue at 10 mg/L and 20 mg/L

| Total Flux of Methylene Blue |               |        |                     |          |
|------------------------------|---------------|--------|---------------------|----------|
| Sample                       | Concentration | abs    | Final Concentration | Reject % |
| Feed                         | 10 mg/L       | 0.1017 | 10.88               |          |
| Concentrate                  | 10 mg/L       | 0.2572 | 21.23               | 97.99    |
| Permeate                     | 10 mg/L       | 0.0507 | 0.43                |          |
| Feed                         | 20 mg/L       | 0.2320 | 19.55               |          |
| Concentrate                  | 20 mg/L       | 0.7636 | 54.91               | 99.72    |
| Permeate                     | 20 mg/L       | 0.0128 | 0.16                |          |

The membrane support was changed from Whatman No. 5 paper filter to 0.45  $\mu\text{m}$  nitrocellulose support. The new support increased flux through the membrane by 50% while maintaining structural support for the membrane. Nitrocellulose was used as a structural support for all experimental runs hereafter.

Granular and nano based CSGO membranes were made by ECM and challenged against methylene blue solutions varying from 1 mg/L to 100 mg/L.

Table 5.2 Average Flux and Recovery of Methylene Blue Through d-n-CSGO After 72 Hours

| Concentration | d-g-CSGO        |              | d-n-CSGO        |              |
|---------------|-----------------|--------------|-----------------|--------------|
|               | Average Removal | Average Flux | Average Removal | Average Flux |
| 100 mg/L      | 98.82           | 2.11         | 99.03           | 2.13         |
| 50 mg/L       | 94.86           | 3.33         | 92.35           | 2.47         |
| 10 mg/L       | 99.59           | 3.49         | 99.27           | 3.11         |
| 1 mg/L        | 91.36           | 2.64         | 89.86           | 4.35         |

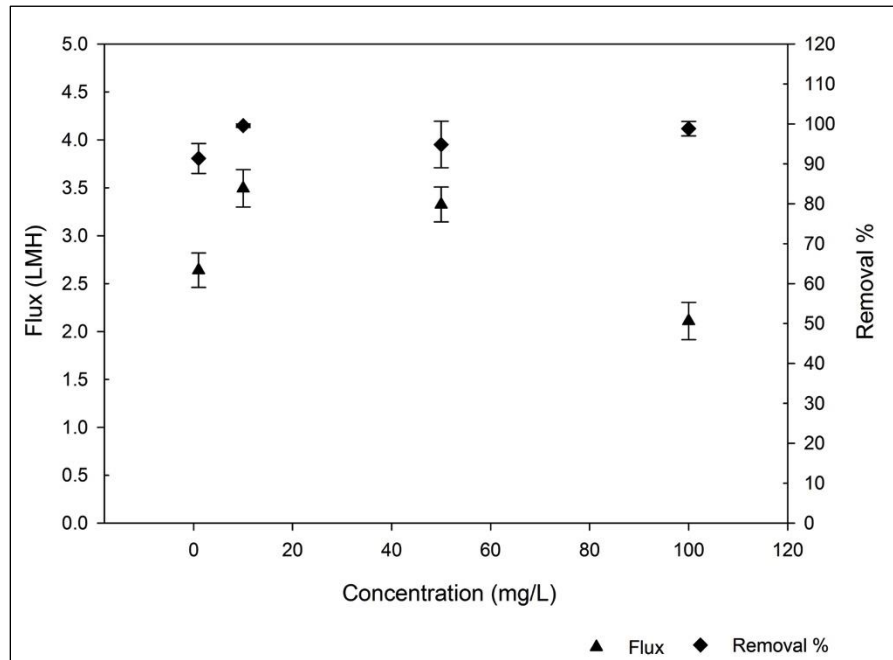


Figure 5.12 d-g-CSGO Flux and Removal Rates Over Various Concentrations of Methylene Blue

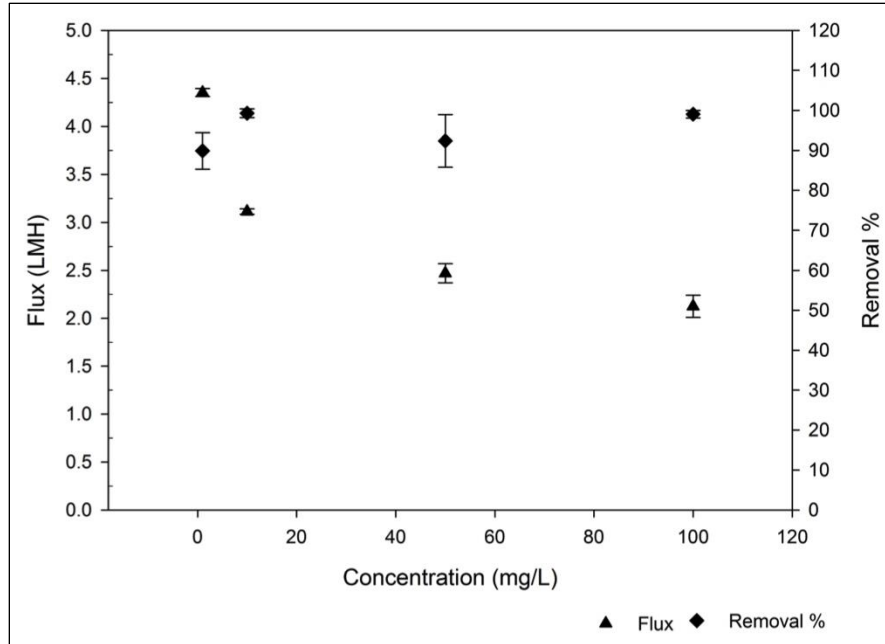


Figure 5.13 d-n-CSGO Flux and Removal Rates Over Various Concentrations of Methylene Blue

The difference in flux for granular and nano CSGO membranes at 345 kPa was not significantly different from one membrane to the other. However, by increasing the pressure exerted upon these membranes the difference in flux can be measured. The d-n-CSGO membranes exhibited about half of the flux of d-g-CSGO membranes at pressures between 1.38 MPa to 4.14 MPa as seen in Figure 5.14.

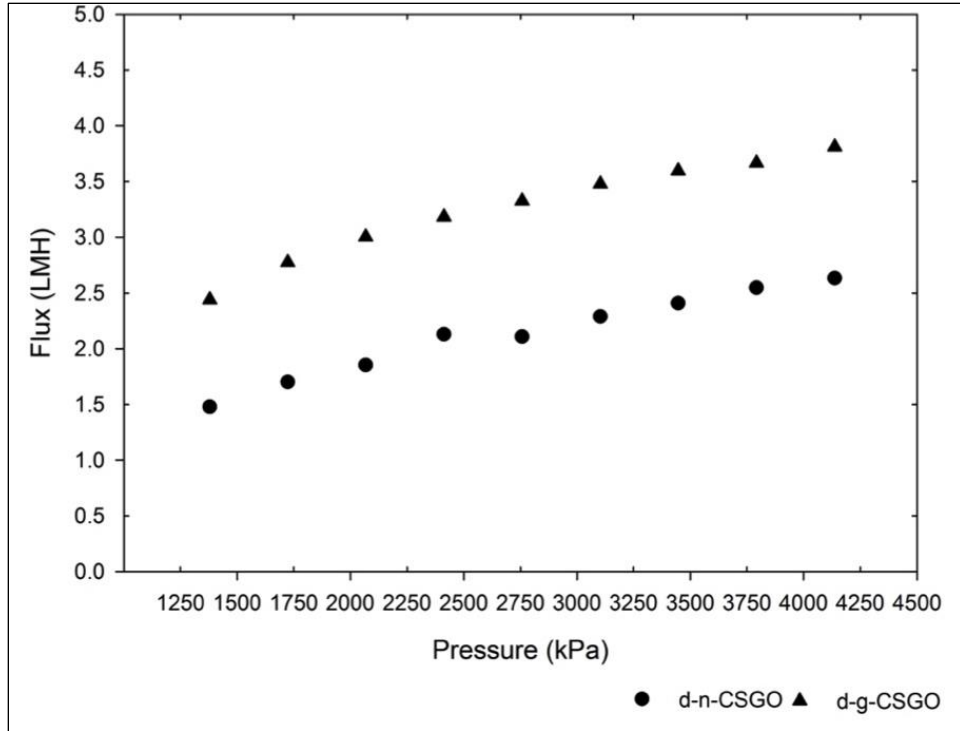


Figure 5.14 d-g-CSGO and d-n-CSGO Water Flux with Varying Pressure

To verify the integrity and removal rate of d-g-CSGO membranes at these pressures a 50 mg/L solution was used as a simulant (Figure 5.15). The membrane was then subjected to four different pressures between 1.38 MPa and 4.14 MPa. Between these pressures flux varied linearly from 2.5 to 3.5 LMH with 100% removal of the dye at each point (Figure 5.15).



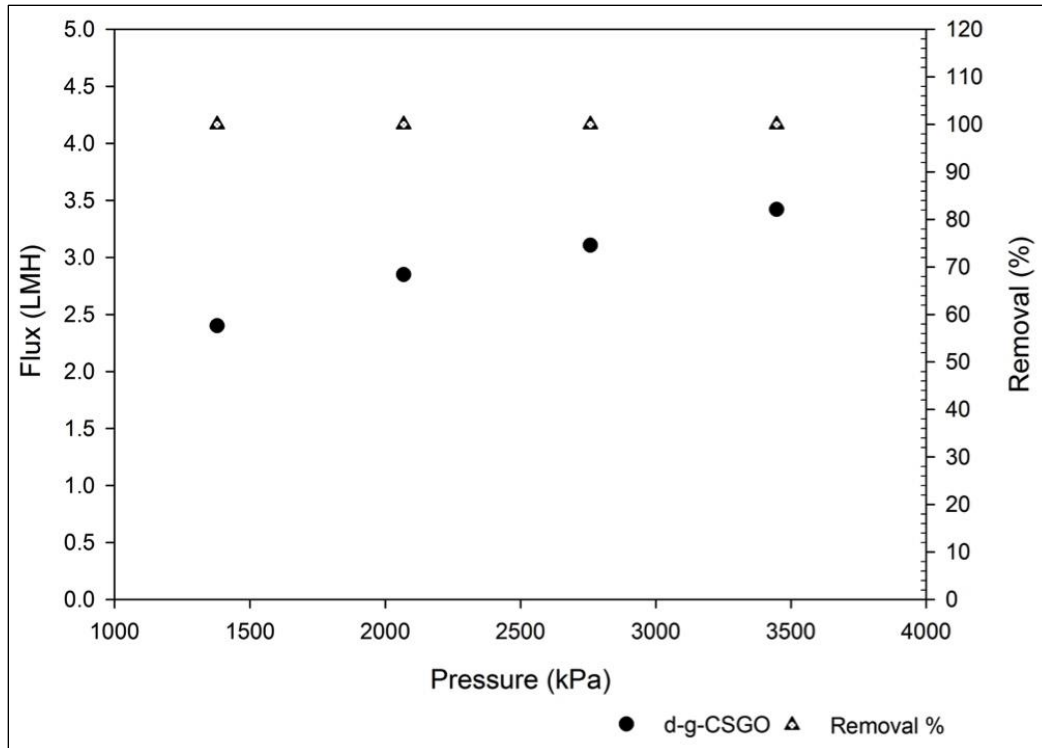


Figure 5.15 Flux vs Pressure for 50 ppm Methylene Blue

## 5.2 Membrane Characterization

Scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD) were carried out. The methods used to obtain the figures below are described in section 4.2.5.

CSGO and Chitosan solutions were created using the ECM and cast as membranes. These were then analyzed via SEM, XPS, and XRD as described in section 4.2.5.

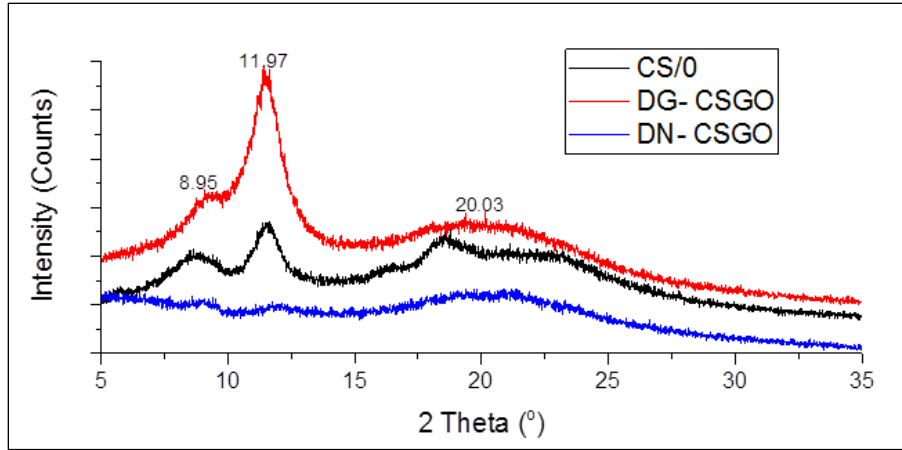


Figure 5.16 XRD Chitosan, d-g-CSGO, d-n-CSGO

Chitosan and CSGO membranes were analyzed via XRD. Peaks were observed around the 12 degree range of 2 Theta (Figure 5.16). This indicates that there is crystallinity and lamellar order present in the analyzed material. Chitosan and d-g-CSGO membrane exhibited this structural behavior with d-g-CSGO being highly ordered compared to the chitosan membrane. However, this property is lost when the membrane is wetted, as it loses its structural stability (Figure 5.17).

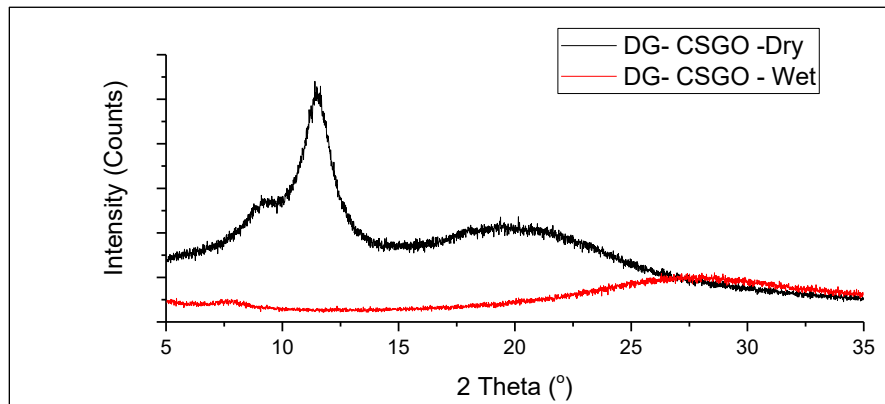


Figure 5.17 XRD of d-g-CSGO Membrane Wet vs Dry

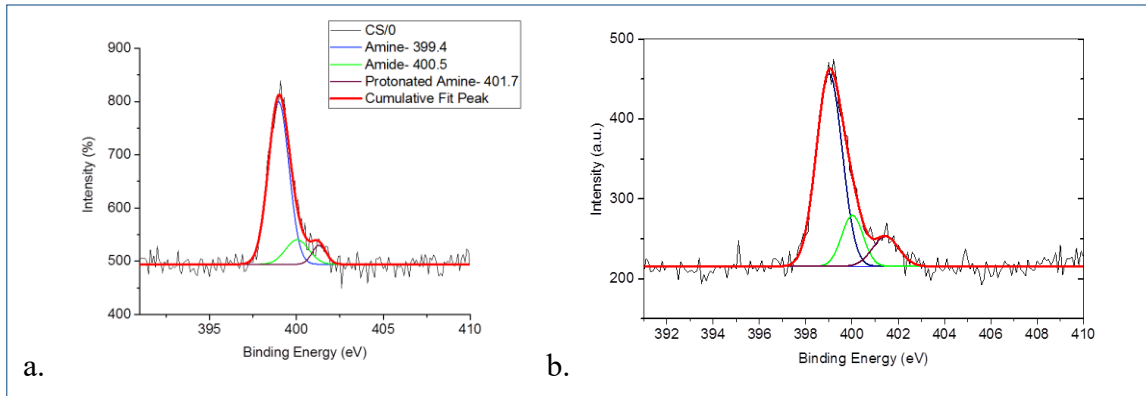


Figure 5.18 XPS, a. Chitosan and b. d-g-CSGO

XPS results for d-g-CSGO in Figure 5.17b indicate an increase in the protonated amine group as compared to a pristine chitosan membrane in Figure 5.17a. The increase in the protonated amine group indicates that new amine bonds are being formed in d-g-CSGO membranes. This indicates strong bonding between chitosan and graphene oxide.

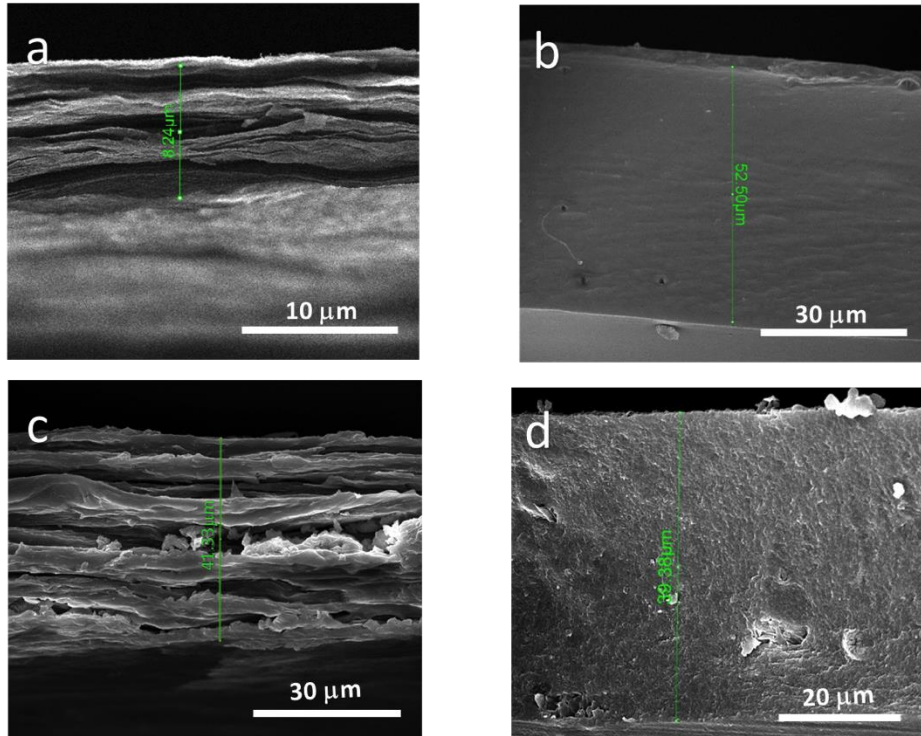


Figure 5.19 SEM Cross Sections: a. Graphene Oxide, b. Chitosan, c. d-g-CSGO, and d. d-n-CSGO

Cross sections of chitosan and CSGO membranes were observed via SEM as designated in Figure 5.19. Their characteristic length and internal structure are also presented. The characteristic lengths for these membranes are shown in Table 5.3.

Table 5.3 Characteristic Lengths by SEM

| Membrane | Characteristic Length ( $\mu\text{m}$ ) |
|----------|---|
| GO       | 8.24                                    |
| Chitosan | 52.50                                   |
| d-g-CSGO | 41.33                                   |
| d-n-CSGO | 39.38                                   |

### 5.3 pH Compatibility

NaOH and HCl solutions were prepared with pH values ranging from 1 to 12. Ten milliliters of each solution was added to a 15 mL glass vial. A coupon cut from a CSGO membrane was placed in each vial and submerged into the liquid (Figures 5.20 and 5.21). Observations were taken at 24 and 336 hours.

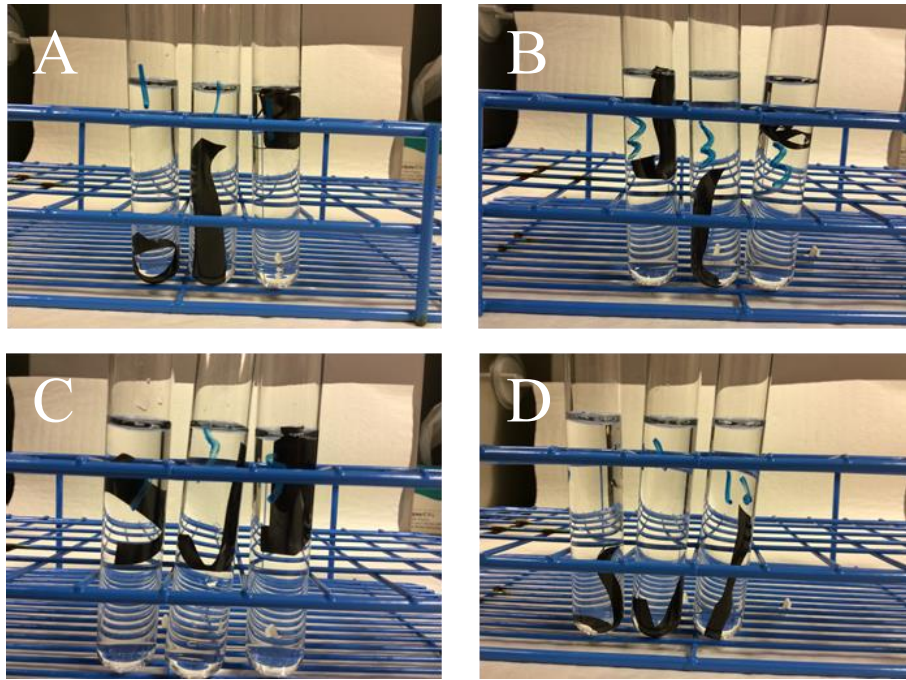


Figure 5.20 Five Minutes After Initial CSGO Coupon Submersion: A. pH 1, B. pH 3, C. pH 7, and D. pH 12

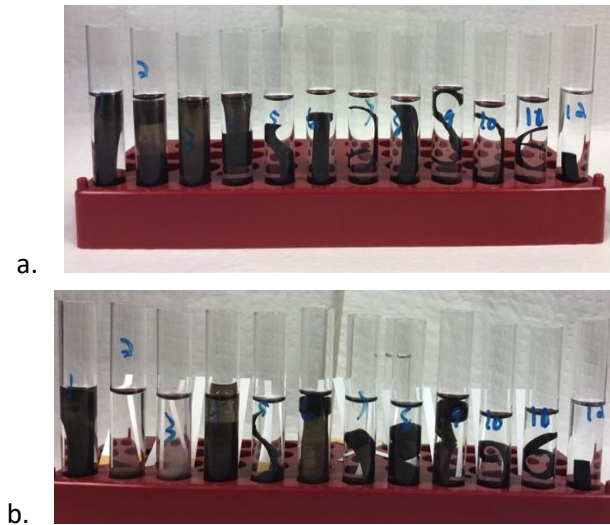


Figure 5.21 1 pH to 12 pH Test of d-g-CSGO Coupons at a. 24 Hours and b. 336 Hours

The CSGO coupons at 24 hours for pH values 1 to 4 had exponentially expanded from their initial size; while those in solution at pH 5 to 12 saw either slight to no expansion as the pH increased. The pH of each solution was determined using color pH indicator strips. After 24 hour, pH values of solutions prepared at pHs 1 to 4 were maintained, while the pH of solutions with initial values between 5 and 11 decreased to pH 5. However, the pH 12 solution was only reduced to a pH of 11 after 24 hours.

The coupons observed again after being submerged for an additional 311 hours. The coupons in solutions at pH 2 and 3 disintegrated completely, while the coupons in solutions at pH 1, 4 to 11 expanded to over twice their original size. The coupon in the pH 12 solution exhibited no sign of expansion or degradation.

#### 5.4 Treated d-g-CSGO Membranes

To further minimize swelling and flux variance of CSGO membranes, the residual acetic acid had to be neutralized. As such, an additional step was added to the

manufacturing process in which the acetic acid was neutralized by either a NaOH base dip, or vaporization at 70°C.

This step was performed to minimize acetic acid interference with the chitosan-GO bonding. The residual acetic acid may be allowing some chitosan to be diluted by the challenge solution, thus creating the variance shown in Figures 5.12 and 5.13.

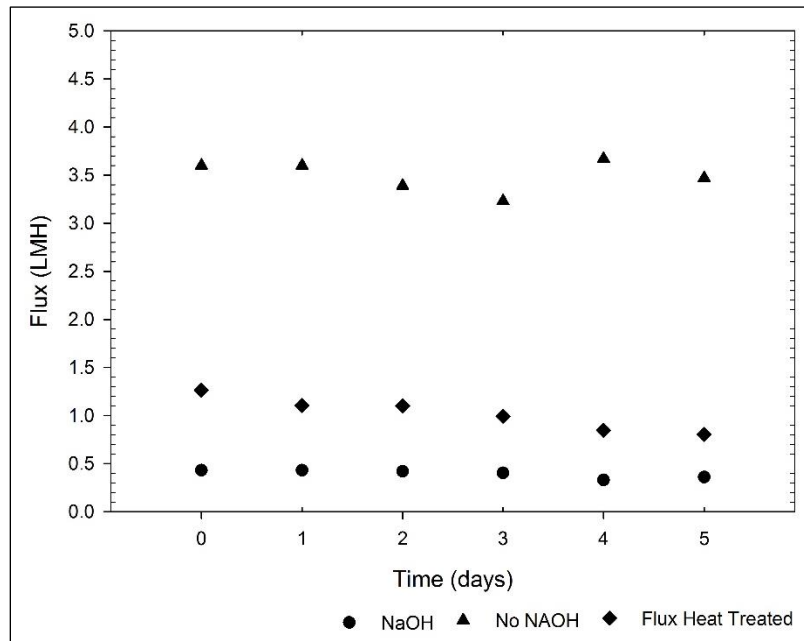


Figure 5.22 Treated d-g-CSGO Membranes at 345 kPa with 10 mg/L MB Solution

Table 5.4 Treated CSGO Membranes Flux and Removal

| Sample       | Average Flux | Average Removal |
|--------------|--------------|-----------------|
| Normal       | 3.49         | 85.25           |
| NaOH Rinse   | 0.41         | 99.83           |
| Heat Treated | 0.95         | 99.85           |

This treatment appeared to be successful at stabilizing the membranes with the drawback of reduced flux at 345 kPa (Figure 5.22). However, at pressures higher than

1.4 MPa the difference in flux is significantly reduced (Figure 5.23). Allowing for the treated membranes to have greater stability without sacrificing flux rates at higher pressures.

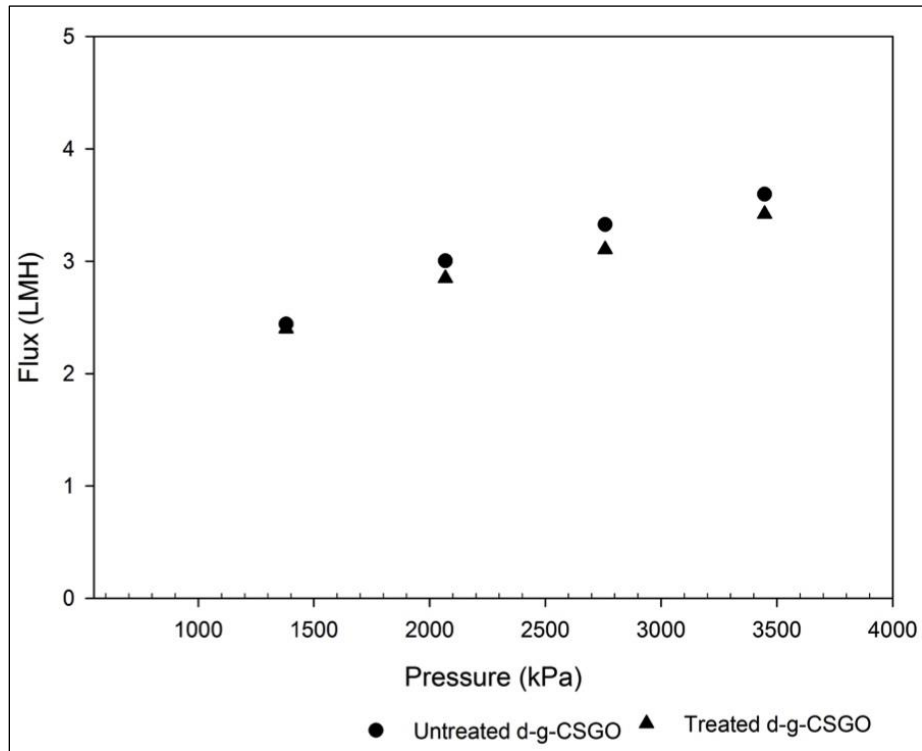


Figure 5.23 Treated and Untreated d-g-CSGO at High Pressures

#### 5.4.1 Scaled Up Membrane

To prove that ECM is a viable method for scaling up of CSGO materials a 30 cm × 42 cm (1260 cm<sup>2</sup>) membrane was produced. The scaled membrane method (SM) was used to produce the scaled up membrane using 720 mL of d-g-CSFO solution poured onto a Plexiglas mold.





Figure 5.24 d-g-CSGO Solution After Pour

A time lapse over 72 hours was recorded while the solution dried, ultimately forming the membrane. The resulting time lapse video (<https://www.youtube.com/watch?v=BplAGoNMz54>) demonstrated how the membrane was set, as well as the effect of the nucleation site on the drying process as it radiated outward. A dry nucleation site formed and expanded until the membrane reached its final state. It took approximately 72 hours for the membrane to dry.



Figure 5.25 Scaled d-g-CSGO Membrane

## CHAPTER VI

### DISCUSSION

#### 6.1 Membrane Formation

When GO is dispersed in solution, it has a metallic-like sheen. The GO sheen is observable when poured into a mold as it visibly moves around in an effort to find its most stable formation. This may be evidence of GO interacting with chitosan. It is also likely that this GO-chitosan self-assembly affects the drying of the chitosan solution. Normally, chitosan solutions prepared in the laboratory has demonstrated its propensity to congeal as it dries in a uniform “top down” fashion. However, when CSGO membranes form, they dry anisotropically while forming the final product.

During the course of this study, it was noted that suspended GO particles form linear patterns when poured into a flat mold. These patterns were observed instantly, and sometimes reformed when agitated. Thereby, suggesting that GO particles are bonding with chitosan and also self-assembling when placed on a flat surface.

During dehydration of the solution, a nucleation site was observed at a single point in the viscous solution which was subsequently reduced. GO lamellar layers appeared to be compressed along the membrane/solution boundary. This action was demonstrated to be irreversible as once the membrane was formed it would not revert back into solution by simple rehydration; rather it would require mechanical and chemical breakdown.

## 6.2 pH Compatibility

The d-g-CSGO coupons were submerged in solution with pH values ranging from 1 to 12. An interesting behavior was observed in which almost all the coupons expanded when submerged, however, the extent of that expansion was affected by the pH. Coupons submerged in acidic solutions expanded to over twice their original size, whereas coupons submerged in basic solutions expanded slightly or not at all (Figure 5.21).

This indicates that the membrane is interacting with the  $H^+$  ions in solution causing deformation and expansion. This behavior does not occur in the basic solutions as the membrane appears to have a lesser affinity for  $OH^-$  ions; hence the absence of swelling of the membrane.

After 336 hours the coupons placed in acidic solutions were either deformed or disassociated completely. While those in basic solutions remained more intact, but still deformed with the exception of the coupon placed in a basic solution at pH 12. This coupon exhibited no sign of deformity when submerged.

This expands upon what was observed in Section 5.4 with treated membranes. After the acetic acid was completely neutralized, the membranes lost flux but gained structural stability that was not demonstrated with the past membranes. This suggests that if the residual acetic acid is not removed, it aids in destabilizing the membrane by solubilizing chitosan (Figure 5.22).

## 6.3 Membrane Characteristics and Performance

The graphene oxides selected for use in this study were the nano and granular graphene oxides purchased from Graphene Supermarket, Inc. The two types of GO

powders were chosen based on particle size, dimensions ranging from 90 nm in diameter for n-GO and 0.3 to 0.07 micron sheets for g-GO, to compare membrane performance.

This difference in particle size resulted in differences across the integral structure of the membrane. The internal characteristics of d-g-CSGO and d-n-CSGO membranes are fundamentally different, as seen in Figure 5.19. The d-g-CSGO forms a lamellar structure similar to that of a GO membrane. While d-n-CSGO incorporates itself throughout the solution forming an amorphous structure similar to that of a chitosan membrane.

The differentiating structures of these membranes depends on how GO particles interact with chitosan. In a d-g-CSGO membrane g-GO uses chitosan as a building block to help assemble its preferred planar structure. While in d-n-CSGO membranes n-GO incorporates itself into chitosan's structure without altering it significantly (Figure 5.19).

The effect of graphene oxide on the internal membrane structure can be confirmed via X-ray powder diffraction (XRD) in Figure 5.14. It was observed that g-GO added a crystalline structure to chitosan's usual amorphous structure, while n-GO had almost no effect on chitosan structure. This confirms the change in a chitosan membrane's structure by g-GO seen in Figure 5.19c.

These characteristics are indicative of a difference between the two membranes at a microscopic level. However, these differences are not perceived when used for water filtration for the ranges tested in this work. As shown in Table 5.2, the average flux and recovery between the two types of membranes are virtually identical with only slight differences between them.

Due to the differences in the membrane's structure, it would be expected that there would be significant differences in the removal or flux rates. But there was no such difference observed. The differentiation of particle shape or size is what can explain the structural difference between the two membranes.

The particle shape and size of GO powders influence the arrangement of chitosan throughout the membrane. Granular graphene oxide powder contains flake sizes ranging from 0.3 to 0.7 microns in which more than 50% are arranged within 1 atomic layer. This allows the granular GO to arrange itself into GO's preferred lamellar structure while also incorporating chitosan into its matrix. This electrostatic interaction observed via XPS in Figure 5.18. Chitosan attaches itself onto the carboxylic acids found around the edges and the surface of GO forming protonated amides. By GO forming these bonds with chitosan it is able to form a stable material that also increases the strength of the chitosan (Lim et al., 2012; Shao et al., 2013; Zuo et al., 2013).

On the other hand, nano GO does not alter these properties to the extent of that of the g-GO. The size of n-GO (90 nm) prohibits significant alteration of the initial chitosan structure. As it incorporates itself throughout the membrane, n-GO makes small adjustments while maintaining chitosan's amorphous structure. Thus, the increased crystallinity and ordered structure observed in d-g-CSGO is not present in d-n-CSGO membranes.

Fluxes and removal rates presented in Table 5.2 are not significantly different between the membrane types even though their internal structures are completely different. This suggests that the internal structure of a CSGO membrane may be

insignificant to its filtration characteristics. Instead thickness and permeable pathways can be considered determining factors for flux in these membranes.

Rather than passing through open channels or pores, water incorporates into the membrane creating hydrated channels. These channels allow water to pass through the membrane while excluding other chemicals. As the membrane continues to hydrate, the channels continue to expand thus allowing a greater percentage of the contaminant to pass through.

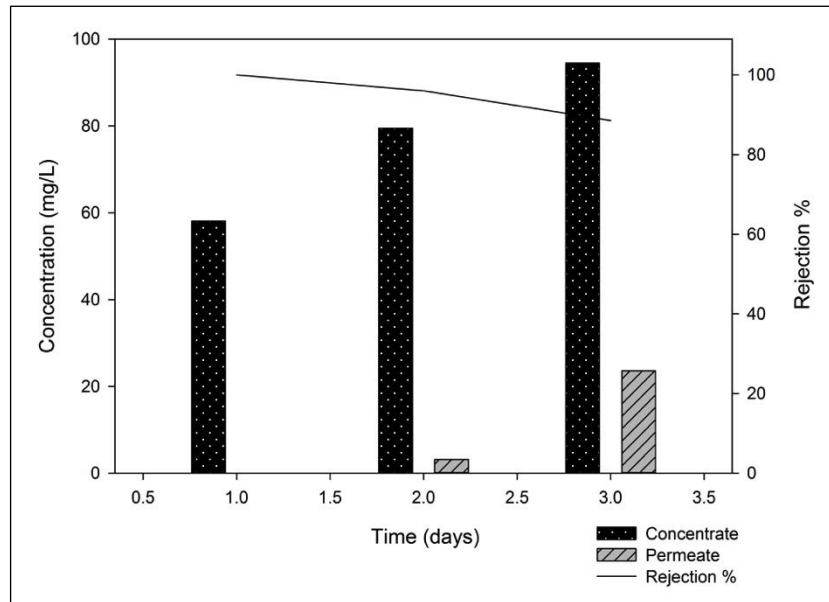


Figure 6.1 Methylene Blue (50 ppm) Concentration vs Time at 345 kPa

This trend is observed when the concentration of the methylene blue permeate increases over time as a result of these expanding channels, which are created due to the degradation of chitosan. This occurs when the residual acetic acid dissolves the chitosan. A clear indication of this is the increasing percentage of dye permeating the untreated membrane versus the treated membrane (Figure 6.2).

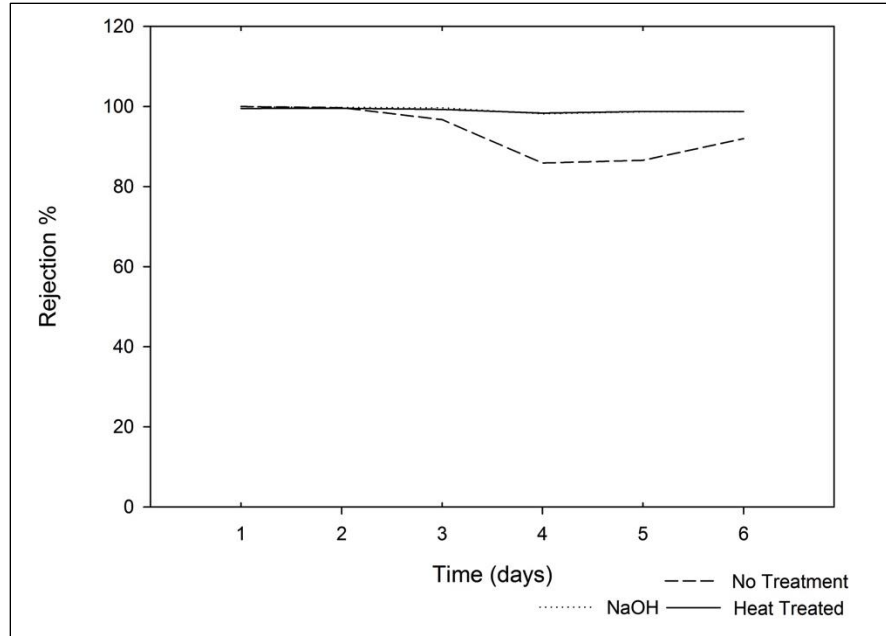


Figure 6.2 Treated and Untreated Rejection Rates of Methylene Blue @ 100 ppm

Removing the acetic acid is essential for the long-term stability of CSGO membranes. Even though flux rates are diminished at low pressures, the differences are negligible at higher pressures (Figure 5.23). The increased structural stability of treated membranes indicates a longer lifespan in comparison to membranes containing residual acetic acid.

#### 6.4 Cost of Manufacture

Graphene oxide can be obtained commercially from a number of sources with varying costs per gram of GO. These usually range from \$100 to \$300 USD per gram of graphene oxide. In this study the graphene oxide obtained from Graphene Supermarket had a markup of \$125 USD per 100 mg for nano GO, while granular GO was marked up as \$250 USD per gram. This cost roughly \$1.25 USD per mg of nano GO and \$0.25 USD

per mg of granular graphene oxide. Making the cost differential per milligram of nano graphene oxide five times greater than that of granular graphene oxide. (Appendix A)

While there is also a cost for chitosan, it can be considered negligible for this calculation. The chitosan for this study cost roughly \$0.011/mg or \$0.55 per membrane. Thus, making graphene oxide the material's cost driver for CSGO membrane manufacture. When manufacturing a 72 cm<sup>2</sup> cross flow membrane nano and granular membranes cost \$125 USD and \$25 USD in materials, respectively.

Table 6.1 Commercial Membrane Costs

| Membrane Type    | Membrane Cost |
|------------------|---------------|
| Reverse Osmosis  | \$25          |
| Nano-Filtration  | \$25          |
| Ultra-Filtration | \$25          |
| d-g-CSGO         | \$25          |
| d-n-CSGO         | \$125         |

When compared to commercial Reverse Osmosis, Nano-Filtration, and Ultra-filtration membranes, sold by Sterlitech to fit the crossflow reactor used in this study, d-g-CSGO membranes can be financially competitive. However, d-n-CSGO membranes on the other hand are considered too expensive as they are roughly five times the cost of what is commercially available with product markups already in place.

This makes d-n-CSGO unfavorable from a financial and budgetary perspective. As d-g-CSGO exhibited similar qualities and properties of d-n-CSGO at a fifth of the cost; making d-g-CSGO the most preferable option when manufacturing CSGO membranes for cross-flow reactors.



## CHAPTER VII

### CONCLUSIONS

The following conclusions were drawn from this work.

- Chitosan and graphene oxide (CSGO) can be mixed together and formed into a membrane via solution casting. This method was proven to be scalable for membranes with an area of up to 1260 cm<sup>2</sup>.
- The structural support provided by Nitrocellulose to CSGO membranes allow these membranes to be used in a cross-flow reactor. Without this extra structural support the external forces acting upon the membrane will cause the membrane to elongate and fail. This is likely due to the presence of residual acetic acid within the membrane. By removing the residual acetic acid these membranes may exhibit low flux at 345 kPa with significantly decreased variability.
- CSGO membranes separated over 95% of methylene blue via size exclusion at various concentrations and pressures using cross-flow filtration. CSGO membranes also exhibited increased durability when the residual acetic acid was removed with no significant decrease in flux at pressures higher than 1.4 MPa.

## CHAPTER VIII

### FUTURE WORK AND STUDY SUMMARY

#### 8.1 Future Work

Moving forward, work with CSGO membranes should focus on the following:

- Improve membrane flux by optimizing the chitosan and graphene oxide composition for high contaminant removal rates;
- Evaluate CSGO membranes for potential removal of negatively charged dyes, radionuclides, salts of difference valencies, and aromatic compounds;
- Investigate possible mechanisms to increase the durability of CSGO membranes over an extended period of time; and comparing the results above against nano-filtration and ultra-filtration membranes.

Table 8.1 Study Summary Table

| Trail                  | Experimental Conditions |                     |                      | Results          |                | Experimental Comments |            |  |
|------------------------|-------------------------|---------------------|----------------------|------------------|----------------|-----------------------|------------|--|
|                        | CSGO Solution           | Variables           | Solution             | Membrane Support | MB Rejection   |                       | Flux (LMH) | Rejection %  |
| CSGO scale up          | CSGO                    | 40 mL in Petri dish | Bell Jar             |                  |                |                       |            | 150µm CSGO Material after 120 hours  |
| CSGO scale up          | CSGO                    | 40 mL in Petri dish | Incubator            |                  |                |                       |            | 150µm CSGO Material after 48 hours   |
| CSGO scale up          | d-CSGO                  | 200 mL in acrylic   | Incubator            |                  |                |                       |            | Plastic-like material after 72 hours   |
| CSGO on CFR            | CSGO                    | 10mL/min            | 50 Psi               | 10ppm MB         | No             |                       |            | Deformed Membrane with Initial filtering   |
| CSGO on CFR            | n-CSGO                  | 10mL/min            | 50 Psi               | 10ppm MB         | No             |                       |            | Impermeable with deformation   |
| Supported membrane     | d-g-CSGO                | 10mL/min            | 50 Psi               | 10ppm MB         | Paper Filter   | 1.25                  | 98         | Material's expansion was contained   |
| Supported membrane 2   | d-g-CSGO                | 10mL/min            | 50 Psi               | 20ppm MB         | Paper Filter   | 1.68                  | 99         | Works as a membrane, Feed solution concentrated  |
| Dye Rejection          | d-g-CSGO                | 10mL/min            | 50 Psi               | 1 ppm MB         | Nitrocellulose | 2.64                  | 92         |  |
| Dye Rejection          | d-g-CSGO                | 10mL/min            | 50 Psi               | 10ppm MB         | Nitrocellulose | 3.49                  | 99         |  |
| Dye Rejection          | d-g-CSGO                | 10mL/min            | 50 Psi               | 50 ppm MB        | Nitrocellulose | 3.33                  | 95         |  |
| Dye Rejection          | d-g-CSGO                | 10mL/min            | 50 Psi               | 100ppm MB        | Nitrocellulose | 2.11                  | 99         |  |
| Dye Rejection          | d-n-CSGO                | 10mL/min            | 50 Psi               | 1 ppm MB         | Nitrocellulose | 4.35                  | 90         | Flux was variable with rejection greater than 90% for all solutions. Both membrane types appear to function in a similar manner.               |
| Dye Rejection          | d-n-CSGO                | 10mL/min            | 50 Psi               | 10ppm MB         | Nitrocellulose | 3.11                  | 99         |  |
| Dye Rejection          | d-n-CSGO                | 10mL/min            | 50 Psi               | 50 ppm MB        | Nitrocellulose | 2.47                  | 92         |  |
| Dye Rejection          | d-n-CSGO                | 10mL/min            | 50 Psi               | 100ppm MB        | Nitrocellulose | 2.13                  | 99         |  |
| Pressure Profile       | d-g-CSGO                | 25 mL/min           | 1.38-4.14 MPa        | Water            | Nitrocellulose | 2.5 - 3.5             |            | d-g-CSGO flux 50% higher than d-n-CSGO   |
| Pressure Profile       | d-n-CSGO                | 25 mL/min           | 1.38-4.14 MPa        | Water            | Nitrocellulose | 1.5 - 2.5             |            | Higher pressures and fluxes do not foul the membrane   |
| Pressure Profile       | d-g-CSGO                | 25 mL/min           | 1.38-4.14 MPa        | 50 ppm MB        | Nitrocellulose | 2.5 - 3.5             | 100        | CSGO deformation is due to solution acidity  |
| pH Test                | d-g-CSGO                | 24 hr               | 336 hr               | pH 1-12          |                |                       |            |  |
| Treated CSGO - Base    | d-g-CSGO                | 1M NaOH             | 30 min treatment     | 100 mg/L         | Nitrocellulose | 0.41                  | 100        | Stability is increased with the drawback of flux significantly being reduced. Thermally Treated membranes may still have residual acetic acid. |
| Treated CSGO - Thermal | d-g-CSGO                | Oven @ 70 °C        | 24 hr @ 70 °C        | 100 mg/L         | Nitrocellulose | 0.95                  | 100        | Membrane was stable with linear increases of Pressure to Flux  |
| Pressure Profile       | d-g-CSGO                | Oven @ 70 °C        | 25 hr / Oven @ 70 °C | Water            | Nitrocellulose | 2.5 - 4               |            | Resulting Material was identical to past membranes   |
| Scaled Membrane        | d-g-CSGO                | Fume Hood           | 720 mL               |                  |                |                       |            |  |

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APPENDIX A  
COST TO MANUFACTURE CSGO MEMBRANES

## Dimensional Parameters for Membrane

$$V := 50 \text{ mL} \quad \text{area} := 5 \text{ in} \cdot 3 \text{ in} = 96.774 \text{ cm}^2 \quad VA := \frac{V}{\text{area}} = 0.517 \frac{\text{mL}}{\text{cm}^2}$$

## Cost per CSGO membrane

$$\text{nano} := \frac{125 \text{ ¢}}{100 \text{ mg}} = 1.25 \frac{\text{¢}}{\text{mg}} \quad \text{granular} := \frac{250 \text{ ¢}}{1 \text{ gm}} = 0.25 \frac{\text{¢}}{\text{mg}}$$

$$\text{nano\_cost} := \frac{\text{nano} \cdot 300 \text{ mg}}{150 \text{ mL}} = 2.5 \frac{\text{¢}}{\text{mL}} \quad \text{granular\_cost} := \frac{\text{granular} \cdot 300 \text{ mg}}{150 \text{ mL}} = 0.5 \frac{\text{¢}}{\text{mL}}$$

$$\text{Nano\_membrane\_cost} := \text{nano\_cost} \cdot 50 \text{ mL} = 125 \text{ ¢}$$

$$\text{Graphene\_membrane\_cost} := \text{granular\_cost} \cdot 50 \text{ mL} = 25 \text{ ¢}$$

## Cost for a Thin Membrane

$$\text{Nano\_membrane\_cost} := \text{nano\_cost} \cdot 25 \text{ mL} = 62.5 \text{ ¢}$$

$$\text{Graphene\_membrane\_cost} := \text{granular\_cost} \cdot 25 \text{ mL} = 12.5 \text{ ¢}$$

## Cost for Scaled Membrane

$$A_{\text{desired}} := 12 \text{ in} \cdot 17 \text{ in}$$

$$\text{Total\_Volume} := VA \cdot (A_{\text{desired}}) = 680 \text{ mL}$$

$$n_{\text{cost}} := \text{nano\_cost} \cdot \text{Total\_Volume} = 1700 \text{ ¢}$$

$$g_{\text{cost}} := \text{granular\_cost} \cdot \text{Total\_Volume} = 340 \text{ ¢}$$