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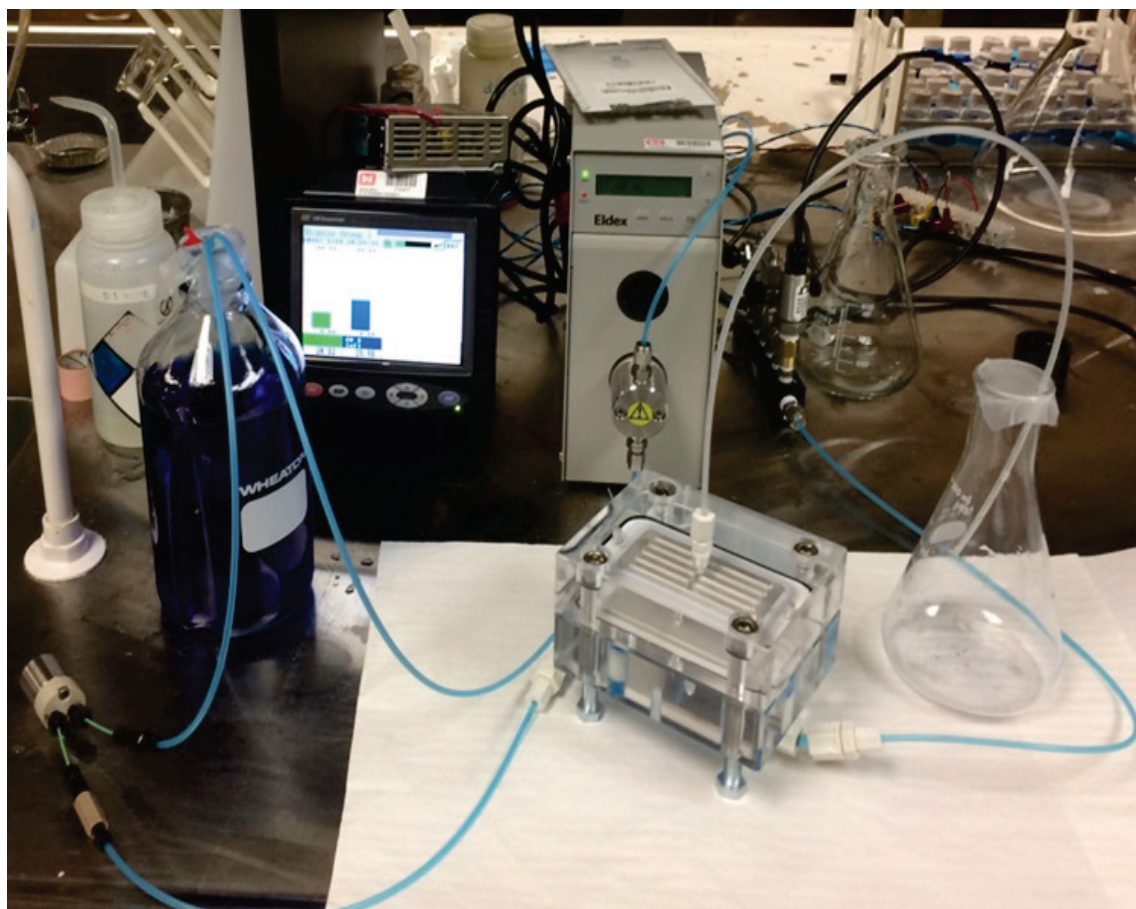


Environmental Quality/Installations

Crosslinking Graphene Oxide and Chitosan to Form Scalable Water Treatment Membranes

Jose Mattei-Sosa, Victor F. Medina, Chris S. Griggs,
and Veera Gnanaswar Gude

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Crosslinking Graphene Oxide and Chitosan to Form Scalable Water Treatment Membranes

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Abstract

Graphene oxide (GO) has emerged within the last decade as a next generation material for water treatment. Fabrication of GO 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 chitosan/graphene oxide (CSGO) sheets. 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 (CFR) and challenged with methylene blue at concentrations ranging from 1 to 100 parts per million (ppm) at 345 kilopascal (kPa), with fluxes ranging from 1 to 4.5 L/(m² hr) and 100% removal via 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.

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Preface

This report is a modification of a thesis prepared by Jose Mattei-Sosa for his Master's Thesis in Civil and Environmental Engineering for Mississippi State University under the guidance of Dr. Veera Gude, an Associate Professor. This report includes characterization data generated by Mojtaba Abolhassani and Lauren Greenlee of the University of Arkansas, and which has been included in Abohassani et al. (2017). The work was published in the thesis supported project titled "Deployable Treatment of Decontamination Effluent," which was the Environmental Quality/Installations Program (EQI) under work unit 448534. The program manager was Mr. John Ballard, Dr. Victor Medina was the Principal Investigator, and Dr. Chris Griggs was the Task Lead for Graphene Oxide membrane studies.

The work was performed by the Environmental Engineering Branch (EPE) of the Environmental Processes and Engineering Division (EP), U.S. Army Engineer Research and Development Center - Environmental Laboratory (USACE-EL). At the time of publication, Dr. Andy Martin was Chief, CEERD-EPE, Mr. Jared Johnson was the Acting Division Chief. Dr. Elizabeth A. Ferguson was the Technical Director of Military Materials in the Environment. The Deputy Director of ERDC-EL was Dr. Jack E. Davis, and the Director of EL was Ilker R. Adiguzel.

COL Ivan P. Beckman was Commander of ERDC, and Dr. David W. Pittman was the Director.

Unit Conversion Factors

Multiply	By	To Obtain
atmosphere (standard)	101.325	kilopascals
bars	100	kilopascals
cubic feet	0.02831685	cubic meters
cubic inches	1.6387064 E-05	cubic meters
cubic yards	0.7645549	cubic meters
degrees Fahrenheit	$(F-32)/1.8$	degrees Celsius
feet	0.3048	meters
gallons (U.S. liquid)	3.785412 E-03	cubic meters
inches	0.0254	meters
microinches	0.0254	micrometers
microns	1.0 E-06	meters
ounces (mass)	0.02834952	kilograms
ounces (U.S. fluid)	2.957353 E-05	cubic meters
pounds (mass)	0.45359237	kilograms

Acronyms and Abbreviations

Acronym	Meaning
ASTM	American Society for Testing and Materials
ATR-FTIR	Attenuated Total Reflection-Fourier Transfer Infrared
Au	Gold
CFM	Cross-flow Method
CFR	Cross-Flow Reactor
CS	Chitosan
CSGO	Chitosan/Graphene Oxide
d-g-CSGO	diluted granular Graphene Oxide
d-GO	dispersed GO
d-n-CSGO	Dilute chitosan and nanoscale graphane oxide
d-x-CSGO	Dilute chitosan and unspecified scale graphane oxide
ECM	Evaporative Casting Method
EL	Environmental Laboratory
EMC	Evaporative Membrane Casting
EPE	Engineering Branch
eV	electronvolt
g-GO	granular Graphene Oxide
GO	Graphene Oxide
H	Hydrogen
kPa	Kilopascal
Kv	Kilovolts
LMH	Liter per Meter Square per-hour
mA	milliamps
MB	Methylene Blue
n-GO	nano-Graphene Oxide
nm	nanometer
OH	hydroxide
Pd	Palladium
PPM	Parts Per-Million
SEM	Scanning Electron Microscope
SM	Scaled Membrane
USACE	U.S. Army Engineer Research and Development Center

UV	Ultraviolet
VASA	Vacuum Assisted Self-Assembly
XPS	X-ray Photoelectron Spectroscopy

1 Introduction

1.1 Background

1.1.1 Membrane filtration

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 that include high capital and operating costs, large quantities of wastewater/concentrate end products, and fouling. New membrane materials are sought to reduce these problems and minimize operation costs.

1.1.2 Graphene oxide (GO)

Graphene oxide (GO) has progressively been studied in computational models and in laboratory studies (Cohen-Tanugi and Grossman 2015). The studies focused on the preparation of laboratory-scale GO membranes and were successful in creating pristine, composite, and coated membranes. The membranes were tested solely in dead end flow systems (Huang et al. 2014; Lim et al. 2012; J. Shen et al. 2014; Shen et al. 2015; Wang et al. 2015; Zhao et al. 2013).

While the GO membranes were successful at separating organic compounds at varying fluxes, most studies have centered on making GO membranes via vacuum assisted self-assembly (VASA) (Hu and Mi 2013; Perreault et al. 2015). Since the membranes are restricted in size by the funnel and filter support, the membranes VASA makes tend to be smaller in shape, therefore, they cannot be used on large cross-flow reactors (CFR).

To overcome the size limitations of VASA, solution casting was used to create a chitosan/graphene oxide (CSGO) composite membrane for cross-flow filtration. Using this method, a membrane of any size can be manufactured.

1.2 Objectives

All GO materials and composites have been produced using vacuum filtration, but the scalability factor of these materials remains an ongoing challenge. The objective of this report is to demonstrate that CSGO membranes can be manufactured, scaled efficiently, and used in a CFR using an evaporative casting approach.

1.3 Approach

Vacuum filtered GO membranes that lack a crosslinking agent tend to dissociate in water and cannot be used for water filtration. The author hypothesized that using chitosan as a crosslinking agent would allow for a CSGO composite to form a scalable membrane that could be used for treatment of aqueous solutions in cross flow filtration.

1.4 Scope

The scope of this project was focused on bench-scale research to explore new methods of casting graphene oxide membranes using an evaporative method allowing for effective upscaling.

2 Literature Review

2.1 GO and its potential uses in water separation

GO 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, and they allow GO to adsorb contaminants such as dissolved metals and organic dyes (Fan et al. 2012a, b; Gao et al. 2011; Najafabadi et al. 2015; Jiao et al. 2015; Liu et al. 2012). Some researchers have created a magnetic form of GO for adsorbent recovery (Li et al. 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 can remove small particles via size exclusion while allowing water to pass through at a high rate (Perreault et al. 2015). Modeling results have suggested that GO membranes can achieve fluxes of 400 to 4000 L m⁻² bar⁻¹ with performance increases of 2 to 3 orders of magnitude higher than reverse osmosis while still rejecting salts (Cohen-Tanugi and Grossman 2012).

While computational studies have demonstrated that this is possible, laboratory studies have encountered many challenges trying to achieve this. In laboratory studies, if a crosslinking agent was not added to stabilize the membrane, the GO would separate over time once submerged in water. Yeh et al. (2015) reported that the use of an anopore disk in a vacuum apparatus stopped dissociation of GO membranes in water. Yeh et al. (2015) discovered that aluminum from the anopore disk leached into the GO solution and incorporated itself into the membrane, thereby strengthening membrane bonds. This allowed the resulting membrane to be tested in water-based solutions. Although this issue was resolved, it remains unclear if these membranes are feasible for commercial use. In addition, GO composites and crosslinking materials require further investigation to resolve stability and scalability issues.

2.2 Chitosan (CS)

Chitosan (CS) is a readily available and inexpensive chemical that is created from the waste products of crustaceans, which include shrimp and crabs. Chitin, which is an essential constituent of a crustacean's exoskeleton, is deacetylated to form chitosan. CS exhibits resistance to most organic solvents and has been studied as a membrane material.

CS 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, however, the group as a whole adds hydrophobicity to the material, which can make it a problem for water filtration. Moreover, 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 CS and GO materials

CS and GO materials have not been thoroughly studied as a membrane material. There have been studies in which a CSGO composite has been tested for mechanical properties, antimicrobial properties, and the absorbance of heavy metals (Hu et al. 2010; Perreault et al. 2015; Xi et al. 2016). During these studies it was discovered 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 et al. 2014). However, the absorbance for Au(III) and Pd(II) were 1,076.649 mg/g and 21.920 mg/g, respectively (Liu et al. 2012). Although these preliminary studies show this composite's promise, more studies are needed to understand its capabilities at various loading ratios.

The characteristics for CSGO materials are summarized in Table 1. CS and GO on their own are unsuitable for membrane filtration, as they are prone to swell, adsorb methylene blue (MB), and/or disintegrate. However, the combination of these materials minimizes or eliminates these characteristics. This is beneficial, as the inability to adsorb MB indicates that CSGO can act as a membrane rather than a sorbent.

Table 1. Desired properties for competent membrane.

Material	Methylene Blue Sorption Capacity (200mg/L)	Aqueous Stability
Graphene Oxide	46% Reduction Qe (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 Qe (46 mg/g)	Stable in wet state at 43.4±1.8 MPa

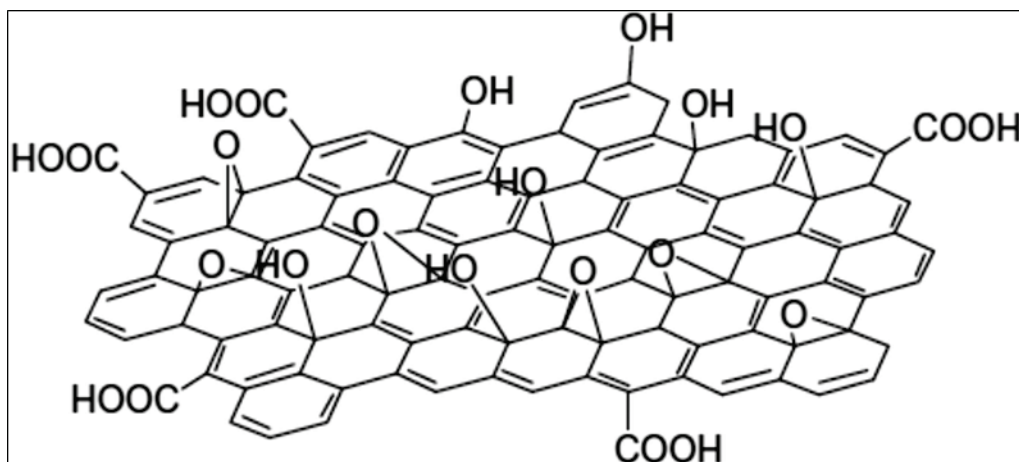
3 Materials and Methods

3.1 Materials

3.1.1 GO

GO was obtained from Graphene Supermarket (graphene-supermarket.com, Calverton, NY) in three different forms (Figure 1). 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 oxide (g-GO), which had a thickness of one atomic layer and a flake size of 0.3 to 0.07 microns. The other powder was called nano-graphene oxide (n-GO), which had a thickness of 1 nanometer (nm) and a diameter of 90 nm.

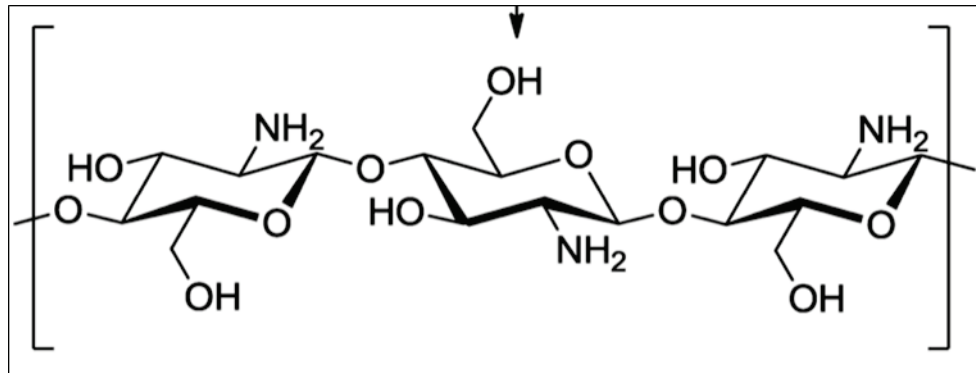
Figure 1. Chemical structure of GO. (Nasrollahzadeh et al. 2015).



3.1.2 CS solution

Fifty grams of medium molecular weight, poly-d-glucosamine chitosan material (SKU 448877-50G) used during this experiment was obtained from Sigma Aldrich (www.sigmaaldrich.com). In addition, an acetic acid, ReagentPlus® ≥99% (Sigma Aldrich SKU A6283-2.5L), was used as a solvent to dissolve chitosan in water (Figure 2).

Figure 2. Chemical structures of chitosan (Heckel et al. 2013).



3.1.3 MB

One hundred grams of MB was purchased from Sigma Aldrich (SKU M9140-100G) for this experiment. The challenge solutions were made by mixing MB and water to form solutions with concentrations ranging from 1, 10, 50, 100, and 130 mg/L. MB 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.

3.1.4 Nitrocellulose millipore membrane

Nitrocellulose membrane rolls (Cat. No. 1620115), which measured 0.45 μm , 30 cm \times 3.5 m were obtained from Bio-Rad (www.bio-rad.com, Hercules, CA).

3.2 Methods

3.2.1 CSGO

CSGO solutions were made with GO powders. A dispersion of GO was also used to initially prototype CSGO materials. These solutions were cast into membranes, which were challenged with MB in a CFR. Efficient flux and removal of these membranes were calculated at a predetermined time interval.

3.2.1.1 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 minutes. Then,

1.5 grams of medium molecular weight chitosan and 1 mL of $\geq 99\%$ acetic acid were added to the solution. The solution was stirred for 72 hours.

3.2.1.2 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 minutes. Then, 1.5 grams of medium molecular weight chitosan and 1 mL of $\geq 99\%$ were added to the solution. The solution was stirred for 72 hours.

3.2.2 Evaporative membrane casting (EMC)

The CSGO solution was poured into a desired casting mold and left to dry in both an incubator and 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.

3.2.3 Scaled membrane (SM)

Seven hundred twenty milliliters of Diluted Granular Graphene Oxide (d-g-CSGO) solution was used to cover an area of 1,394 cm² 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.

3.2.4 Cross-flow method (CFM)

Two CFRs were obtained from Sterlitech (www.sterlitech.com) for this experiment. One of them was an acrylic CF042A reactor, while the other was a stainless steel CF042SS. CSGO membranes were created by pouring 50 mL of an Unspecified Diluted Graphene Oxide (d-x-CSGO) solution in a 97 cm² mold. The molds were die cut and placed on one of the CFRs. The membranes were tested in both a supported, and unsupported mode or configuration. Although most of the experiments were conducted using the acrylic reactor, both types were arranged in a continuous flow configuration with a recycling loop, this allowed for extended run times over several days. Unless specified otherwise, the CFR experiments were conducted at a flow rate of 10 mL/min with an operating pressure of 345 kPa. Flux data, concentrate, and permeate samples were taken and placed in scintillation vials every 24 hours (Figures 3–6).

Figure 3. Block flow diagram of experimental setup for CFR.

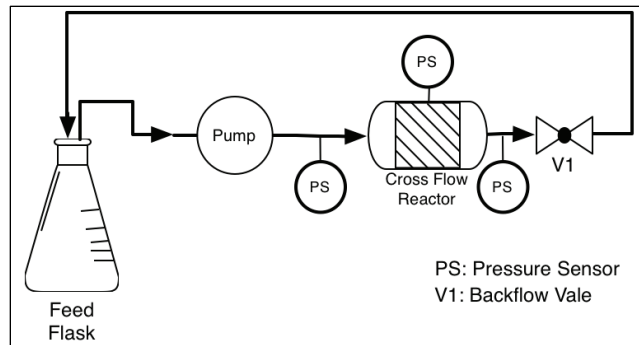


Figure 4. Cross-flow membrane experimental setup for acrylic reactor.

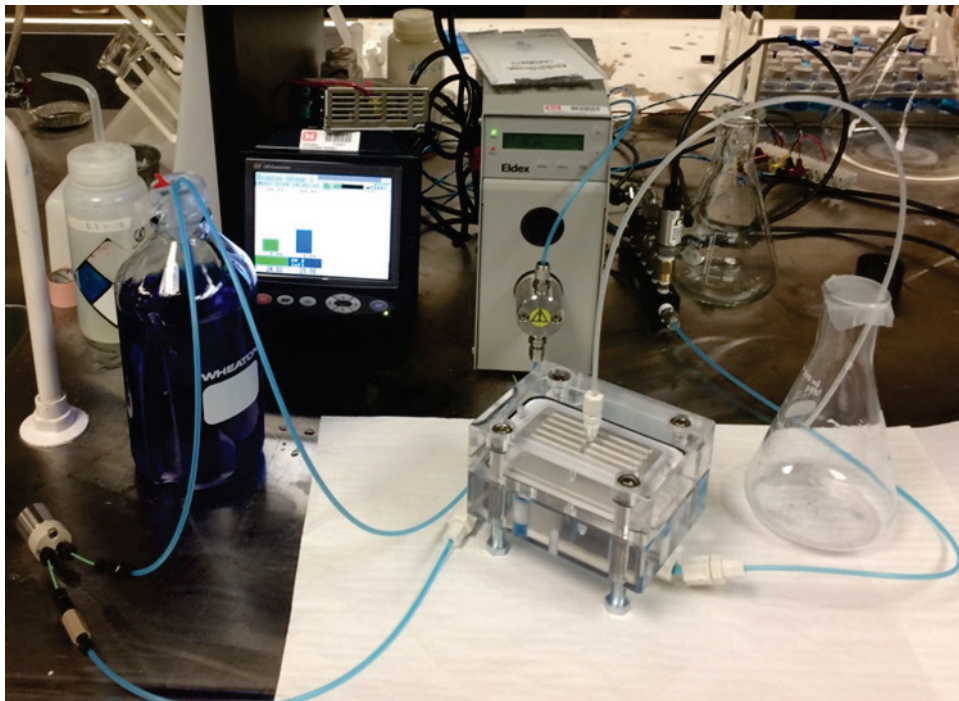


Figure 5. Sterlitech membrane die (12 cm × 6 cm).

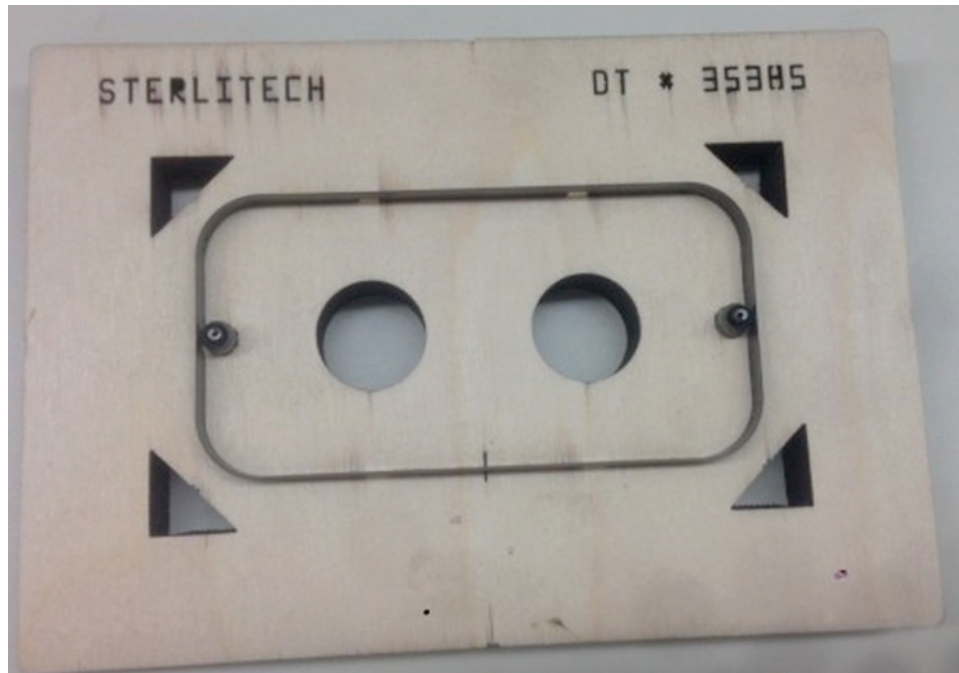
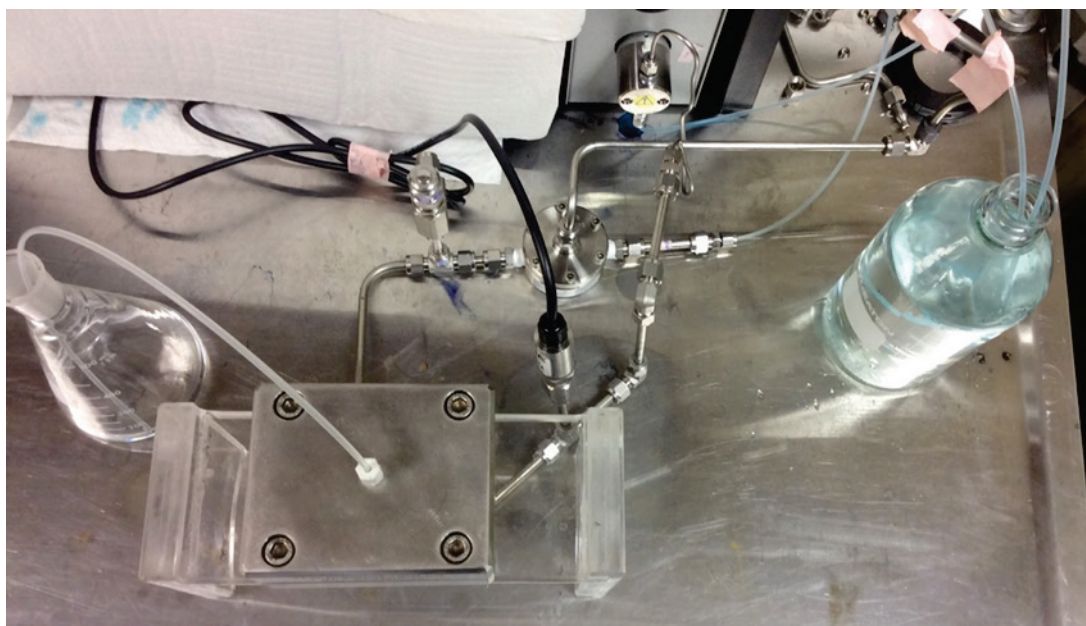


Figure 6. Cross-flow membrane experimental setup for stainless steel reactor.



MB was used as the model contaminant in this study. MB 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 the American Society for Testing and Materials (ASTM) E275. A dilution ratio of 1:10 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 shown in Figures 7 and 8.

Figure 7. MB calibration curve at 660 nm.

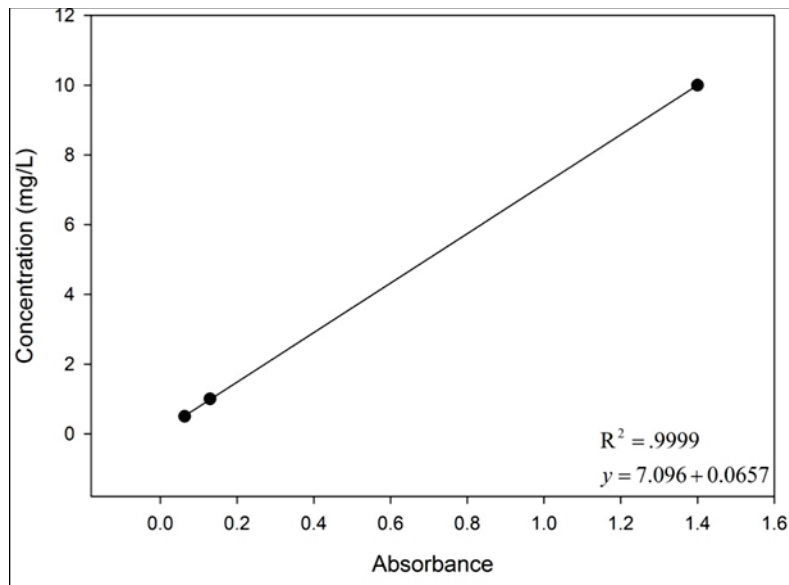
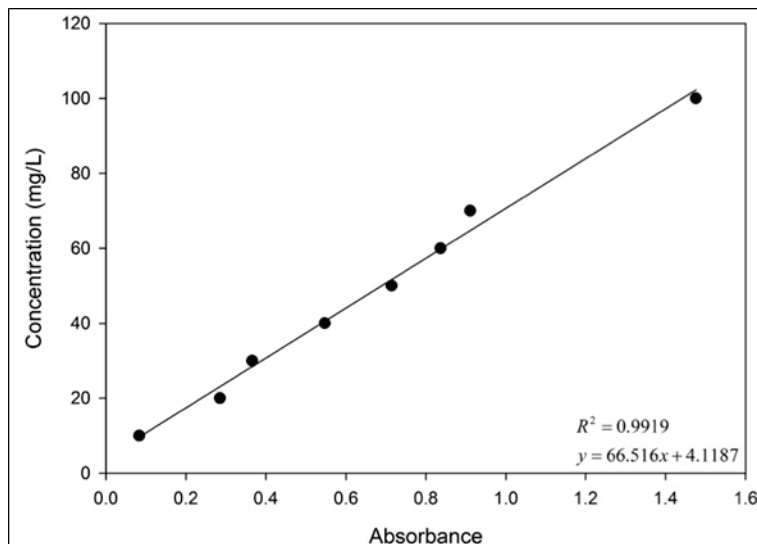


Figure 8. MB calibration curve at 660 nm.



3.2.5 Morphological and chemical analysis

The surface and cross-section morphologies for samples were studied using a scanning electron microscope (SEM), specifically the Nova Nanolab 200 with 15 kilovolts (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 the SEM. An Attenuated Total Reflection-Fourier Transfer Infrared (ATR-FTIR) spectrophotometer, specifically, a Spectrum BX FTIR spectrometer equipped with a Pike technology accessory was used to study the molecular interaction between GO and chitosan. The spectra were used at 8 cm^{-1} resolutions in the range of 4,000 to 500 cm^{-1} . An X-ray photoelectron spectroscope (XPS), specifically, a PHI VersaProbe 5,000 with PHI multipack data analysis software was used to evaluate the chemical composition of the films. Initial survey scans (0 – 1400 electronvolt [eV] binding energy) were followed by detailed scans for carbon (275 – 295 eV) and nitrogen (390 – 410 eV). High-resolution X-ray diffraction, specifically, Philips X'Pert- MRD diffractometer with 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 minute^{-1} at the voltage of 45.0 kV and a current of 40.0 milliamps (mA).

3.2.6 CSGO membrane pH compatibility

The 5.1 cm \times 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.

3.2.7 NaOH treated CSGO membranes

The d-g-CSGO membranes were treated with a pH 14 solution of Sodium Hydroxide (NaOH) at 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.

3.2.8 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.

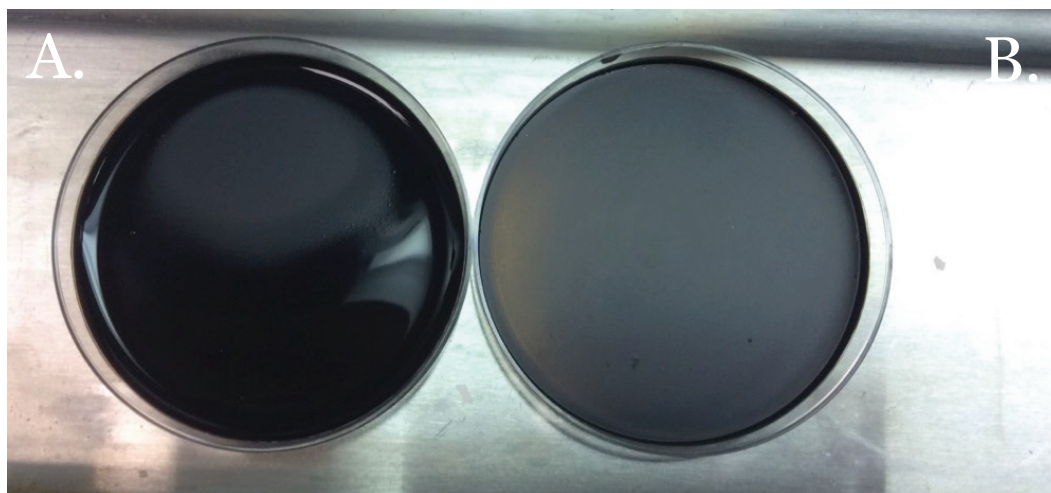
4 Results

4.1 Manufacturing scalable CSGO membranes

4.1.1 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 μm 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 9).

Figure 9. CSGO solution after drying for 24 hours: (A) CSGO solution dried in a bell jar; (B) 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 9. This behavior is characteristic of CSGO materials as it occurred while drying every sample.

A CSGO membrane capable of fitting a CFR 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 CF (Figures 10 and 11).

Figure 10. Mold with 200 mL of CSGO dispersion solution.

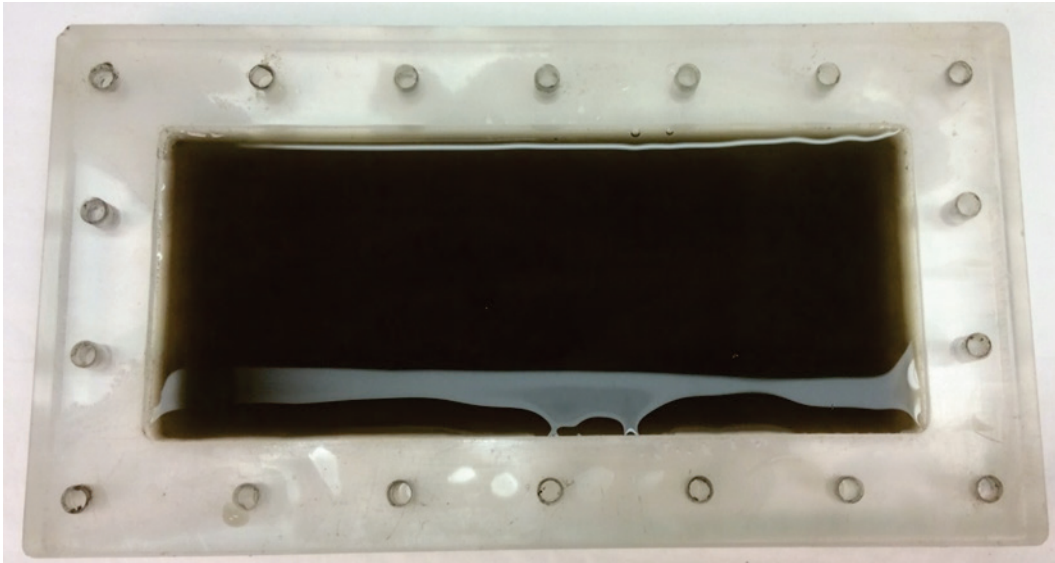


Figure 11. Dried diluted CSGO membrane after 72 hours of incubation.



4.1.2 CSGO membranes in a cross flow reactor

A CSGO membrane using diluted GO was prepared using ECM and placed in a CFR. 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, however, the membrane failed soon after causing MB 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 (Figures 12–15).

Figure 12. d-CSGO membrane on CFR.



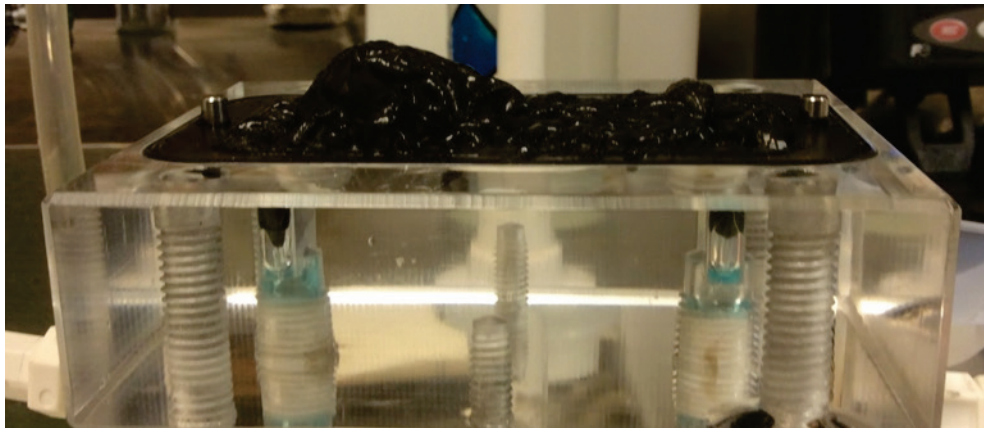
Figure 13. Membrane filtering MB (10 mg/000).



Figure 14. Top View of d-CSGO membrane after failure.



Figure 15. Side view of d-CSGO membrane after failure.



A nano CSGO membrane was cast and tested using a CFR (Figure 16). This membrane was virtually impermeable after six hours on the CFR 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 17).

Figure 16. (A) Nano CSGO membrane after trimming; (B) Nano CSGO membrane in CFR.

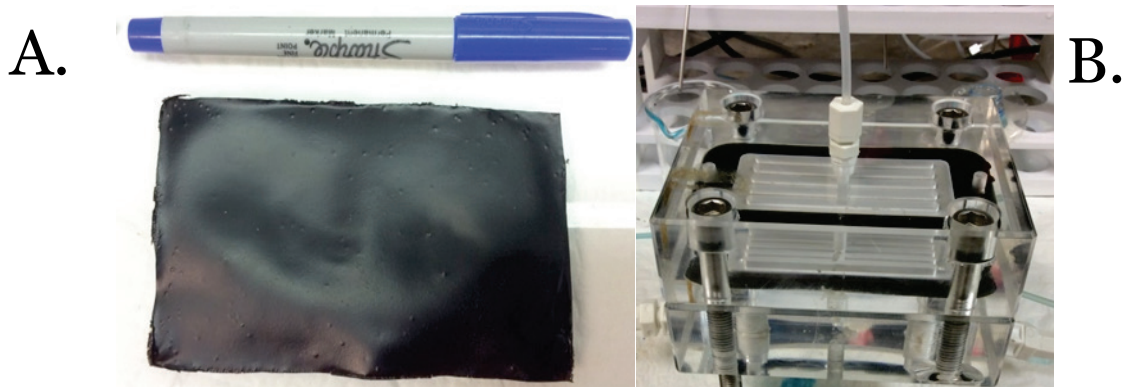
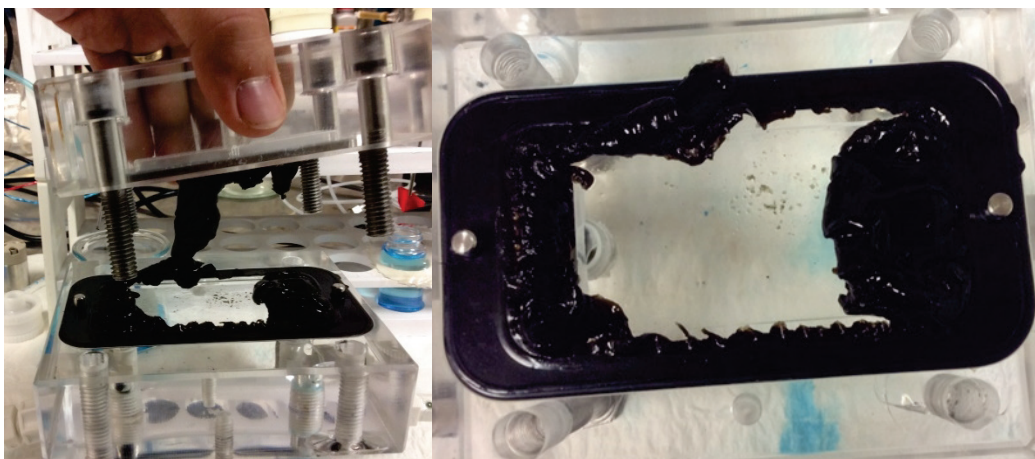


Figure 17. n-CSGO membrane failure after six hours in a CFR.



This kind of behavior was not seen in dead end filtration, as constant pressure throughout the membrane prevents swelling. However, in cross-flow filtration, forces exerted on a membrane are in tangential direction. CSGO membranes also swelled to several times their original thickness, which exacerbated 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 new method allowed membrane to swell within the confines of the support, while still allowing the membrane to be used for cross-flow filtration.

4.1.3 Membrane performance

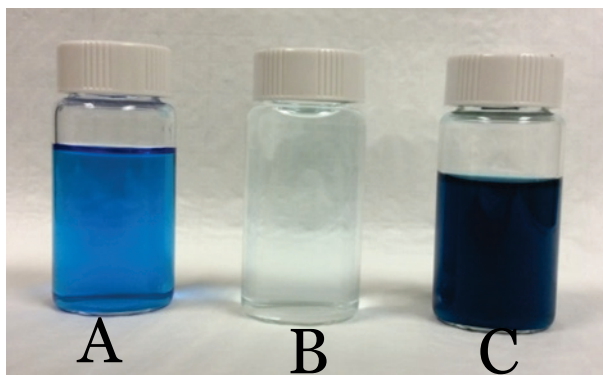
The new membranes were designated as d-x-CSGO and created and tested in a CFR (Figure 18). These membranes were permeable with low swelling that could be controlled by external supports. As such, d-g-CSGO membranes were challenged with MB at 10 mg/L with a feed rate of 10 mL/min at 344.74 kPa over 72 hours. The resulting flux was 1.25 Liter/(meter²*hour) (LMH).

Figure 18. Bottom of the CFR.



Using the same membrane, a subsequent experiment was performed in which the membrane was challenged with a 20 mg/L solution of MB 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 MB, which suggested that the mechanism of removal was size exclusion (Figure 19).

Figure 19. (A) 10 mg/L methylene feed, (B) membrane permeate, and (C) feed concentrate.



Samples were analyzed via ultraviolet (UV)-visible spectroscopy using ASTM E257 (Table 2). Concentrations were calculated using the calibration curves found in Figures 7 and 8.

Table 2. d-g-CSGO flux of MB 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 μm 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 attempts hereafter.

ECM made granular and nano based CSGO membranes and challenged them against MB solutions varying from 1 mg/L to 100 mg/L (Table 3 and Figures 20 and 21).

Table 3. Average flux and recovery of MB 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 20. d-g-CSGO flux and removal rates over various concentrations of MB.

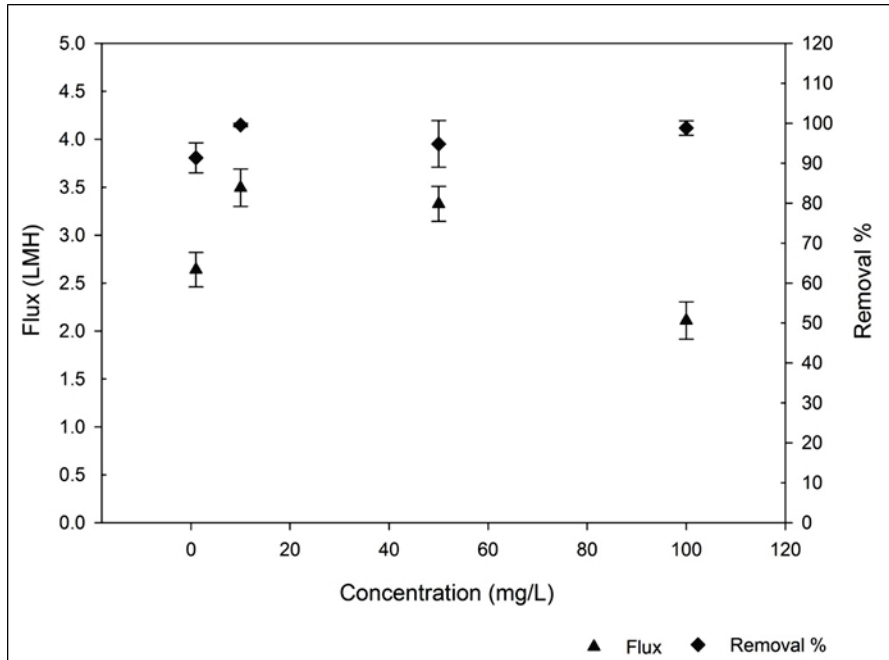
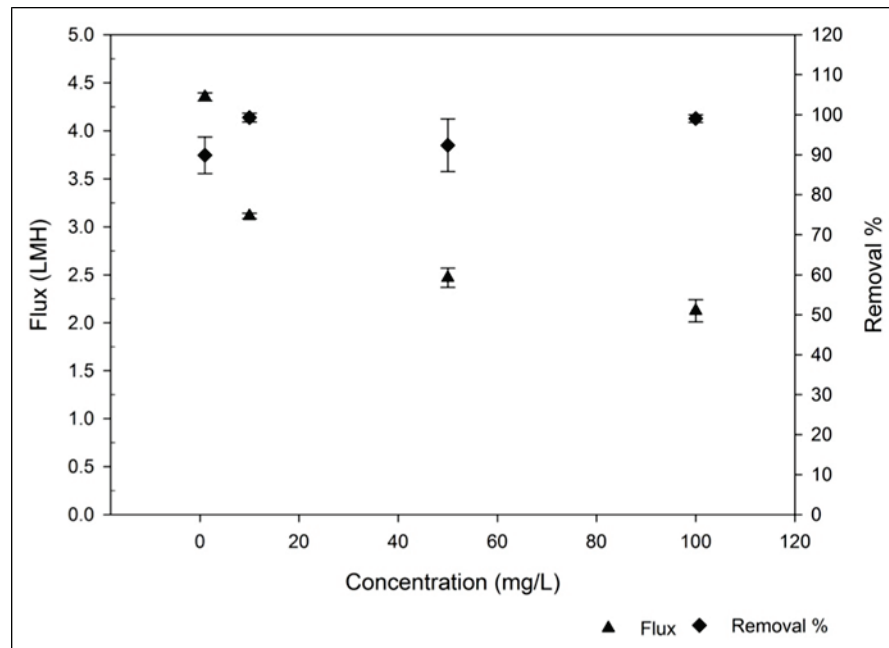


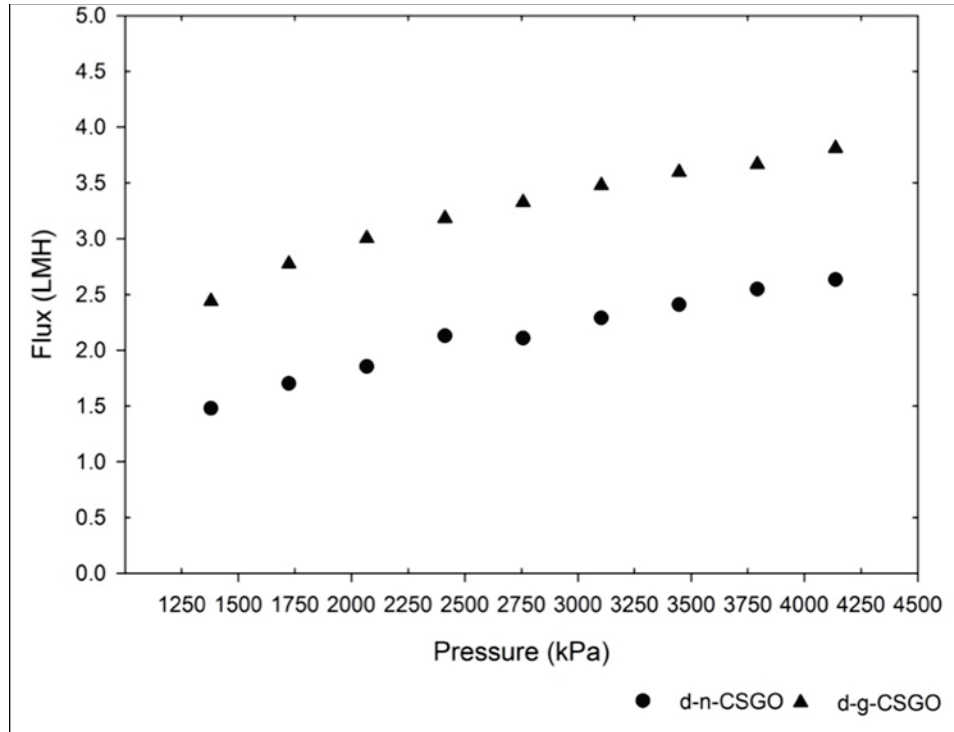
Figure 21. d-n-CSGO flux and removal rates over various concentrations of MB.



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

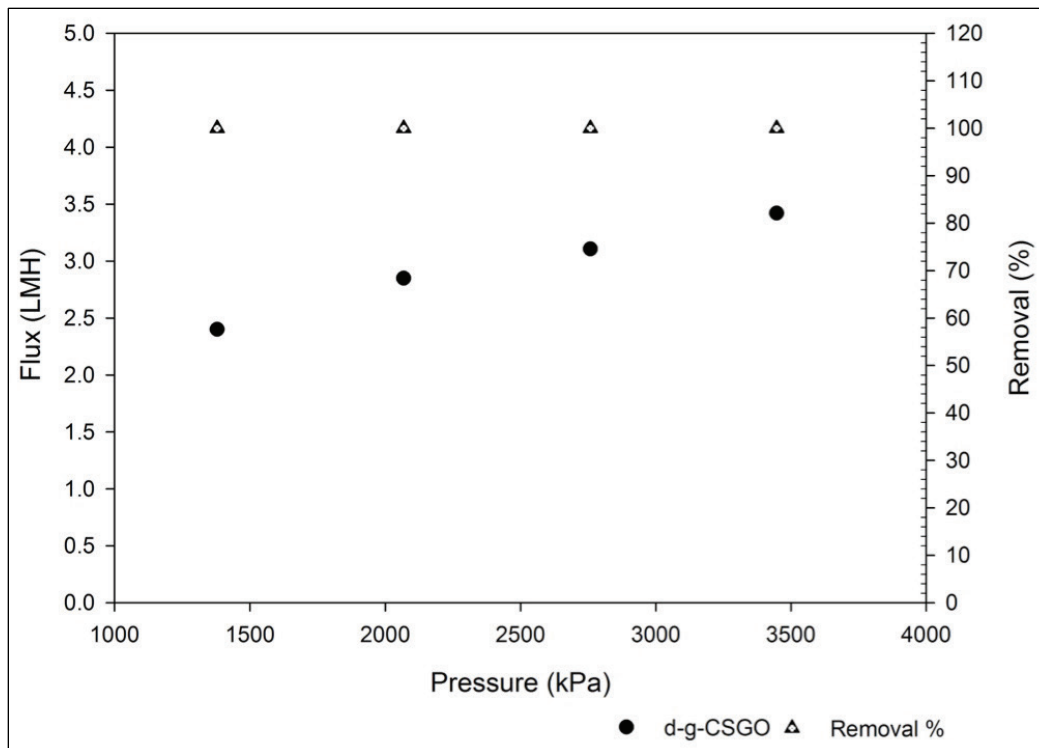
of the flux of d-g-CSGO membranes at pressures between 1.38 megapascal (MPa) to 4.14 MPa as seen in Figure 22.

Figure 22. 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 23). Then, the membrane was 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 23).

Figure 23. Flux vs. pressure for 50 ppm MB.

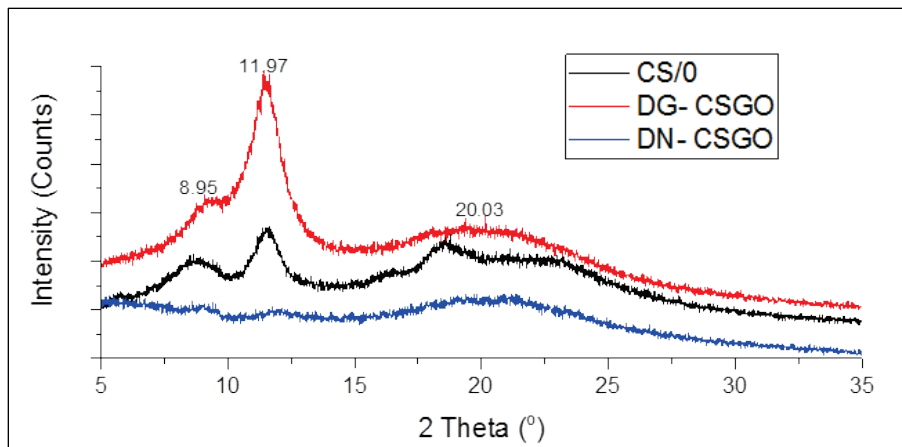


4.2 Membrane characterization

SEM, XPS, and XRD were carried out during this research (Figure 24). The methods used to obtain the figures below are described in section 3.2.5.

CSGO and chitosan solutions were created using the ECM and cast as membranes. These were later analyzed using SEM, XPS, and XRD.

Figure 24. XRD Chitosan, d-g-CSGO, d-n-CSGO.



CS and CSGO membranes were analyzed via XRD. Peaks were observed around the 12 degree range of 2 theta (Figure 25). This indicates that there is crystallinity and lamellar order present in the analyzed material. CS 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 26).

Figure 25. XRD of d-g-CSGO membrane wet vs. dry.

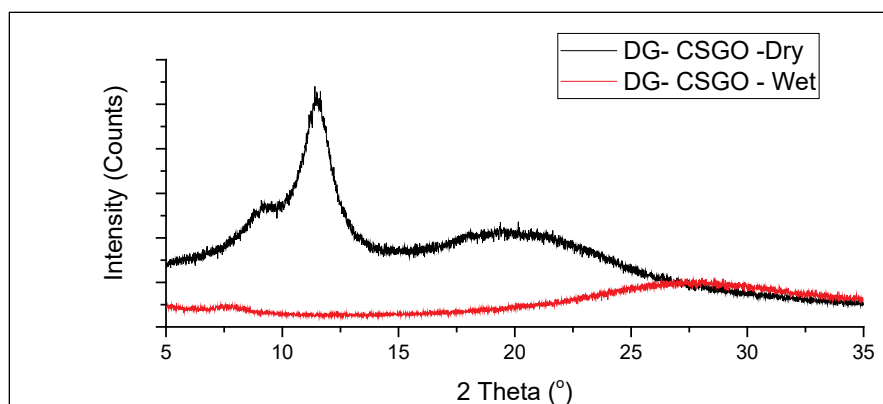
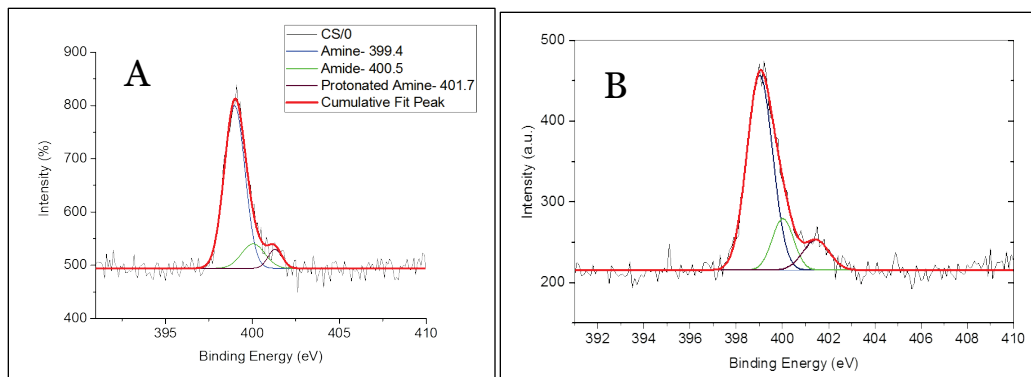
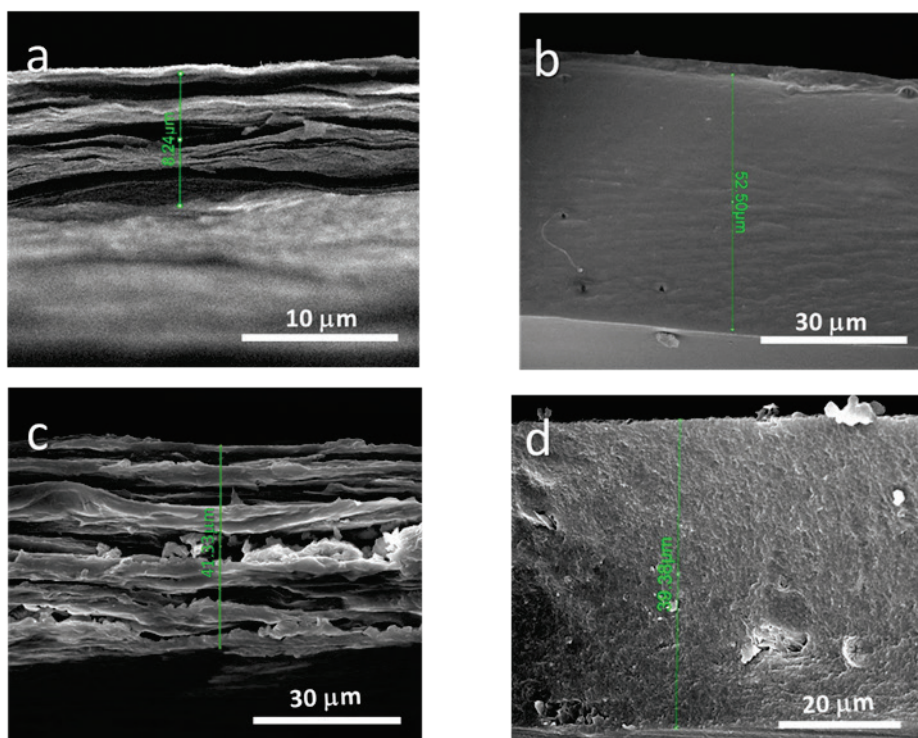


Figure 26. XPS, (A) chitosan and (B) d-g-CSGO.



XPS results for d-g-CSGO in Figure 27 (b) indicate an increase in the protonated amine group as compared to a pristine chitosan membrane in Figure 27 (a). The increase in the protonated amine group indicates that new amine bonds are being formed in d-g-CSGO membranes and shows strong bonding between chitosan and GO.

Figure 27. 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 during SEM as designated in Figure 27. Their characteristic length and internal structure are also presented. The characteristic lengths for these membranes are shown in Table 4.

Table 4. Characteristic lengths by SEM.

Membrane	Characteristic Length (μm)
GO	8.24
CS	52.50
d-g-CSGO	41.33
d-n-CSGO	39.38

4.3 pH compatibility

NaOH and hydrochloric acid (HCl) solutions were prepared with pH values ranging from 1 to 12. Ten milliliters of each solution were 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 28 and 29). Observations were taken at 24 and 336 hours.

Figure 28. Five minutes after initial CSGO coupon submersion: (A) pH 1, (B) pH 3, (C) pH 7, and (D) pH 12.

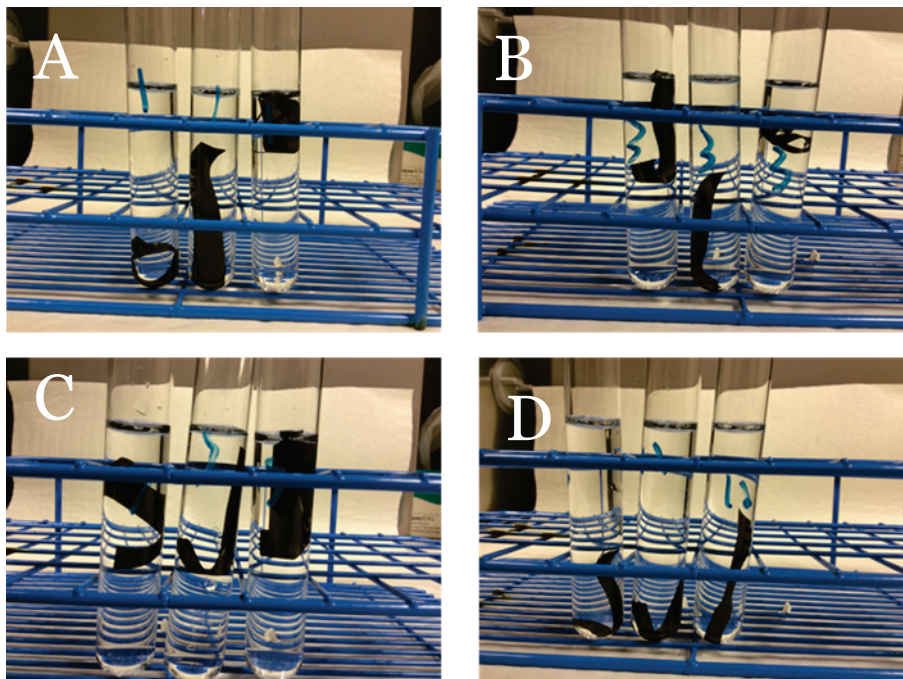
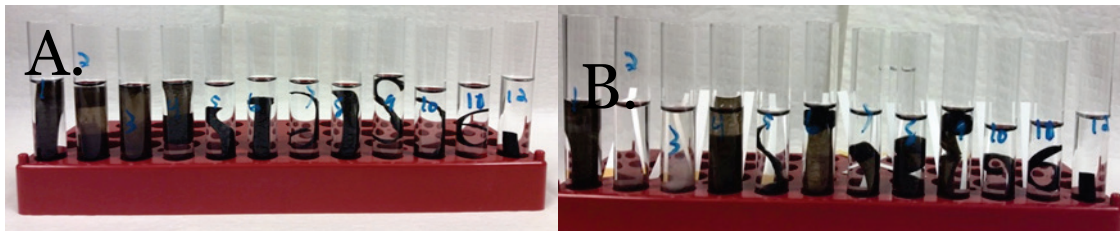


Figure 29. 1 pH – 12 pH test of d-g-CSGO coupons at (A) 24 hours, and (B) 336 hours.



The CSGO coupons at 24 hours for pH values 1 – 4 had exponentially expanded from their initial size, while those in solution at pH 5 – 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 hours, pH values of solutions prepared at pHs 1 – 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 were 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 – 11 expanded to over twice their original size. The coupon in the pH 12 solution exhibited no sign of expansion or degradation.

4.4 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 an NaOH base dip or vaporization at 70° C (Table 5).

This step was performed to minimize acetic acid interference with the CSGO bonding. The residual acetic acid may be allowing some chitosan to be diluted by the challenge solution, thus creating the variance shown in Figures 30 and 31.

Figure 30. Treated d-g-CSGO membranes at 345 kPa with 10 mg/L MB solution.

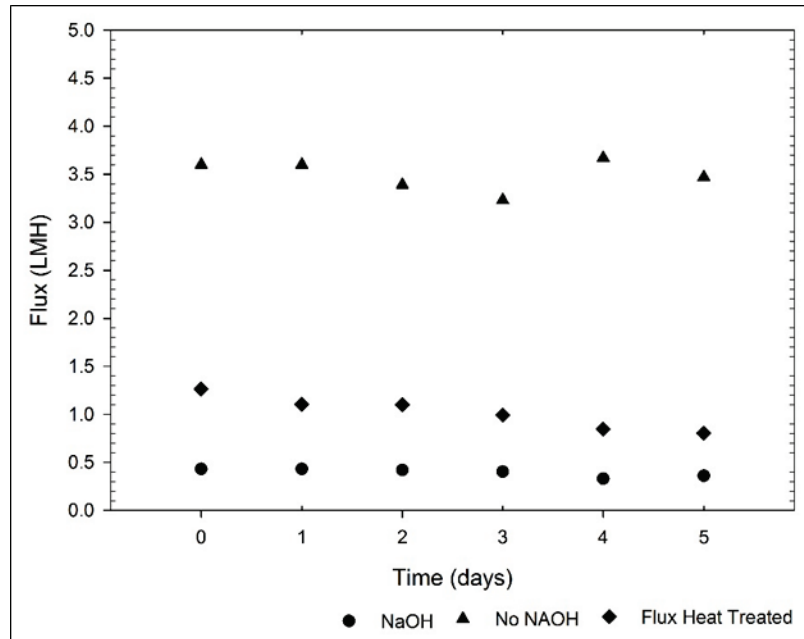
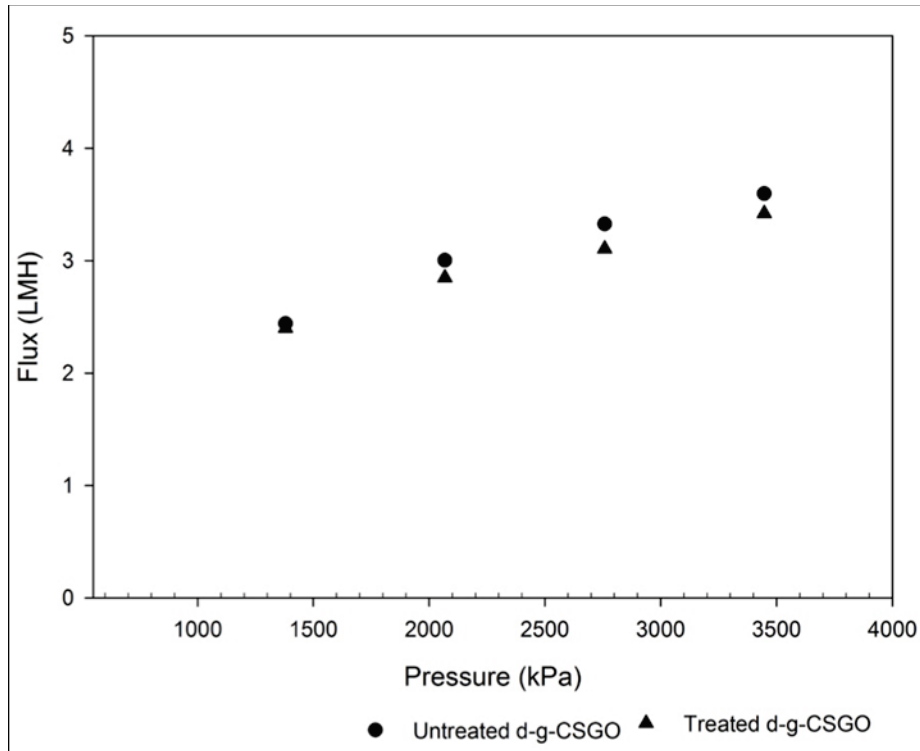


Table 5. Treated CSGO membranes flux and removal.

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 30). However, at pressures higher than 1.4 MPa, the difference in flux is significantly reduced (Figure 31), which allows for the treated membranes to have greater stability without sacrificing flux rates at higher pressures.

Figure 31. Treated and untreated d-g-CSGO at high pressures.



4.5 Scaled up membrane

To prove that ECM is a viable method for scaling up CSGO materials, a 30 cm × 42 cm (1260 cm²) membrane was produced. The scaled membrane (SM) method was used to produce the scaled up membrane using 720 mL of d-g-CSGO solution poured onto a Plexiglas mold (Figure 32).

Figure 32. d-g-CSGO solution after pouring onto Plexiglass mold.



A time lapse of over 72 hours was recorded while the solution dried and formed the membrane. The resulting time lapse video (Medina 2016) demonstrated how the membrane was set including 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 33).

Figure 33. Scaled d-g-CSGO membrane.



5 Discussion

5.1 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 demonstrate a propensity to congeal as they dry in a uniform “top down” fashion, however, when CSGO membranes form, they dry anisotropically while forming the final product.

During the course of this research, 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, which suggested that GO particles were bonding with chitosan and 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, instead, it would require mechanical and chemical breakdown.

5.2 pH compatibility

The d-g-CSGO coupons were submerged in solution with pH values ranging from 1 – 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 29). This indicates that the membrane is inter-acting with the hydrogen (H⁺) ions in the solution, thereby causing deformation and expansion. This behavior does not occur in the basic solutions as the membrane appears to

have a lesser affinity for hydroxide (OH⁻) ions, hence, the absence of membrane swelling.

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 observation expands upon what was observed in Section 4.3 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 30).

5.3 Membrane characteristics and performance

The GOs selected for use in this research were nano and granular GO powders purchased from Graphene Supermarket, Inc. These GO powders were chosen based on particle size and dimensions ranging from 90 nm in diameter n-GO and 0.3 to 0.07 micron sheets for g-GO in order 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 27. 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. In d-n-CSGO membranes, n-GO incorporates itself into chitosan's structure without altering it significantly (Figure 27).

The effect of GO on the internal membrane structure can be confirmed using XRD, as shown in Figure 25. It was observed that g-GO added a crystal-line 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 27c.

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 research. As shown in Table 3, 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 structures, it would be expected that there would be significant differences in the removal or flux rates, however, 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 GO powder contains flake sizes ranging from 0.3 – 0.7 microns in which more than 50% are arranged within one atomic layer. This allows the g-GO to arrange itself into GO's preferred lamellar structure while also incorporating chitosan into its matrix. This electro-static interaction was observed via XPS and shown in Figure 26. CS attaches itself onto the carboxylic acids found around the edges and the surface of GO forming protonated amides. Because GO formed these bonds with chitosan, it was able to form a stable material that also increased the strength of the chitosan (Lim et al. 2012; Shao et al. 2013; Zuo et al. 2013).

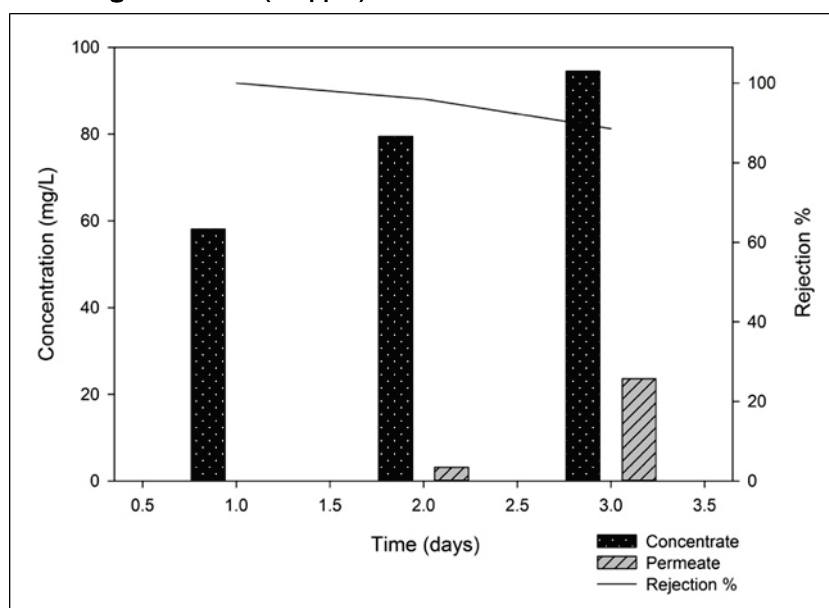
On the other hand, n-GO does not alter these properties to the same extent as g-GO. The size of n-GO (90 nm) prohibits significant alteration of the initial chitosan structure. As it incorporates itself throughout the membrane, n-GO makes small adjustments while maintaining chitosan's amorphous structure. 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 3 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.

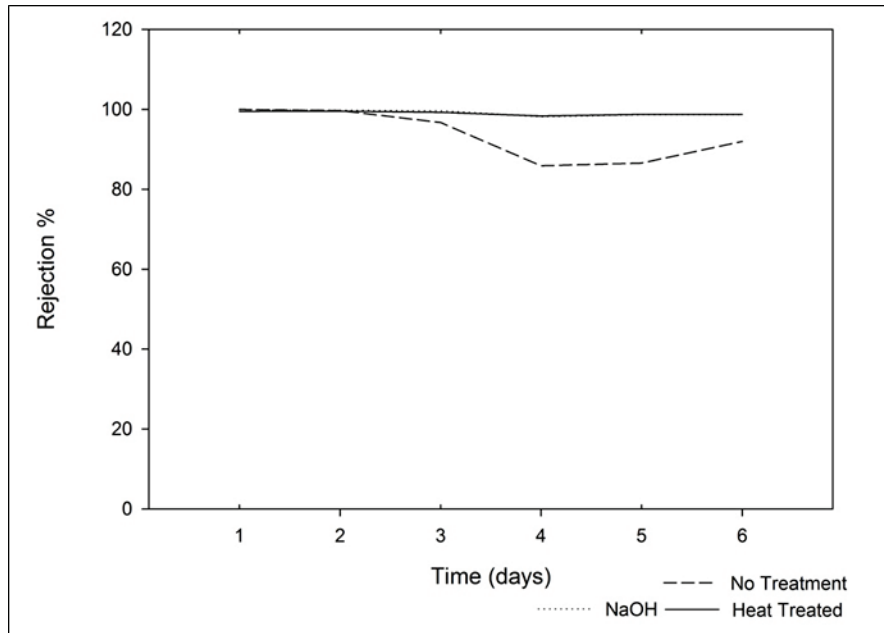
Rather than passing through open channels or pores, water incorporates into the membrane creating hydrated channels. These channels allow water to pass through the membrane while excluding other chemicals. As the membrane continues to hydrate, the channels continue to expand, thus allowing a greater percentage of the contaminant to pass through (Figure 34).

Figure 34. MB (50 ppm) concentration vs. time at 345 kPa.



This trend is observed when the concentration of the MB 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 35).

Figure 35. Treated and untreated rejection rates of MB at 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 31). The increased structural stability of treated membranes indicates a longer lifespan in comparison to membranes containing residual acetic acid.

5.4 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 – \$300 per gram of GO. For this research, the GO obtained from the Graphene Supermarket exhibited a markup of \$125 per 100 mg for n-GO and \$250 per gram for g-GO, which equated to approximately \$1.25 per mg of n-GO and \$0.25 per mg of g-GO. This cost differential per milligram made n-GO five times greater in value than g-GO (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 GO the material's cost driver for CSGO membrane manufacture. When manufacturing a 72 cm² cross flow membrane nano and granular membranes cost \$125 USD and \$25 USD in materials, respectively (Table 6).

Table 6. 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 cross flow reactor used in this research, 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. d-g-CSGO exhibited similar qualities and properties of d-n-CSGO at a fifth of the cost, thus making d-g-CSGO the most preferable option when manufacturing CSGO membranes for CFR.

6 Conclusions

The following conclusions were drawn from this work:

- CS and GO can be mixed together (CSGO) and formed into a membrane via solution casting. This method was proven to be scalable for membranes with an area of up to 1,260 cm².
- The structural support nitrocellulose provided to CSGO membranes allows these membranes to be used in a CFR. 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 MB 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.

7 Future Work

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

- Improving membrane flux by optimizing the CSGO composition for high contaminant removal rates.
- Evaluating membranes for potential removal of negatively charged dyes, radionuclides, salts of difference valencies, and aromatic compounds.
- Investigating 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.

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Appendix A: Model Style for Equations

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

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

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

$$\text{n_cost} := \text{nano_cost} \cdot \text{Total_Volume} = 1700 \text{ ¤}$$

$$\text{g_cost} := \text{granular_cost} \cdot \text{Total_Volume} = 340 \text{ ¤}$$

Appendix B: Literature Review Table

Paper	Authors	Year	Journal	Premise	Difference in CSGO work
Graphene-based antibacterial paper	Hu, Wenbing et al	2010	ACS nano	Using GO paper for antibacterial applications making Nanoelectromechanical systems and papertlike composites by using computational models and hydrogen bondings	Computational studies is not the focus of CSGO work
Hydrogen bond networks in graphene oxide composite paper: structure and mechanical properties.	Medhekar, Nikhil V et al	2010	ACS nano	Explores the mechanical properties of a well dispersed CSGO material	The material presented in the paper has similar aspects to our CSGO membrane. The percentages of GO to CS are different but the paper focuses on the mechanical properties of the CSGO material
Well-Dispersed Chitosan/Graphene Oxide Nanocomposites	Yang, Xiaoming et al	2010	ACS applied Material and interfaces	The authors are able to functionalize sand that was then coated with GO and used as an adsorbent for heavy metals and an organic dye	Our work is trying to make CSGO into a flat membrane for size exclusion filtration vs chemical adsorption
Engineered Graphite Oxide Materials for Application in Water Purification	Gao, Wei	2011	ACS applied Material and interfaces	Graphene nano sheets are exfoliated and used as an adsorbent of Pb (II)	Our material and experiments concern size exclusion of contaminants vs adsorption of contaminants in a GO dispersed solution.
Adsorption of Lead(II) Ions from Aqueous Solution on Low-Temperature Exfoliated Graphene Nanosheets	Huang, Zheng Hong	2011	Langmuir	Explores the mechanical properties of a mix of chitosan and graphene oxide over several wt %s	The material presented in the paper has similar aspects to our CSGO membrane. The percentages of GO to CS are different but the paper focuses on the mechanical properties and optics of the CSGO material
Green fabrication of chitosan films reinforced with parallel aligned graphene oxide	Pan, Yongzheng	2011	Carbohydrate Polymers	Explores the adsorptive properties of a magnetic chitosan and graphene oxide material.	The material magnetic chitosan/graphene oxide material was tested for its adsorptive properties of methylene blue. Where as our material is used as a membrane filter
Fabrication of novel magnetic chitosan grafted with graphene oxide to enhance adsorption properties for methyl blue	Fan, Lulu	2012	Journal of Hazardous Materials	Explores the adsorptive properties of a magnetic chitosan and graphene oxide material.	The material magnetic chitosan/graphene oxide material was tested for its adsorptive properties of methylene blue. Where as our material is used as a membrane filter
Preparation of novel magnetic chitosan/graphene oxide composite as effective adsorbents toward methylene blue	Fan, Lulu	2012	Bioresourc Technology	CSGO composites in this paper were created to try to strengthen CS materials. GO as a nano filler using 2 different hummer's methods which produced different qualities of GO.	Our material and experiments concern size exclusion of contaminants vs adsorption of contaminants in a GO dispersed solution.
Facile preparation of graphene-based chitosan films: Enhanced thermal, mechanical and antibacterial properties	Lim, H.N.	2012	Journal of Non-Crystalline Solids	Graphene nano sheets are exfoliated and used as an adsorbent of Pd (II) & Au (III)	CSGO materials in this paper were tested for their mechanical strengths and antibacterial properties. These were tested against a pure CS material. While these properties are a good basis for our material it's focus was end goal is different than our CSGO.
Preparation and characterization of chitosan/graphene oxide composites for the adsorption of Au(III) and Pd(II)	Liu, Li	2012	Talanta	Created GO membranes are impermeable to liquids, vapors, and gases inc He. But these membranes allow water to permeate unimpeded.	This study focuses on a thin GO membrane that is basically impermeable to everything but water. They go on to explain why this can happen. While Our work does include the permeation of water our work concentrates on water and contaminat filtration vs permeability of gases and vapors. Also our work involves GO composites rather than a 100% GO membrane.
Unimpeded Permeation of Water Through Helium-leak-Tight Graphene-Based Membranes	Nair, R. R.	2012	Science		
New Routes to Graphene, Graphene Oxide and Their Related Applications	Zhu, Yu	2012	Advanced Materials		Our Material is a composite vs this paper uses only GO
Enabling Graphene Oxide Nanosheets as Water Separation Membranes	Hu, Meng	2013	Environmental Science and Technology		Our material is a different type of GO composite. Also the paper's membranes were crosslinked with 1,3,5-benzenetricarbonyl trichloride on a polydamine-coated PS support. Where as our membrane is a freestanding membrane created by solution casting.
Salt concentration, pH and pressure controlled separation of small molecules through lamellar graphene oxide membranes	Huang, Hubiao	2013	Chemical Communications		

Fabrication of novel magnetic nanocomposite with a number of adsorption sites for the removal of dye	Li, Lilei	2015	International Journal of Biological Macromolecules	An Fe ₃ O ₄ /chitosan/GO material was synthesized and tested in batch adsorption tests of methylene blue. The equilibrium adhered to Langmuir isotherms and had an adsorption capacity of 260 mg/g	This hydrogel was made for adsorption while our membranes were created as flat sheet membranes for size exclusion processes.
Preparation of poly(vinyl alcohol)/chitosan hydrogel compounded with graphene oxide to enhance the adsorption properties for Cu(II) in aqueous solution	Li, Luchong	2015	Journal of Polymer Research	Graphene Oxide/CSGO 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.
Highly Porous Core-Shell Structured Graphene-Chitosan Beads	An Ouyang	2015	ACS Applied Materials & Interfaces		
High-Efficiency Water-Transport Channels using the Synergistic Effect of a Hydrophilic Polymer and Graphene Oxide Laminae	Huang, Kang	2015	Advanced Functional Materials		
Environmental applications of graphene-based nanomaterials	Perreault, François	2015	Chem. Soc. Rev.		
A ZnO decorated chitosan-graphene oxide nanocomposite shows significantly enhanced antimicrobial activity with ROS generation	Say Chowdhuri, Angshuman	2015	RSC Adv.	The membrane in the paper had ZnO added to it's CSGO structure in an effort to enhance the antimicrobial properties of CS and GO.	Work on CSGO is not focused on antibacterial properties
Enhanced Performance of a Novel Poly(vinyl Amine)/Chitosan/Graphene Oxide Mixed Matrix Membrane for CO ₂ Capture	Shen, Yijia	2015	ACS Sustainable Chemistry & Engineering	PVA CS solution was coated onto a PS support. GO was later grafted onto the support with poly(ethyleneimine). This material was tested against CO ₂ /N ₂ has separation tests to determine the permeance of CO ₂ .	CSGO membranes are being used for water filtration not Gas Selectivity.
Polymer-Graphene Oxide Quadlayer Thin-Film Assemblies with Improved Gas Barrier	Tzeng, Ping	2015	Langmuir		CSGO membranes are being used for water filtration not Gas Selectivity.
O-(Carboxymethyl)-chitosan Nanofiltration Membrane Surface Functionalized with Graphene Oxide Nanosheets for Enhanced Desalting Properties	Wang, Jiall	2015	ACS Applied Materials and Interfaces	NF membrane was coated with GO and the resulting material was characterized and was tested against salts. It was presented that the membrane had higher flux and salt rejection compared to the pristine NF membrane	CSGO is a free standing membrane and is not coated onto another material. We have also no filtered salts as with the membrane from this paper.
On the origin of the stability of graphene oxide membranes in water	Che-Ning Yeh	2015	Nature Chemistry	Discusses the reasons in which an anopore disc is needed for vacuum filtration formation of Graphene Oxide	We use chitosan as a binder to form CSGO membranes via solution casting vs vacuum filtration. Also our membranes are composites vs pristine graphene oxide
High Performance of Alkaline Anion-Exchange Membranes Based on Chitosan/Poly (vinyl) Alcohol Doped with Graphene Oxide for the Electrooxidation of Primary Alcohols	García-Cruz, Leticia	2016	Journal of Carbon Research	a 50/50 PVA/CS solution 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.	CSGO membranes do not contain PVA. Though I had created PVA/CSGO membranes in the past but disassociate when either submerged or used for water filtration.
Declining flux and narrowing nanochannels under wrinkles of compacted graphene oxide nanofiltration membranes	Wei, Yi	2016	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 investigated and discussed in the paper	We use a different method and solution to form CSGO membranes via solution casting vs vacuum filtration. Also our membranes are composites vs pristine graphene oxide. Also this membrane is a thinner allowing higher over all fluxes.
Graphene Oxide Membranes with Strong Stability in Aqueous Solutions and Controllable Lamellar Spacing	Xi, Yue-Heng	2016	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 CSGO membranes via solution casting instead of mixing reduced GO into the pristine GO dispersion.
High flux MWNTs-interlinked GO hybrid membranes survived in cross-flow filtration for the treatment of strontium-containing wastewater	Zhang, Lin	2016	Journal of Hazardous Materials	MWNTs 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	CSGO membranes do not use MWNT 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.

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14. ABSTRACT Graphene oxide (GO) has emerged within the last decade as a next generation material for water treatment. Fabrication of GO 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 chitosan/graphene oxide (CSGO) sheets. 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 (CFR) and challenged with methylene blue at concentrations ranging from 1 to 100 parts per million (ppm) at 345 kilopascal (kPa), with fluxes ranging from 1 to 4.5 L/(m ² hr) and 100% removal via 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.					
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