# GO-Based Filtration Membrane for Removal of Endocrine Disrupting Compounds (EDCs) from Water

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## ABSTRACT

In the present study, an attempt is made to utilize the superior water selective transport properties of Graphene Oxide (GO) laminates as filtration membranes for Endocrine Disrupting Compounds (EDCs) with high permeate flux rates. A layer-by-layer (L-b-L) approach was utilized to prepare thin film composite membranes with a polymer support and a few layers of GO interlinked via poly(allylamine hydrochloride) (PAH). The prepared membrane showed a fourfold increase in the permeate flux in comparison to the commercially available nanofiltration (NF) membranes. The rejection performance of the membrane was evaluated by studying the permeation of ibuprofen and a rejection rate of 75% was obtained.

***Keywords***: Graphene Oxide, Water Filtration, Membrane Technology

## 1 INTRODUCTION

Endocrine Disrupting Compounds (EDCs) are a class of micro-pollutants that affect the endocrine (hormonal) system by interfering with the developmental processes of humans and wildlife species. EDCs are currently used in a wide range of chemicals including Pharmaceutically Active Compounds (PhACs), pesticides, fire retardants, industrial chemicals, and Personal Care Products (PCPs). The effects of EDCs are dependent on the level of exposure as well as the timing, with exposure during developmental stages being the most dangerous. Studies [1-3] have concluded that EDCs have adverse effects on reproductive outcomes (infertility, malformations,etc.), thyroid function, brain, function, and obesity. Removal of these EDCs by waste water treatment plants through conventional means (flocculation, coagulation, precipitation) has proven to be inefficient, particularly for low molecular weight EDCs in the range of 100-500 Da [4-6]. Parametric studies concerning rejection of EDCs through current nanofiltration (NF) and reverse osmosis (RO) membranes suggest that the dominant rejection mechanisms are based on size exclusion (steric hindrance) and charge exclusion [7,8]. Realization of a membrane that can easily alter its size exclusion aspect while retaining the charge exclusion could result in increased rejection of common EDCs.

Graphene Oxide (GO) is an oxygen-functionalized derivative of graphene, consisting of a skeleton of 2D sheets of $sp^2$ hybridized carbon atoms in a honeycomb crystal lattice with covalently attached oxygen-functional groups on the basal plane and edges of these sheets. The presence of these oxygen-containing functional groups render GO electrically non-conductive and highly hydrophilic with a net negative surface charge. GO has exhibited unusually high water permeation upon hydration [9, 10], which has led to its use in desalination, water purification, and fuel cell applications. Alteration of synthesis conditions of GO have been shown to affect the flake size and interlayer spacing of GO laminates, which in turn influence the mass transport capability of the membrane [11,12]. The presence of a net negative surface charge along with highly tunable flake/interlayer size provides GO with the necessary properties to develop a highly selective EDC filtration membrane which retains both size and electrostatic exclusion rejection mechanisms.

In the present study, GO is employed in a layer-by-layer (L-b-L) assembly to create a membrane assembly for use as a filtration membrane of EDCs. The L-b-L membrane consists of a polyacrylonitrile (PAN) support polymer with GO layers interlinked with poly(allylamine hydrochloride) (PAH) located above it. This membrane assembly is then tested with 2-bilayers of GO-PAH on the polymer support using ibuprofen as the precursor molecule. Comparison of rejection rates and permeate flux rates to commercially available nanofiltration (NF) membranes is then presented.

## 2 EXPERIMENTAL SETUP

### 2.1 Synthesis of GO

The graphene in this study was synthesized following the modified Hummer's method outlined by Kovtyukhova [13]. Pre-oxidized graphite was obtained by mixing graphite flakes with a solution of $H_2SO_4$, $K_2S_2O_8$, and $P_2O_5$ at 80°C for 4.5 hours. This solution was then diluted with 0.5L of de-ionized (DI) water and filtered with a DI water wash until a neutral pH was obtained. Hummer's method was then used to oxidize this graphite [14], wherein 3 grams of pre-oxidized graphite were added to a mixture of $NaNO_3$ and $KMnO_4$ in concentrated $H_2SO_4$ placed in an ice bath. This mixture was maintained at 35 °C for 2 hours, after which the solution was diluted with DI water and heated to 98 °C for 15 minutes. Any unreacted manganate (VII) ions were removed by rinsing with DI water and addition of hydrogen peroxide. The solution was then centrifuged for 30 minutes, the supernatant poured off from the tubes, and then the precipitate washed with 30% hydrochloric acid (HCl). This centrifugation process is

repeated multiple times with washing using DI water until a neutral pH is obtained. The solution is then sonicated for some time to break down the graphite oxide laminates into graphene oxide flakes.

## 2.2 Layer-by-Layer Assembly

The L-b-L method is a technique used for creating an interlinked laminate of two or more materials/molecules via chemical or electrostatic interactions. This technique has been widely used in polymer membrane synthesis [15-17]. Electrostatic interactions are used as the interlinking mechanism in this study, using a polycation as the interlinking molecule due to the net negative surface charge associated with GO. Polyacrylonitrile (PAN) was used as a support substrate due to its high water flux, micro-porous structure, and mechanical robustness [18]. In order to provide PAN with the surface negative charge required to interact with the chosen polycation, PAN was soaked in NaOH at 47 °C for 1.5 hours. Excess NaOH was poured off from the reaction vessel and poly(allylamine hydrochloride) (PAH) was added above the hydrolyzed PAN (hPAN) substrate for 30 minutes. PAH was removed from the vessel and the membrane/vessel were washed with Millipore water, and dried using nitrogen for 4-5 minutes. GO was added to the PAN-PAH membrane and let sit for 30 minutes. The excess GO was removed and the same washing/drying process was repeated. This addition of PAH/GO was repeated until membranes with two (GO-2-BL) and five (GO-5-BL) bilayers were achieved (c.f. Figure 1).

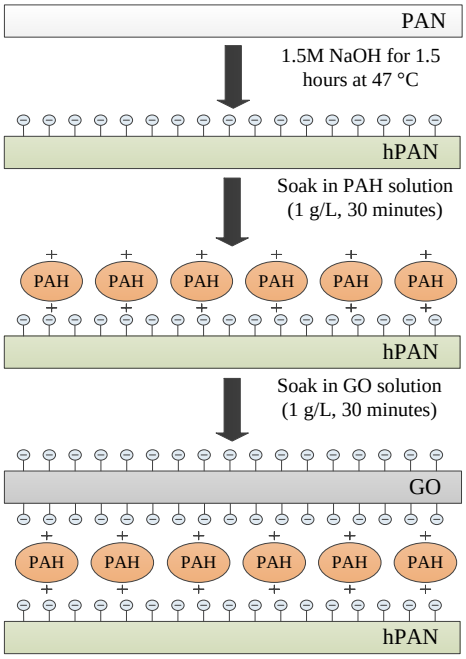


Figure 1: Schematic of the L-b-L assembly for GO membrane

## 2.3 EDC Rejection Setup

To test the rejection rate of EDCs for the membranes prepared using the above process, negatively charge ibuprofen (mol. wt. = 206.1) was chosen as a representative EDC. Rejection rates of ibuprofen for the GO-2-BL and GO-5-BL membranes were tested using a dead-end, solvent resistant stirred diffusion cell (Millipore, MD) which contained a 5 cm test membrane located at the bottom of the enclosure (c.f. Figure 2).

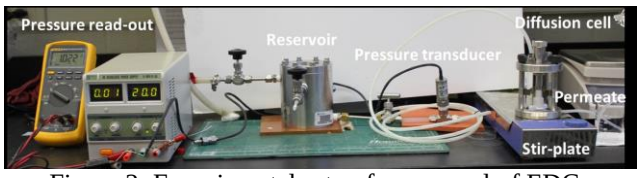


Figure 2: Experimental setup for removal of EDCs

The EDC solution was pressurized on the membrane using ultra-pure nitrogen and a pressure transducer was installed to measure the dilution feed pressure. Permeate from the diffusion cell was collected periodically to determine the concentration of filtrated solution, and thus quantify the amount of EDC rejection across the membrane. UV-Vis spectroscopy (Hitachi U-2900) was used to determine the concentration of EDC in the permeate. An initial calibration curve of multiple known concentrations versus their respective absorbance was prepared, and the resulting absorbance of each permeate sample was then used to determine concentration.

# 3 RESULTS

In order to test the rejection rates of the L-b-L membranes, two separate membranes were prepared. After initial preparation of the PAN support was completed, two and five-bilayers of PAH-GO were deposited onto the substrate. FTIR analysis was carried out for both iterations of the membrane to verify the addition of PAH-GO to the base hPAN substrate (c.f. Figure 3).

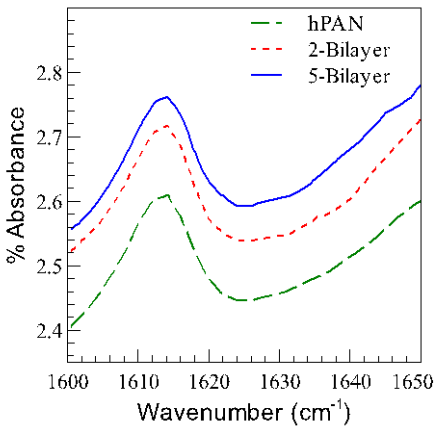


Figure 3: Absorbance of carboxylic group on L-b-L membranes


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From Figure 3, an increase in absorbance at the carboxylic group peak is observed upon addition of PAH-GO bilayers compared to the base hPAN substrate. This indicates the increased presence of carboxylic groups as more bilayers are added to hPAN, it has been shown that these carboxylic groups decorate the edges of GO flakes [19, 20]. The prepared GO-2-BL, GO-5-BL, and GE Osmonic membranes were tested with the previously described precursor EDC and rejection percent/permeate flux was measured.

The results of these studies are presented in Figure 4, where it is observed that the GO-5-BL membrane was able to achieve a rejection of ~80% with a permeate flux comparable to the GE Osmonic membrane. The two nanofiltration membranes tested by Nghiem et al [21], and Quintanilla et al. [22] were able to achieve comparable rejection performance to GO-5-BL for the case of NF-270. However, these nanofiltration membranes were able to operate at higher permeate flux (~2-2.5x), making these NF membranes energetically favorable when operating at the permeate flux of the GO-5-BL and GE Osmonic membranes. These NF membranes only utilize size exclusion as a rejection mechanism for ibuprofen, meaning that rejection performance could be further improved by implementing a membrane with charge exclusion at similar size exclusion properties.

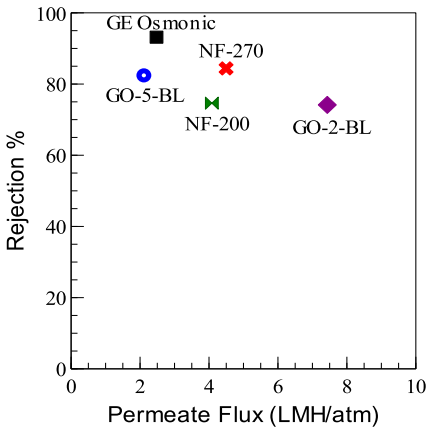


Figure 4: Rejection of Ibuprofen for several membranes.

While the GO-2-BL membrane showed lower rejection rates of ibuprofen, the permeate flux achieved was fourfold that of the GE Osmonic or GO-5-BL cases. The GO-2-BL case presented the highest achieveable permeate flux out of all membranes, including typical nanofiltration membranes covered in literature [21, 22]. Operating the GO-2-BL membrane at lower permeate flux requires a lower transmembrane pressure, making it a more energy efficient membrane compared to the other tested membranes at the same working conditions. From these tests, the GO-5-BL membrane provided negligible increases in rejection when considering the much lower permeate flux tested compared to GO-2-BL. . As shown in Figure 5, the primary mass transport pathway for GO laminates is through the interlayer spacing, with lateral transport occuring only through surface defects or flake edges. This increased rejection at much lower permeate flux can be attributed to increased tortuosity in the GO-5-BL membrane, which is a characteristic of GO laminate stacking

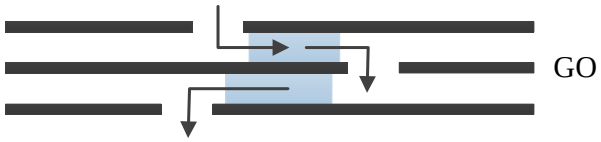


Figure 5: Mass transport across GO laminates. Areas in blue indicate interlayer space between GO sheets

The presence of more PAH-GO layers in the GO-5-BL assembly leads to increased transport resistance, resulting in a lower operable permeate flux. Due to identical synthesis conditions for GO-5-BL and GO-2-BL, there is no difference in EDC separation mechanism between the two, resulting in a similar rejection rates. The interlayer spacing of PAH-GO is much larger than typical GO laminate interlayer spacing (~9Å [18]) due to the presence of the PAH molecule. This interlayer spacing is larger than the calculated molecular diameter of Ibuprofen (~8.1Å [7]), indicating that steric hindrance of Ibuprofen is not the dominant rejection mechanism. The relatively high rejection performance of the L-b-L membranes despite this size difference indicates that the primary rejection mechanism is electrostatic in nature. Due to the Debye length of Ibuprofen, there is sufficient interaction with the negative surface charge of GO to cause electrostatic repulsion, inhibiting the transport of Ibuprofen across the L-b-L membrane.

## 4 CONCLUSION

In this study, a layer-by-layer membrane using PAN-PAH-GO was successfully prepared and tested for rejection of Ibuprofen, a precursor EDC. Two membranes were prepared under the same synthesis conditions with varying number of bilayers above a hPAN substrate. Th rejection performances and permeate fluxes of these two GO-based membranes was then compared to commercially available nanofiltration membranes in a dead-end diffusion cell. The GO-5-BL membrane was found to yield comparable rejection performance (~80%) to other nanofiltration membranes, but at a lower operating permeate flux. GO-2-BL was also found to produce similar rejection performances as the other nanofiltration membranes (~75%) at 2-3 times higher permeate flux, including the commercially available GE Osmonic membrane. This indicates that operating the GO-2-BL assembly at the permeate flux of other nanofiltration membranes requires a lower transmembrane pressure, resulting in a more energy efficient membrane while retaining comparable rejection. Further optimization of L-b-L membranes can be pursued in

order to improve rejection performance while maintaining high permeate flux conditions.

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