MODIFICATION OF POLYETHERSULFONE MEMBRANES WITH FRACTIONATED NATURAL ORGANIC MATTER FOR INCREASED FLUX AND GREENER WATER FILTRATION

Cyndey Johnson-Edler [†], Basmala Aleman*, Jessica DeLair*, Tanner Flickema*, Anna Gross*,*Abbie Lund*, Nathaniel Pekas*, Julia Radtke* and Isaac Ventura*

Augustana University, Department of Chemistry and Biochemistry, Sioux Falls SD 57197

Abstract

This investigation modified polyethersulfone membranes with fractionated natural organic matter obtained from two source materials using ultraviolet assisted grafting at 254 nm. This study also investigated the effect of using milder cleaning conditions than are currently used in water treatment of ultrafiltration membranes. Cross-flow filtration was used to determined permeate flux of laboratory produced and environmental water samples. The modified membranes were characterized to determine changes in surface hydrophilicity when compared to unmodified membranes. Resulting data from this study determined that modification of the membranes increased hydrophilicity an average of 8.6% for Leonardite and Pahokee peat modified membranes. Permeate flux, also increased for Leonardite modified membranes by 64% when compared to unmodified membranes. In addition, using milder cleaning conditions was comparable to the extreme cleaning conditions for the unmodified membranes, however was determined to not be as effective for cleaning of modified membranes.

†Corresponding author: cjohnsonedler@augie.edu

Introduction

Polyethersulfone [Poly(oxy-1,4-phenylenesulfonyl-1,4-phenylene)] (PES), are thermally, hydrolytically, oxidatively and chemically stable and are commonly used in the manufacture of ultrafiltration membranes used in water treatment. However, hydrophobic properties for PES cause these membranes to have high water contact angles, and also increase the probability of proteins, microbes, and organic substances to attach to its surface leading to fouling which lowers the efficiency of the membrane due to a decrease in permeate flux. This fouling must be rectified through extensive cleaning and or membrane replacement.[1] In an attempt to reduce the fouling tendency of PES membranes many modification techniques have been developed to increase surface hydrophilicity. These techniques range from ultraviolet light grafting,[2–4] blending of polymer materials,[5,6] and coating the PES membranes with various materials to increase membrane hydrophilicity.[7–10]

Natural organic matter (NOM) is ubiquitous in surface waters and is known to foul ultrafiltration and nanofiltration membranes used in water treatment facilities. It is comprised of humic substances and organic molecules consisting of lipids, carbohydrates, proteins etc.,[11] which contain aromatic and aliphatic functional groups.[11–13] Given this diverse functionality contributes to NOMs ability to self-assemble and also bind environmental pollutants in surface water, drinking water and wastewater such as hydrophobic organic pollutants (HOPs) like polycyclic aromatic hydrocarbons (PAHs) and chlorinated biphenyls and pesticides.[14–16] Conversely, NOM is also a precursor to disinfection byproducts (DBPs) created during the wastewater disinfection process.[17,18] The presence of NOM inhibits permeate flux through filtration membranes making it necessary to clean them using harsh acids, bases, and oxidants at pH values of approximately 2 and 11.[19–21]

The use of natural materials to modify filtration membranes has become a focus of the advancement of water treatment in re-

cent years. Nadir determined the addition of cannabinoids to PES membranes increased flux for modified membranes when compared to the unmodified counterparts.[22] Cannabinoids and NOM have many structural similarities as determined by ^{13}C NMR studies.[23,24] NOM, however, can be fractionated into five distinctly components with distinctly different solubility characteristics dependent upon pH.[25,26] Interestingly enough, these components of NOM have strikingly similar chemical functional groups regardless of the origin of the bulk soil material used.[23,25,26] The isolated amphiphilic component, hereafter referred to as HA_2, is the focus of this study. Although naturally occurring NOM does create issues with water filtration membranes due to the tendency to foul said membranes, the modification of PES membranes with substances of varying functionality as previously mentioned have resulted in increased membrane surface hydrophilicity and permeate flux. This investigation used UV-grafting to modify the surface of PES membranes with aqueous solutions of the amphiphilic HA_2 component of NOM that has been isolated from two different bulk soil types.

Experimental Methods

Fractionation of NOM

Source materials used in this study were obtained from the International Humic Substances Society (IHSS). The organic matter from IHSS Leonardite (Lot# BS104L) and IHSS Pahokee Peat (Lot# BS103P) was extracted using a traditional alkali extraction method.[11] Further fractionation was achieved by Soxhlet extraction using a benzene:methanol azeotrope (3:1, v:v). Followed finally by an additional alkali extraction which yields the target amphiphilic component of HA_2 and a lipid component.[25]

Membrane Modification

PES flat sheet membranes (Microdyn Nadir, PM UP150, 150kDa, UF) were modified using a modified method based on Yamagishi.[4] Membranes were placed in Type 1 water (Barnsted Gen Pure CAD Plus system) with stirring for 24 hours, then dried

under nitrogen for 24 hours. Once cleaned and dried the membranes were submerged in a 15 mg/L solution of the amphiphilic fraction of NOM at pH ~ 8 for 20 minutes. Excess solution was discarded and membranes were placed on a quartz plate in a Luzchem LZC-4V Photoreactor which was then purged with nitrogen for 20 minutes. Samples were then irradiated for 30 minutes at 254 nm while continuing the nitrogen purge. After irradiation the membranes underwent a series of washings in Type 1 water at pH 7, pH 9 and pH 5 each for 24 hours to remove unreacted NOM from the membrane surface. The membranes were then dried in a nitrogen purged desiccator containing Drierite™ with indicator, 4 mesh (Thermo Scientific).

Membrane Characterization

All following membrane characterization and water filtering efficiency analyses were performed on NOM modified and unmodified membranes.

The Attenuated Total Reflectance (ATR) accessory on a Thermo Fisher iS50 Fourier Transform Infrared (FTIR) spectrometer was employed to characterized the surface functional groups on PES membranes. ATR-FTIR was also used to determine effects of the pH of cleaning solutions on membrane surface functionally after filtration.

An Ossila L2004A contact angle goniometer with camera, was used to determine surface hydrophilicity. A 40 μL droplet of water was place on 2 cm^2 portions of all membranes analyzed using Ossila contact angle software to determine left and right contact angles which were then averaged by one-way ANOVA.

Surface Zeta Potentials were determined by a Malvern Panalytical Zetasizer ZS90 with surface accessory to explore how water samples containing NOM influence the charge on the membrane surface. PES samples (7 mm x 4 mm) were mounted in the surface potential cell (ZEN1020), placed in a disposable plastic cuvette (Fisher Scientific) containing either a lab created sample of NOM (8 mg/L) in a 5 mM solution of NaCl or a standard transfer solution (Disodium tetraborate-Malvern Panalytical;0.1%, w:v).

Water Filtering Efficiency

An Explorer Cross/Tangential flow filtration apparatus (Sterlitech Corp, Auburn, WA) was used to compare differences in permeate flux of PES membranes. Laboratory produced solutions of the HA$_2$ fraction of NOM designed to mimic environmental water samples at a concentration of 8 mg/L(pH~7.5), and water samples collected from the Viking Oasis pond (Sioux Falls, SD) were run at 50 psi until one liter of permeate was collected. Viking Oasis samples were filtered (Whatman #1) to remove any large particulates then used as is.

Fluorescence spectroscopy was completed using a Horiba Scientific Fluoromax-4 spectrometer with FluorEssence software. 3D spectra were obtained for excitation and emission from 300-600 nm, at one nm increments employing a 1.00 nm slit width. Triplicate 3D spectra were obtained on lab created and Viking Oasis water samples before and after filtration. Reduction of NOM in water samples were calculated using maximum (ex:em) intensity values for each plot.

Results and Discussion

Successful modification of PES membranes with the HA$_2$ fraction of NOM is evidenced by Figure 1. This figure includes representative FTIR spectra of the solid HA$_2$ fraction of NOM (a), a modified PES membrane (b), and an unmodified PES membrane (c). The increased intensity of the carboxylic acid peak in Figure 1b at approximately 3400 cm^{-1} and its associated carbonyl peak at approximately 1700 cm^{-1} indicates the addition of carboxylic acid functional groups due to binding of solid HA$_2$ fraction in Figure 1a to the membrane surface when compared the unmodified PES membrane spectra in Figure 1c.

Contact angle measurements also indicate modification of the surface of PES membranes. One way ANOVA results determined the control sample of PES had average contact angles of ($F_{(2,33)}$ = 50.06 ± 0.08°, p = 0.98). By comparison, PES membranes modified with the HA$_2$ component of either source material exhibited contact angle measurements of ($F_{(2,30)}$ = 43.42 ± 0.31°, p = 0.93). Resulting in an average increase in membrane surface hydrophilicity of 13.2%.

Table 1. shows the average liquid zeta potential of HA$_2$ solutions by source material (8 mg/L in 5 mM NaCl) and a reference standard solution of disodium tetraborate (Malvern Panalytical – 40.0 ± 5.0 mV). This concentration of HA$_2$ was chosen for its similarity to NOM concentrations usually found in natural surface waters. The magnitude of the liquid zeta potentials of the solutions used to determine the surface zeta potentials of the membranes are all greater than 30 mV indicating that according to Derjaguin, Landau, Vervey, and Overbeek (DLVO) theory they are stable colloid systems.[27] These solutions were used to determine the effect of the HA$_2$ NOM solutions on the surface of the membranes when compared to a standard reference solution. The surface zeta potential data show a decrease in magnitude (less negative) of membranes exposed to a solution of NOM when compared to a standard solution of disodium tetraborate. This decrease in magnitude is due to
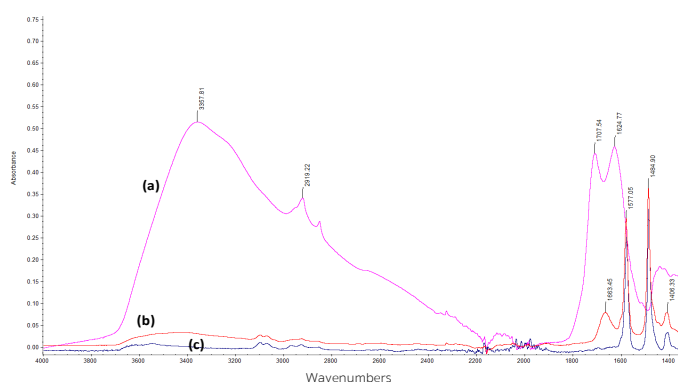

Figure 1. ATR-FTIR spectra of the solid HA$_2$ fraction of NOM (a), a modified PES membrane (b); and an unmodified PES membrane (c).

Table 1. Surface zeta potentials for PES membranes, and liquid zeta potentials of solutions

Sample	Surface ZP in Standard (mV)	Liquid ZP of Standard particles (mV)	Surface ZP in NOM (8 mg/L) (mV)	Liquid ZP of NOM particles (mV)
LHA2	-15.2 ± 3.0	-41.4*	-10.3 ± 0.9	-38.2 ± 0.9
PHA2	-20.5 ± 2.7	-40.0*	-10.6 ± 2.5	-39.5 ± 1.4
PES Control	-21.2 ± 1.9	-40.7*	-15.7 ± 2.8	-40.0 ± 5.0

*Standard Transfer Solution (Malvern Panalytical) std ±5.0

a reduction of the repulsive electrostatic forces between the membrane surface and the particles in solution which increases the likelihood of attachment of NOM to the membrane surface. Although this decrease in magnitude of surface zeta potential was foreseen the magnitude of the decrease is smaller than anticipated. Given the decrease of surface zeta potentials were 35%, 48%, and 25% for Leonardite, Pahokee Peat and the control PES, respectively it can be determined that the colloidal particles of NOM in the lab created solutions have overcome the repulsive forces that keep the particles from accumulating on the membrane surface.

The effect of the increased hydrophilicity of the modified membranes on filtration effectiveness and permeate flux was investigated by cross-flow filtration. Permeate flux rates were calculated using Equation 1.

$$Flux(J) = \frac{permeate\ flow\ rate\left(\frac{L}{hr}\right)}{membrane\ area\ (m^2)} \tag{1}$$

The average permeate flux rate for modified membranes was 6666 ± 25 L*hr^{-1}*m^{-2} which was significantly higher (2.8x) than the average rate for unmodified membranes at 2403 ± 15 L*hr^{-1}*m^{-2}. This increase in flux reinforces the increase in membrane functionality and hydrophilicity seen in contact angle and ATR-FTIR analyses.

In addition to filtration studies lab created and environmental water samples were analyzed by 3D fluorescence spectroscopy before and after filtration. All plots contained with Figures 2, 3 and 4 are representative of the data collected. Figure 2. shows plots for water samples before and after filtration through unmodified PES membranes. Figure 2a shows the fluorescence intensity of a lab created Pahokee Peat HA$_2$ water sample (8 mg/L) prior to any filtration. Using the maximum intensity at 360:480 nm (ex:em).

Figure 2b indicates that 75% of NOM contained in the water sample had been removed. In comparison, Figure 2c shows the florescence of a water sample obtained from the Viking Oasis pond (Sioux Falls, SD). Comparing the maximum intensity at 350:445 nm (ex:em) with Figure 2d the reduction of NOM is 67%. Figure 3a & 3b compare the fluorescence of a Leonardite HA$_2$ NOM water sample (8 mg/L) pre- and post-filtration through a Leonardite modified membrane. The increased fluorescence intensity in Figure 3a when compared to 2a indicates that even though the HA$_2$ component of both materials have comparable chemical characteristics and behave similarity throughout this investigation, Leonardite HA$_2$ has more fluorescence active functional groups than Pahokee Peat HA$_2$. Figure 3b indicates that the Leonardite modified
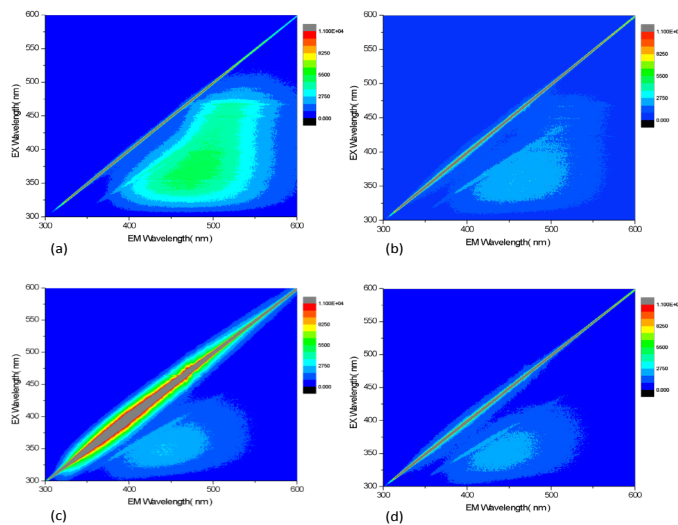

Figure 3. Leonardite HA$_2$ Modified PES membrane fluorescence results. Prefiltration lab created solution of Leonardite HA$_2$ (8 mg/L) (a); Post filtration lab created sample of Leonardite HA$_2$ (b), reduction of NOM =67%. Prefiltration sample (Viking Oasis – Sioux Falls, SD) (c); Post filtration (Viking Oasis – Sioux Falls, SD) (d), reduction of NOM = 33%
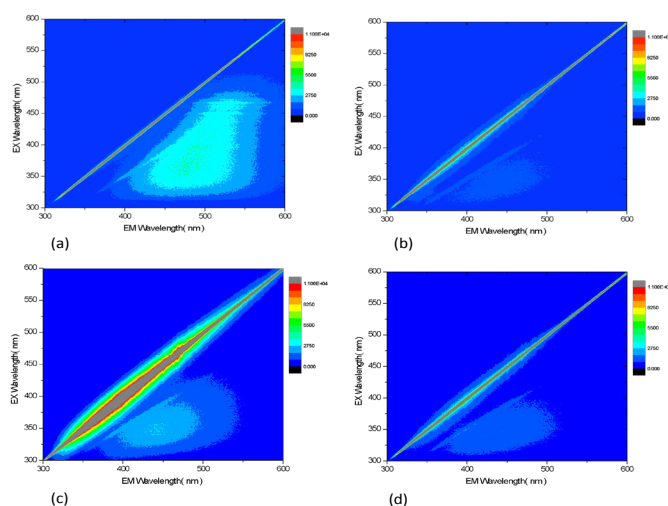

Figure 2. Unmodified PES membrane fluorescence results. Prefiltration lab created solution of Pahokee Peat HA$_2$ (8 mg/L) (a); Post filtration lab created sample of Pahokee Peat HA$_2$ (b), reduction of NOM =75%. Prefiltration sample (Viking Oasis – Sioux Falls, SD) (c); Post filtration (Viking Oasis – Sioux Falls, SD) (d), reduction of NOM = 67%
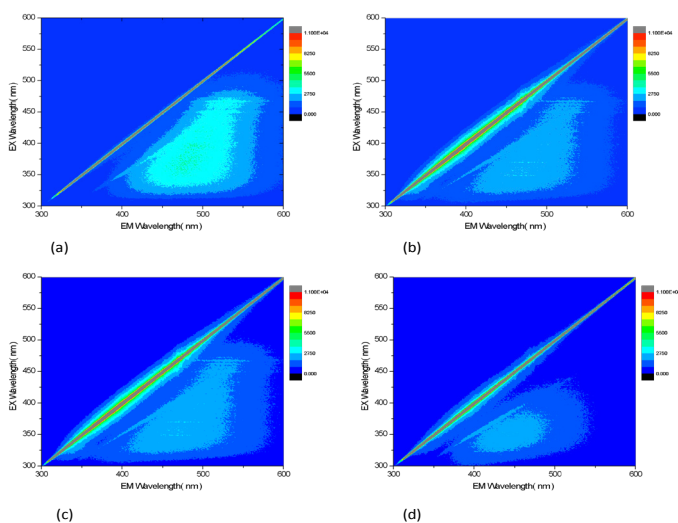

Figure 4. Pahokee Peat HA$_2$ Modified PES membrane fluorescence results. Prefiltration lab created solution of Pahokee Peat HA$_2$ (8 mg/L) (a); Post filtration lab created sample of Pahokee Peat HA$_2$ (b), reduction of NOM =50%. Prefiltration sample (Viking Oasis – Sioux Falls, SD) (c); Post filtration (Viking Oasis – Sioux Falls, SD) (d), reduction of NOM = 20%

membranes were able to remove 67% of the NOM contained in the lab created sample at 375:480 nm (ex:em). However, the sample from the Viking Oasis in Figures 3c and 3d show a reduction of NOM at 350:445 nm (ex:em) of 33%. Figure 4a and 4b compare the fluorescence of a Pahokee Peat HA_2 NOM water sample (8 mg/L) pre- and post-filtration through a Pahokee Peat modified membrane. The membrane used to filter the water in Figure 4b removed 50% of the NOM from the original sample shown in Figure 4a at 360:480 nm (ex:em). In comparison, the Viking Oasis post-filtration sample in Figure 4d indicates a reduction of NOM by 20% when compared to its pre-filtration counterpart in Figure 4c at 350:445 nm (ex:em). These results indicate that all membranes tested show greater efficiency to remove NOM from lab created samples over environmental collected samples, likely due to variables such as ionic strength and pH. Leonardite modified membranes showed higher filtration efficiency than Pahokee Peat modified membranes possibly due to it having more fluorescent active functional groups as evidenced in Figure 2a. Fluorescent active groups such as aromatic rings and conjugated double bonds are covalently bonded to the PES membrane surface during the irradiated process during membrane modification.[2,3]

Leonhardite's larger concentration of these moieties would enable this material an increased likelihood to interact with similar functional groups of NOM in the water samples.

Following filtration, used membranes were washed using consecutive acid/base baths of Type 1 water adjusted to the conventional pH's of 2 and 11 using HCl and NaOH, respectively. To compare washing methods, duplicate post filtration membranes were also washed using consecutive acid/base baths of Type 1 water adjusted to pH's of 5 and 9 to determine cleaning efficiency by examination of the ATR_FTIR carboxylic acid peak at 3400 cm^{-1}. Figure 5 shows ATR-FTIR results for unmodified membranes using both cleaning regiments. As can be seen when comparing the post-filtration (b), mild (c) and conventional cleaning (d) spectra, both cleaning methods have similar cleaning efficiency at approximately 90%. This indicates that milder cleaning pH's can be employed with similar results for unmodified PES membranes. While no significant difference can be discerned from the spectra in Figure 5 for unmodified PES membranes, slight differences can be seen in both Figures 6 and 7 for membranes modified with Leonardite and Pahokee Peat, respectively. Membranes modified by both materials appear to more efficiently cleaned using the solutions of conventional pH rather than the milder pH solutions. Milder cleaning resulted in a reduction at 3400 cm^{-1} of 26% and 28% for Leonardite and Pahokee Peat, respectively. With the conventional cleaning method giving a 34% reduction for membranes regardless of material used in modification.

Conclusions

These results indicate that the modification of PES membranes using the HA_2 component of NOM increases membrane hydrophilicity, which greatly increases the permeate flux of water and decreases membrane contact angle. The decrease in magnitude of surface zeta potentials seen herein indicate that although more water may be filtered through the modified membranes it is likely that NOM will accumulate at the modified membrane surface similar to unmodified membranes. Although NOM tends

to accumulate at the surface of all membranes used in this study, the ATR-FTIR results for the cleaning efficiency study show similarities in NOM reduction between the modified membranes regardless of material used, and the two cleaning methods employed for the unmodified membranes show no significant difference in NOM reduction. Fluorescence measurements indicate the modified membranes show the same trend in fluorescence reduction as the unmodified membranes, although removal of NOM from lab created and environmental samples was less efficient when using
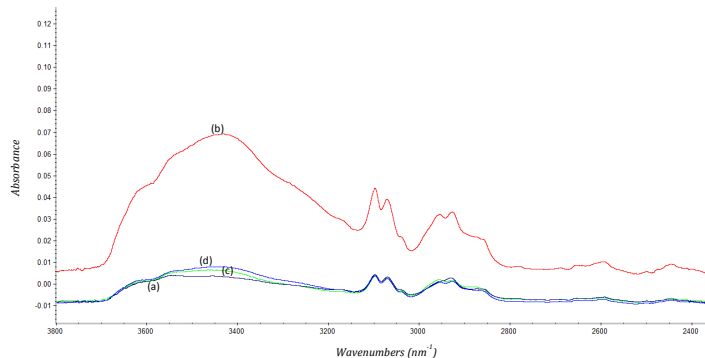

Figure 5. ATR-FTIR results for cleaning efficiency investigation for unmodified membranes. Pre-filtration (a), post-filtration (b), post mild cleaning (c), post conventional cleaning (d)
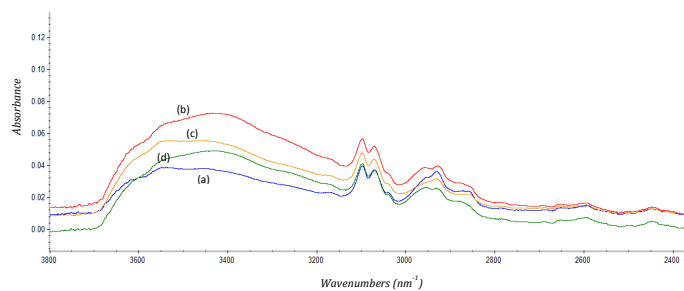

Figure 6. ATR-FTIR results for cleaning efficiency investigation for Leonardite modified membranes. Pre-filtration (a), post-filtration (b), post mild cleaning (c), post conventional cleaning (d).
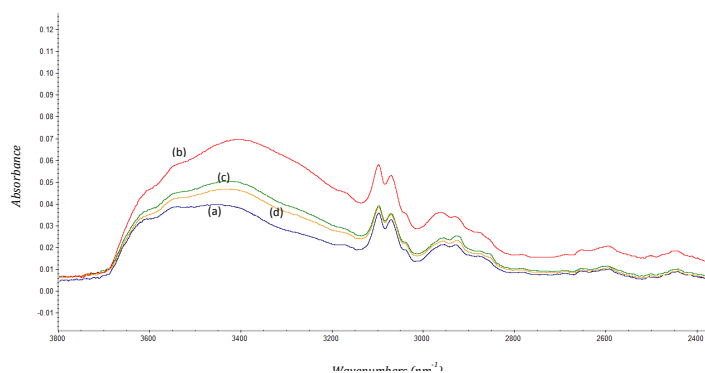

Figure 7. ATR-FTIR results for cleaning efficiency investigation for Pahokee Peat modified membranes. Pre-filtration (a), post-filtration (b), post mild cleaning (c), post conventional cleaning (d).

the modified membranes.

References

1. Sabri, S.; Najjar, A.; Manawi, Y.; Eltai, N.; Al-Thani, A.; Atieh, M.; Kochkodan, V. Antibacterial Properties of Polysulfone Membranes Blended with Arabic Gum. *Membranes* **2019**, *9* (2), 29. https://doi.org/10.3390/membranes9020029.

2. Pieracci, J.; Crivello, J. V.; Belfort, G. UV-Assisted Graft Polymerization of N-Vinyl-2-Pyrrolidinone onto Poly(Ether Sulfone) Ultrafiltration Membranes Using Selective UV Wavelengths. *Chem. Mater.* **2002**, *14*, 256–265.

3. Taniguchi, M.; Pieracci, J.; Samsonoff, W. A.; Belfort, G. UV-Assisted Graft Polymerization of Synthetic Membranes: Mechanistic Studies. *Chem. Mater.* **2003**, *15* (20), 3805–3812. https://doi.org/10.1021/cm020283p.

4. Yamagishi, H.; Crivello, J. V.; Belfort, G. Development of a Novel Photochemical Technique for Modifying Poly (Arylsulfone) Ultrafiltration Membranes. *J. Membr. Sci.* **1995**, *105* (3), 237–247. https://doi.org/10.1016/0376-7388(95)00063-I.

5. Lafreniere, L. Y.; Talbot, F. D. F.; Matsuura, T.; Sourirajan, S. Effect of Poly(Vinylpyrrolidone) Additive on the Performance of Poly(Ether Sulfone) Ultrafiltration Membranes. *Ind. Eng. Chem. Res.* **1987**, *26* (11), 2385–2389. https://doi.org/10.1021/ie00071a035.

6. Kouhestani, F.; Torangi, M. A.; Motavalizadehkakhky, A.; Karazhyan, R.; Zhiani, R. Enhancement Strategy of Polyethersulfone (PES) Membrane by Introducing Pluronic F127/Graphene Oxide and Phytic Acid/Graphene Oxide Blended Additives: Preparation, Characterization and Wastewater Filtration Assessment. *Desalin Water Treat.* **2019**, *171*, 44–56. https://doi.org/10.5004/dwt.2019.24769.

7. Kim, K. J.; Fane, A. G.; Fell, C. J. D. The Performance of Ultrafiltration Membranes Pretreated by Polymers. *Desalination* **1988**, *70* (1–3), 229–249. https://doi.org/The performance of ultrafiltration membranes pretreated by polymers.

8. Kim, K. J.; Fane, A. G.; Fell, C. J. D. The Effect of Langmuir-Blodgett Layer Pretreatment on the Performance of Ultrafiltration Membranes. *J. Membr. Sci.* **1989**, *43* (2–3), 187–204. https://doi.org/10.1016/S0376-7388(00)85097-8.

9. Hvid, K. B.; Nielsen, P. S.; Stengaard, F. F. Preparation and Characterization of a New Ultrafiltration Membrane. *J. Membr. Sci.* *53* (3), 189–202. https://doi.org/10.1016/0376-7388(90)80014-D.

10. Ulbricht, M.; Belfort, G. Surface Modification of Ultrafiltration Membranes by Low Temperature Plasma II. Graft Polymerization onto Polyacrylonitrile and Polysulfone. *J. Membr. Sci.* **1996**, *111* (2), 193–215. https://doi.org/10.1016/0376-7388(95)00207-3.

11. Stevenson, F. J. *Humus Chemistry*; Wiley & Sons: New York, NY, 1982.

12. Six, J.; Guggenberger, G.; Paustine, K.; Haumaier, L.; Elliott, E. T.; Zech, W. Sources and Composition of Soil Organic Matter Fractions Between Soil Aggregates. *Eur. J. Soil Sci.* **2001**, *52*, 607–618.

13. Wershaw, R. L. The Study of Humic Substances -- In Search of a Paradigm. In *Humic Substances*; Woodhead Publishing, 2000; pp 1–7.

14. Chiou, C. T. Water Solubility Enhancement of Some Organic Pollutants and Pesticides by Dissolved Humic and Fulvic Acids. *Environ. Sci. Technol.* **1986**, *20* (5), 502–508. https://doi.org/10.1021/es00147a010.

15. Evans, H. E. The Binding of Three PCB Congeners to Dissolved Organic Carbon in Freshwaters. *Chemosphere* **1988**, *17* (12), 2325–2338. https://doi.org/10.1016/0045-6535(88)90143-9.

16. Rav-Acha, Ch. Binding of Organic Solutes to Dissolved Humic Substances and Its Effects on Adsorption and Transport in the Aquatic Environment. *Water Res.* **1992**, *26* (12), 1645–1654. https://doi.org/10.1016/0043-1354(92)90164-Y.

17. Tak, S.; Vellanki, B. P. Natural Organic Matter as Precursor to Disinfection Byproducts and Its Removal Using Conventional and Advanced Processes: State of the Art Review. *J. Water Health* **2018**, *16* (5), 681–703. https://doi.org/10.2166/wh.2018.032.

18. Bellar, T. A.; Lichtenberg, J. J.; Kroner, R. C. The Occurrence of Organohalides in Chlorinated Drinking Waters. *J. Am. Water Works Assoc.* 66 (12), 689–744. https://doi.org/10.1002/j.1551-8833.1974.tb02129.x.

19. Shi, X.; Tal, G.; Hankins, N. P.; Gitis, V. Fouling and Cleaning of Ultrafiltration Membranes: A Review. *J. Water Process Eng.* **2014**, *1*, 121–138. https://doi.org/10.1016/j.jwpe.2014.04.003.

20. Trägårdh, G. Membrane Cleaning. *Desalination* **1989**, *71* (3), 325–335. https://doi.org/10.1016/0011-9164(89)85033-7.

21. Mohammadi, T.; Madaeni, S. S.; Moghadam, M. K. Investigation of Membrane Fouling. *Desalination* **2003**, *153* (1–3), 155–160. https://doi.org/10.1016/S0011-9164(02)01118-9.

22. Nadir, I.; Rana, N. F.; Ahmad, N. M.; Tanweer, T.; Batool, A.; Taimoor, Z.; Riaz, S.; Ali, S. M. Cannabinoids and Terpenes as an Antibacterial and Antibiofouling Promotor for PES Water Filtration Membranes. *Molecules* **2020**, *25* (3), 691–701. https://doi.org/10.3390/molecules25030691.

23. Johnson-Edler, C. Self-Assembled Architecture of Natural Organic Matter, South Dakota State University, 2017. https://openprairie.sdstate.edu/etd/2177.

24. Archer, R. A.; Johnson, D. W.; Hagaman, E. W.; Moreno, L. N.; Wenkert, E. Carbon-13 Nuclear Magnetic Resonance Spectroscopy of Naturally Occurring Substances. 47. Cannabinoid Compounds. *J. Org. Chem.* **1977**, *42* (3), 490–495. https://doi.org/10.1021/jo00423a021.

25. Chilom, G.; Bruns, A. S.; Rice, J. A. Aggregation of Humic Acid in Solution: Contributions of Different Fractions. *Org. Geochem.* **2009**, *40* (4), 455–460.

26. Khalaf, M. M. R.; Chilom, G.; Rice, J. A. Comparison of the Effects of Self-Assembly and Chemical Composition on Humic Acid Mineralization. *Soil Biol. Biochem.* **2014**, *73*, 96–105. https://doi.org/10.1016/j.soilbio.2014.02.013.

27. Verwey, E. J. W. Theory of the Stability of Lyophobic Colloids. *J. Phys. Colloid Chem.* **1947**, *51* (3), 631–636. https://doi.org/10.1021/j150453a001.