Antifouling properties of ultrafiltration membranes modified with perfluorophenylazide molecules for use in membrane bioreactors

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Introduction:

Due to the lack of access to clean water worldwide and the large cost associated with water transport, communities must seek efficient systems to locally treat wastewater for re-use. Membrane bioreactors (MBRs) can produce high quality water from wastewater, with a relatively small footprint compared to traditional treatment processes.[1] Membranes are used to separate a mixed liquor containing high concentrations of biomass and the purified water, thus, the membranes quickly foul, greatly reducing production efficiency. Due to the microorganisms' sensitivity to chemicals, membranes used in MBRs can only be treated with mild, ineffectual reagents during operation and must be removed completely from the system for more aggressive cleaning. Membranes modified to be self-cleaning or resistant to fouling would make MBR technology more economically feasible.

Still, many of the surface modifications require exotic reaction conditions, long reaction times, and expensive reagents that are not compatible with the roll-to-roll manufacturing of state-of-the-art commercial membranes. Herein, we present a scalable process to functionalize the surface of commercial UF membrane with small molecule PFPA derivatives to impart anti-fouling properties.

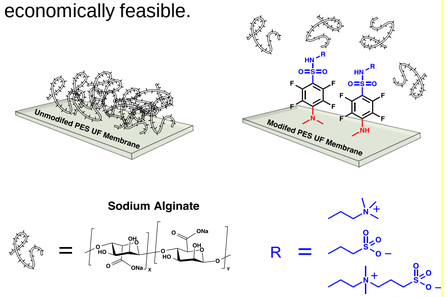


Figure 1: . Illustration of sodium alginate adhesion to PES ultrafiltration membranes unmodified (left) and modified with PFPA derivatives (right).

Modification of Membrane Surfaces:

Previously, we have developed a novel photochemical surface modification of polymeric reverse osmosis membranes.[2] Photoactive perfluorophenyl azides (PFPAs) were utilized to generate highly reactive nitrenes (when exposed to UV light, 254nm) that can covalently bind to the membranes' surfaces. Therefore, the membrane surfaces can be modified under ambient conditions and be completed within minutes, maintaining the roll-to-roll scalability of membrane manufacturing.

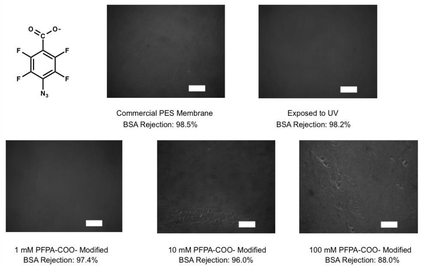
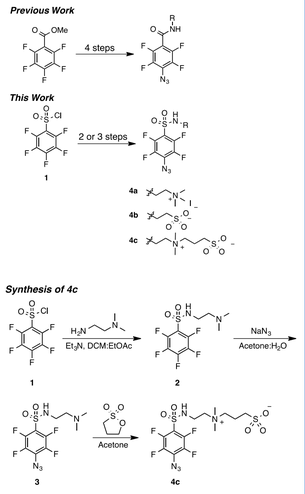


Figure 2: Optical microscope images demonstrating visible membrane degradation at higher concentrations of a PFPA derivative (scale bar = 100 µm). Rejection of bovine serum albumin (BSA) is shown below each image.



Scheme 1: Synthesis of PFPA's from pentafluorophenyl sulfonyl chloride.

Modeling Interfacial Forces:

Fouling largely occurs at the surface of a polymer membrane. The key interfacial factors between the interface of liquid media and the solid surfaces can be quantitatively described using interfacial forces/free energies.[2]

Interfacial forces between membrane and foulant:

Lischfitz van der Waals force $F_{LW} = 2\pi h_0^2 \Delta G_{132}^{LW} a_p \left(\frac{1}{h^2}\right)\left(1+\frac{5.32h}{l_{LW}}\right)^{-1}$ Acid-Base force $F_{AB} = 2\pi h_0 \Delta G_{132}^{AB} a_p \exp\left(-\frac{h_0 - h}{l_{AB}}\right)$

Electrostatic force $F_{EL} = 4\pi\varepsilon\left(\frac{zF}{RT}\right)^2\left(\frac{g_s g_m}{l_{EL}}\right) a_p \exp\left(-\frac{h}{l_{EL}}\right)$

Interfacial free energies: $\Delta G_{132}^{Tot} = \Delta G_{132}^{LW} + \Delta G_{132}^{AB}$

Lischfitz van der Waals free energy $\Delta G_{132}^{LW} = 2\left(\sqrt{g_3^{LW}} - \sqrt{g_1^{LW}}\right)\left(\sqrt{g_2^{LW}} - \sqrt{g_3^{LW}}\right)$

Acid-Base free energy $\Delta G_{132}^{AB} = 2\sqrt{g_3^-}\left(\sqrt{g_1^+} + \sqrt{g_2^-} - \sqrt{g_3^+}\right) + 2\sqrt{g_3^+}\left(\sqrt{g_1^+} + \sqrt{g_2^+} - \sqrt{g_3^+}\right) - 2\sqrt{g_1^+ g_2^-} - 2\sqrt{g_1^- g_2^+}$

Modified membrane surface characterization:

After PES membranes were modified with the three PFPA derivatives, X-ray photoelectron spectroscopy (XPS) and sessile drop contact angle (CA) measurements with different liquids were conducted to analyze chemical and physical changes to the surface of the membranes.

Extended Young-Dupré Equation: $(1+\cos q)g_l^{TOT} = 2\left(\sqrt{g_s^{LW} g_l^{LW}} + \sqrt{g_s^+ g_l^-} + \sqrt{g_s^- g_l^+}\right)$

Membrane	Surface Fluorine (at. %)	CA (DI water)	CA (Ethylene Glycol)	CA (Diiodomethane)	ΔG^{lw} (mJ/m²)	ΔG^{Y+} (mJ/m²)	ΔG^{Y-} (mJ/m²)	ΔG^{mlm}
PES	-	49.8	28.9	17.7	48.4	4E-07	29.4	-3.0
PES UV	-	48.8	29.9	23.3	46.8	1E-03	31.3	1.6
PES PFPA(-)	0.5%	46.8	25.3	21.6	47.3	1E-02	32.1	2.3
PES PFPA(+)	0.4%	45.7	23.2	23.7	46.6	4E-02	32.8	3.9
PES PFPA(+-)	0.7%	40.4	20.1	19.2	48.0	9E-03	38.4	12.5

Table 1: Surface properties of modified and unmodified PES.

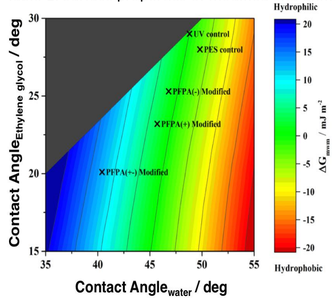


Figure 3: Hydrophilicity of unmodified and modified membranes based on the ΔG^{mwm} surface energy.

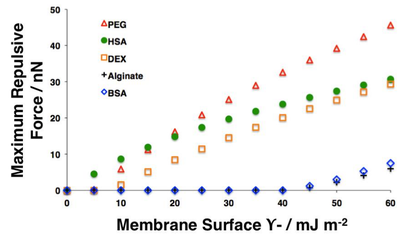


Figure 4: The effect of high ϒ- on repulsive forces between several foulants and a PES membrane. PEG = polyethylene glycol, HSA = human serum albumin, DEX = dextran, BSA = bovine serum albumin

Membrane fouling experiments:

Membranes were compacted at 300psi using DI water. Permeate flux was then adjusted to 3.2 mL/min and once stable the feed was then switched to 200 ppm sodium alginate Flux was maintained until 300 mL of permeate was collected. Trans-membrane pressure: $TMP = (P_{in} - P_{ret})/2 - P_{perm}$, recorded throughout.
Rejection of BSA determined by total organic compound (TOC) analysis of the first fouling stage's permeate

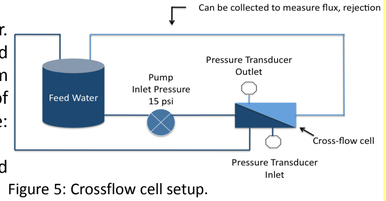


Figure 5: Crossflow cell setup.

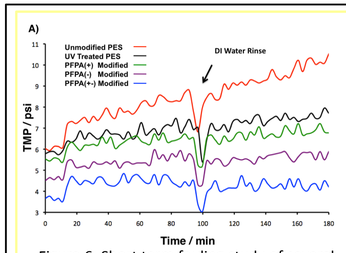


Figure 6: Short term fouling study of several surface modifications.

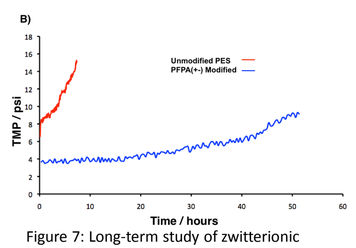


Figure 7: Long-term study of zwitterionic membrane modification.

Membrane	1st Stage Fouling Rate (psi/h)	2nd Stage Fouling Rate (psi/h)	Pure Water Permeability (LMH/bar)	Rejection of SA
Unmodified PES	0.85	1.28	1.069	98.0 %
PES UV Treated	0.54	0.54	1.136	98.8 %
PES-PFPA(+)	0.32	0.41	1.202	98.3 %
PES-PFPA(-)	0.22	0.22	1.603	97.7 %
PES-PFPA(+-)	-0.04	-0.06	1.804	98.7 %

Table 2: Surface properties of modified and unmodified PES.

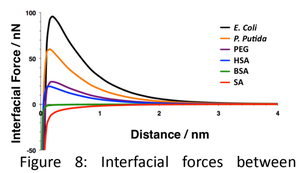


Figure 8: Interfacial forces between selected foulants in MBRs and PES. *E. coli* = *Escherichia coli*, *P. putida* = *Pseudomonas putida*, PEG = polyethylene glycol, HSA = human serum albumin, BSA = bovine serum albumin, SA = sodium alginate

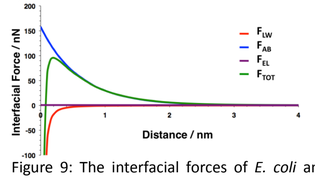


Figure 9: The interfacial forces of *E. coli* and PES broken down into its components

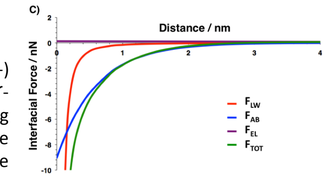


Figure 10: The interfacial forces between sodium alginate and PES broken down into its components.

Among the modified membranes, the PFPA(+-) coated membrane demonstrates the greatest ϒ- and greatest anti-fouling ability. Our modeling data highlights the importance of controlling the ϒ- of the membrane surface to enhance the repulsion of foulants and thus we have synthesized novel PFPA small molecules demonstrating a scalable synthesis to produce photoactive PFPA small molecules in large quantities for use in MBRs.

References:
[1] A. N. L. Ng, A. S. Kim, *Desalination* **2007**, *212*, 261
[2] B. T. McVerry, M. C. Y. Wong, K. L. Marsh, J. A. T. Temple, C. Marambio-Jones, E. M. V Hoek, R. B. Kaner, *Macromol. Rapid Commun.* **2014**, *35*, 1528.
[3] S. Kim, M. Marion, B.-H. Jeong, E. M. V Hoek, *J. Memb. Sci.* **2006**, *284*, 361.

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