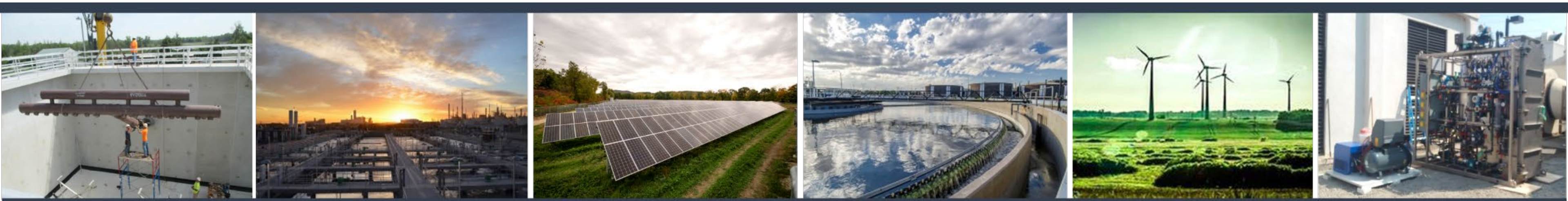
AMERICAN ACADEMY OF ENVIRONMENTAL ENGINEERS & SCIENTISTS®

Thank you to our Patrons

Geosyntec consultants
AECOM
SCS ENGINEERS Environmental Consultants and Contractors
The Metropolitan Water District of Southern California
OC SAN Orange County Sanitation District
carollo
BLACK & VEATCH
CDM Smith
DSWA Delaware Solid Waste Authority
Los Angeles County Sanitation Districts Converting Waste Into Resources
Stanley Consultants
LA DWP Los Angeles Department of Water & Power

We will begin our presentation in a few minutes…



Leadership and Excellence in Environmental Engineering and Science

Multifunctional Membranes Towards PFAS Remediation

D. Bhattacharyya (DB)*, Alumni Chair Professor, Chemical and Materials Engineering and Director of Center of Membrane Sciences, UK NIEHS-SRP Project 3 PI, University of Kentucky, Lexington, KY USA

Collaborators : Current/Recent Students/Res Engineer: S. Thompson, R. Mills , S. Basu, M. leach, J. Bukowski, T. Coolidge, A. Aher, F. Leniz, A. Saad, H. Wan, M. Detisch, A. Gutierrez
Faculty/Industry: Kelly Pennell (Civil Eng, and Director UK NIEHS SRP)), J. Balk, Z. Hilt, I. Escobar, T. Dziubla, L. Ormsbee (Chemical and Materials Eng; Civil Eng)), D. Y. Kim (Chemistry), T. Hastings (Electrical eng), B. Weaver (Solecta Membrane, now with Toray), N. Meeks (Southern Co.)

* **email: DB@UKY.EDU; phone: 859-312-7790**

AAEES Webinar
January 22, 2025

Lecture Outline

- PFAS aspects

- Membrane Advances (background)

- Some new NF approaches

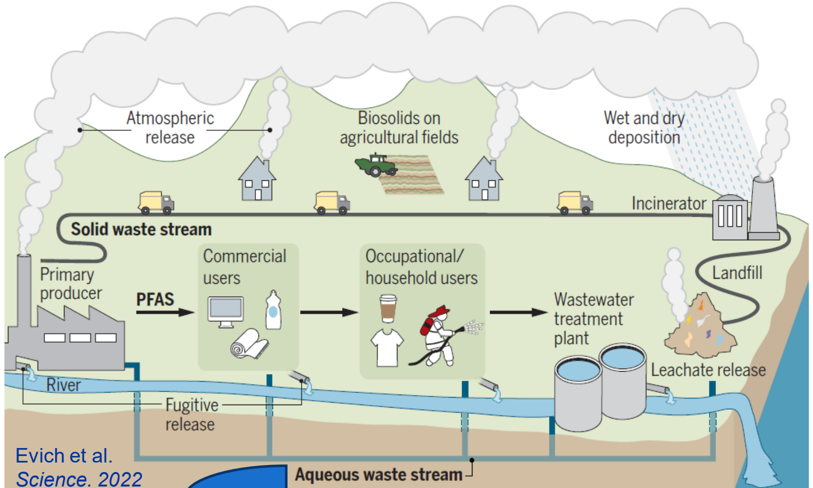
- Membrane pore and surface functionalization approaches

- PFAS Adsorption/desorption (Temperature responsive to amine functionalized membrane pores and fibers)

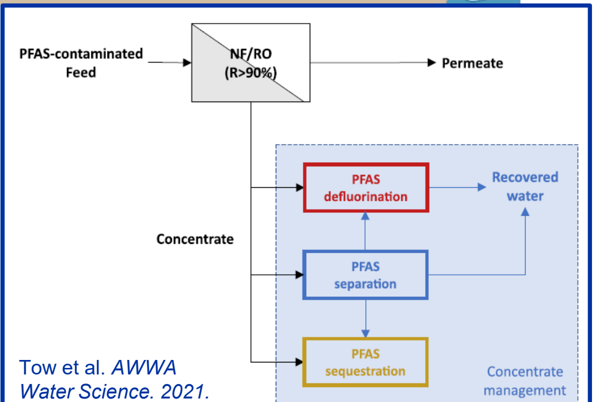
- Metal catalyst synthesis in MF pores and UF surface towards halo-organic detoxification

UK Superfund Research Center

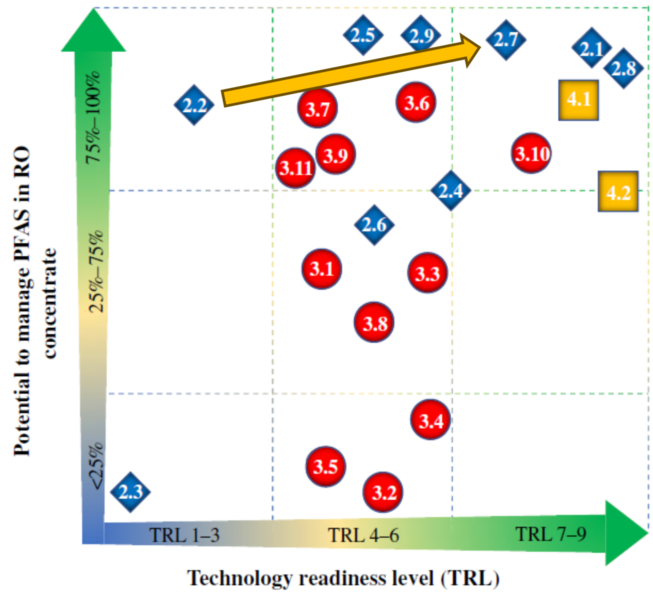
PFAS REMEDIATION TECHNOLOGIES



Evich et al. *Science. 2022*



Tow et al. *AWWA Water Science. 2021.*



2.1. Reverse osmosis and nanofiltration
2.2. Emerging membrane processes
2.3. ED–RO hybrid systems
2.4. Foam fractionation
2.5. Electrocoagulation
2.6. Evaporation ponds
2.7. Brine concentrator with crystallizatio
2.8. Adsorption
2.9. Coagulant aids
3.1. Biological treatment
3.2. Ultraviolet irradiation
3.3. Photocatalysis
3.4. Advanced oxidation
3.5. Solvated electrons
3.6. Plasma-based treatment
3.7. Electron beam
3.8. Zero-valent iron
3.9. Sonochemical treatment
3.10. Incineration
3.11. Supercritical water oxidation
4.1. Deep well injection
4.2. Landfill

Amine Sorbents

+Recyclability	-Scalability
+Tunability	-Removal Rate
+Removal Efficiency	

Ateia et al. *Env Sci & Tech. 2019*

Membrane Technology (Background)

Dense Membranes
- Reverse Osmosis(RO)
- Forward Osmosis (FO)
- Pervaporation(PV)
- Electrodialysis(ED)

Nanofiltration (NF)

Other surface modif

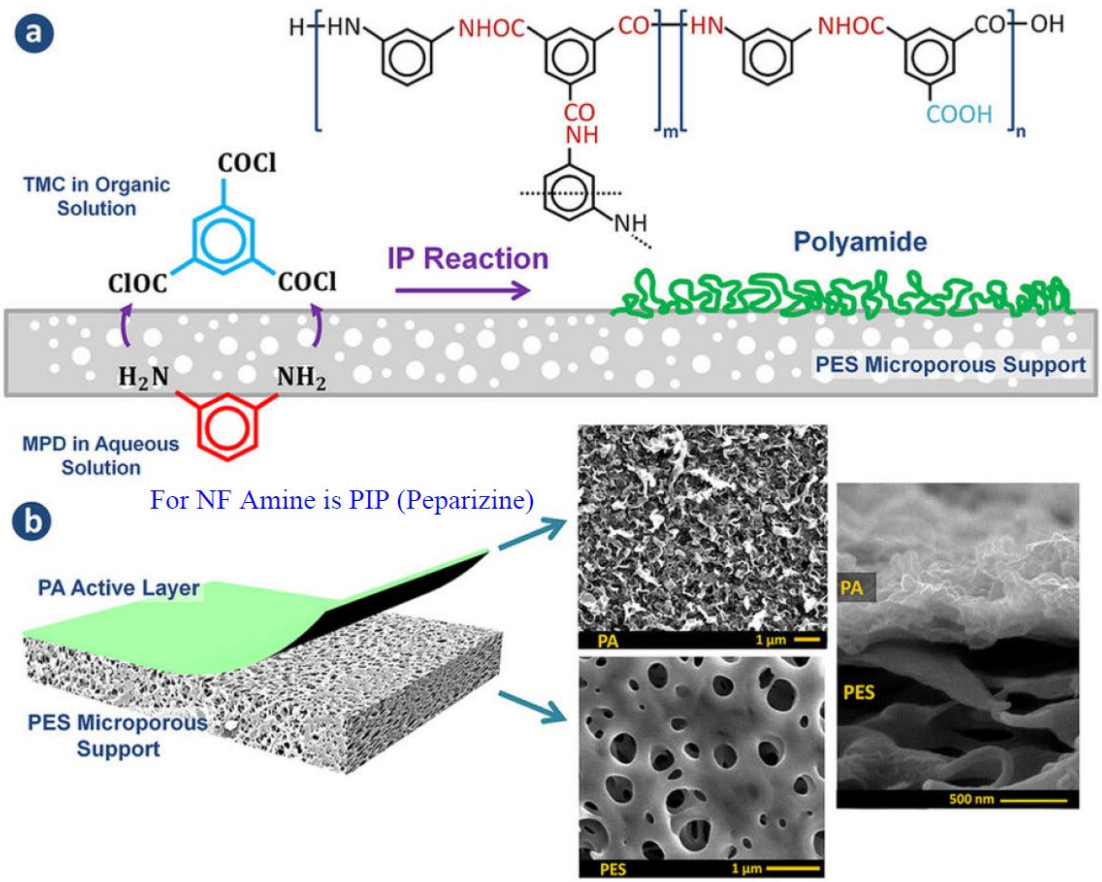
Ultrafiltration (UF)

Microfiltration (MF)

CDI, ED, MD, SLM, etc.

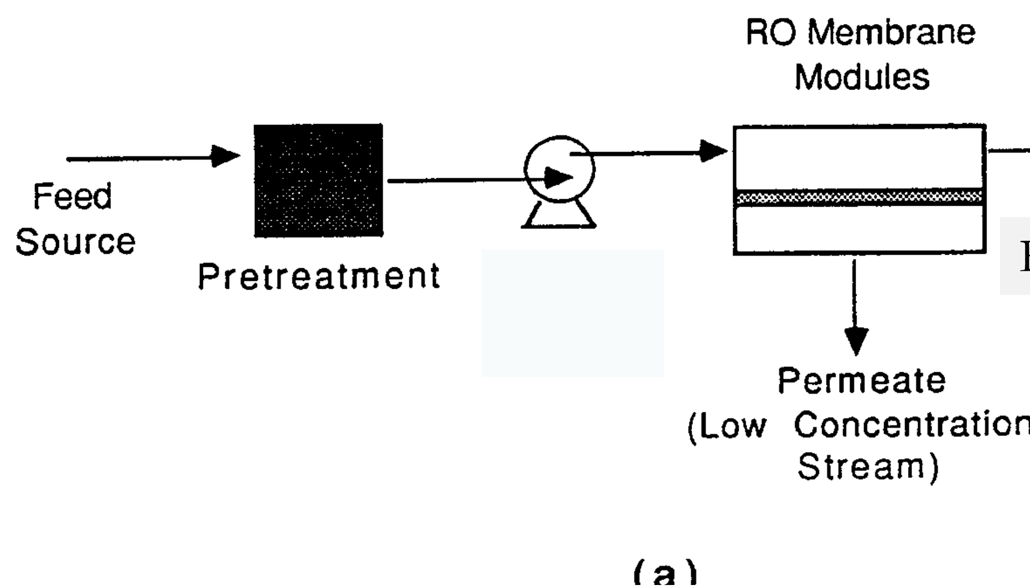
Advanced Functionalized Membranes: Responsive and Adsorptive Membranes, In-situ Catalytic-Nanoparticles to thin film, GO, Bioinspired

RO/NF interfacial polymerization(surface reactions)



Khorshidi, et al, Scientific reports (2016)

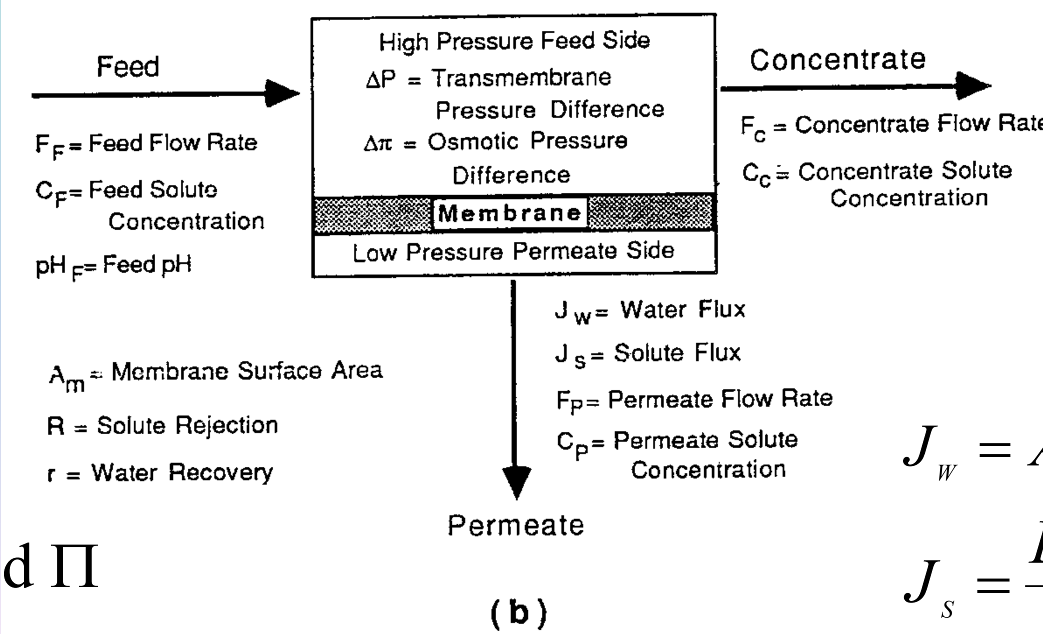
Schematic of (a) a Membrane Process and (b) the Process Streams



(a)

Retentate Stream

No place to dispose retentate
(except seawater)
May need other hybrid processes
to recover materials or to dispose
Most cases require very high recovery

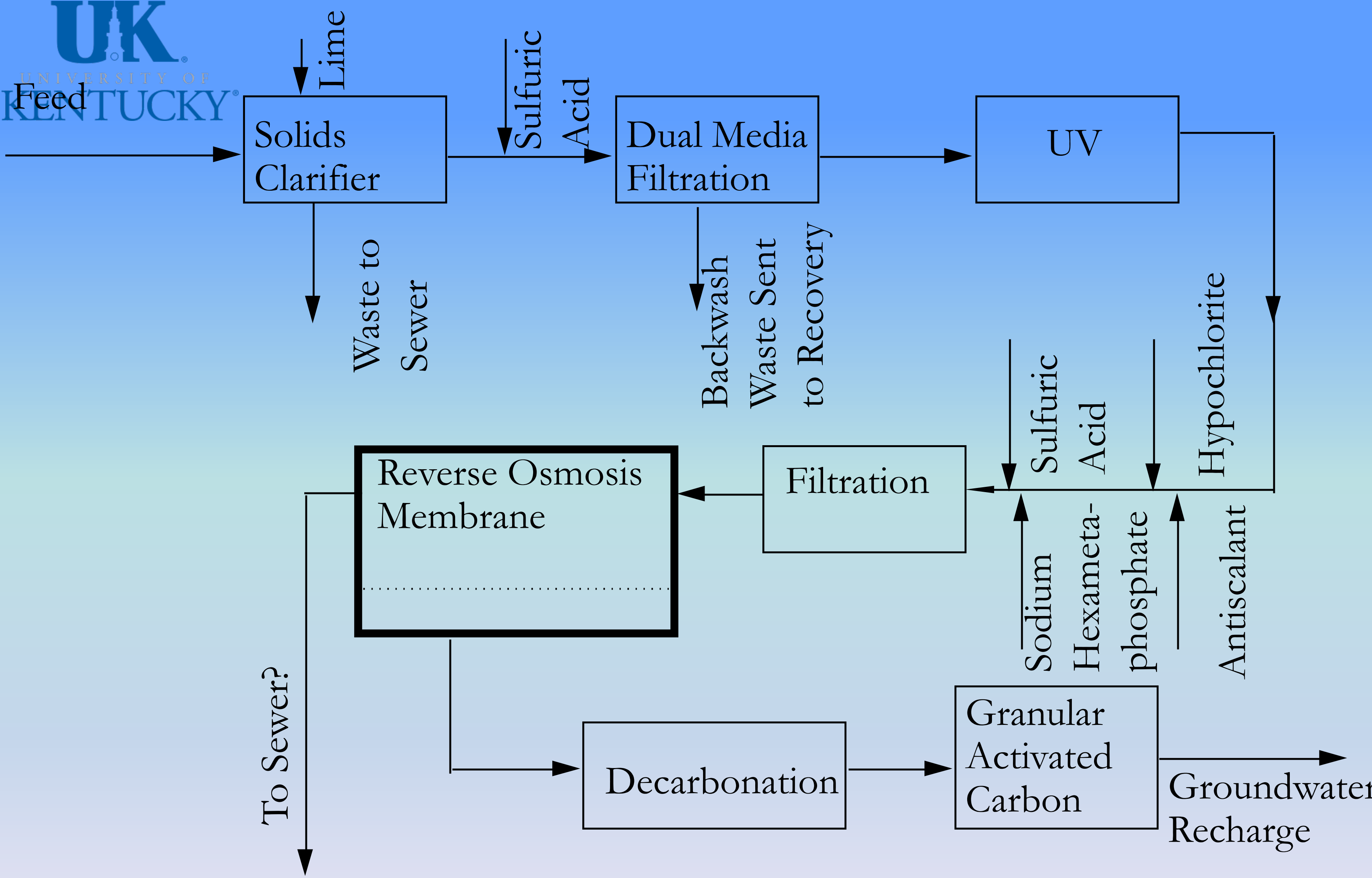


(b)

$$J_W = A(\Delta P - \Delta \Pi)$$

$$J_S = \frac{D_S K}{L}(C_B - C_P)$$

r ∝ feed Π



Need to look at PFAS now

Reverse Osmosis for Treatment of Municipal Wastewater (Secondary Effluent) at Orange County, CA

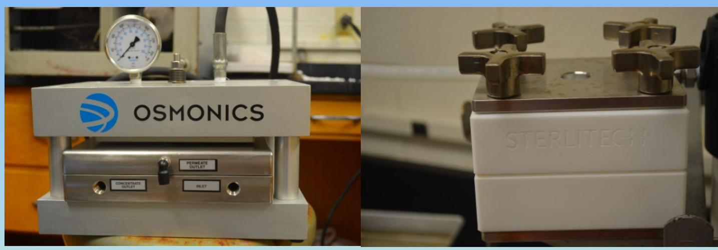
Some RO/NF membranes PFAS separation Results

Pollutant (Concentration, ppm)	Membrane Technology Used	Conditions	Water Matrix	Rejection
PFOS: 0.5–1500	RO	pH 4 25 °C 200 psi 24 h	Real wastewater	>99%
Perfluorobutanoic acid (PFBA), perfluorobutane sulfonate (PFBS), perfluorooctanoic acid (PFOA), and perfluorooctane sulfonate (PFOS): 0.001	NF and RO	87–116 psi 22–28 °C pH 7.4	Tap water	95–99.9%
PFXxA: 0.0001–0.0003	RO, NF, and UF	pH 7	MilliQ water	69–99.2%
9 types of PFAS	NF	pH 6.7 18 °C 125 psi	Artificial ground water	95–99%
PFOA: 1	NF (negatively charged)	pH ~7 25 °C 100 psi	Simulated groundwater	~90%

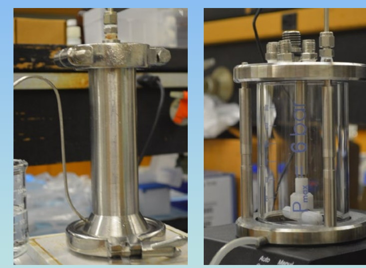
Das and Ronen. "A Review on Removal and Destruction of Per- and Polyfluoroalkyl Substances (PFAS) by Novel Membranes". *Membranes*. (2022)

Membrane Test Cells and Modules

Cross-flow cell



Dead-end cell



Membrane modules

Automated cross-flow NF and Functionalized MF membranes System (4 cross flow cells, one spiral module) with temperature control, etc.)

Modeling of NF Membrane Separation

Extended Nernst-Planck Equation

$$j_i = -c_i D_{i,p} \frac{d(\ln \gamma_i)}{dx} + \frac{c_i D_{i,p}}{RT} V_i \frac{dP}{dx} - K_{i,d} D_{i,\infty} \frac{dc_i}{dx} - \frac{z_i c_i D_{i,p}}{RT} F \frac{d\psi}{dx} + K_{i,c} c_i v$$

The flux of the ionic species i

The activity gradient

The effect of pressure on chemical potential

Negligible due to small pressure drop

Solute diffusion

Transport due to the electric field gradient (equals zero for uncharged solutes)

Solute convection

Bowen and Welfoot, Chem. Eng. Sci..2002, 57(7), 1121-1137.

Bowen and Welfoot, Desalination.2002, 147, 197-203.

See-Toh et al. J. Membrane Sci. 2008, 324, 220–232.

Francisco, Escobar, Liu, and Bhattacharyya et al , JMS (2021)

Some NF (Nanofiltration) Advances Towards PFAS

Synthesis of Negative ot positive charge NF Membranes

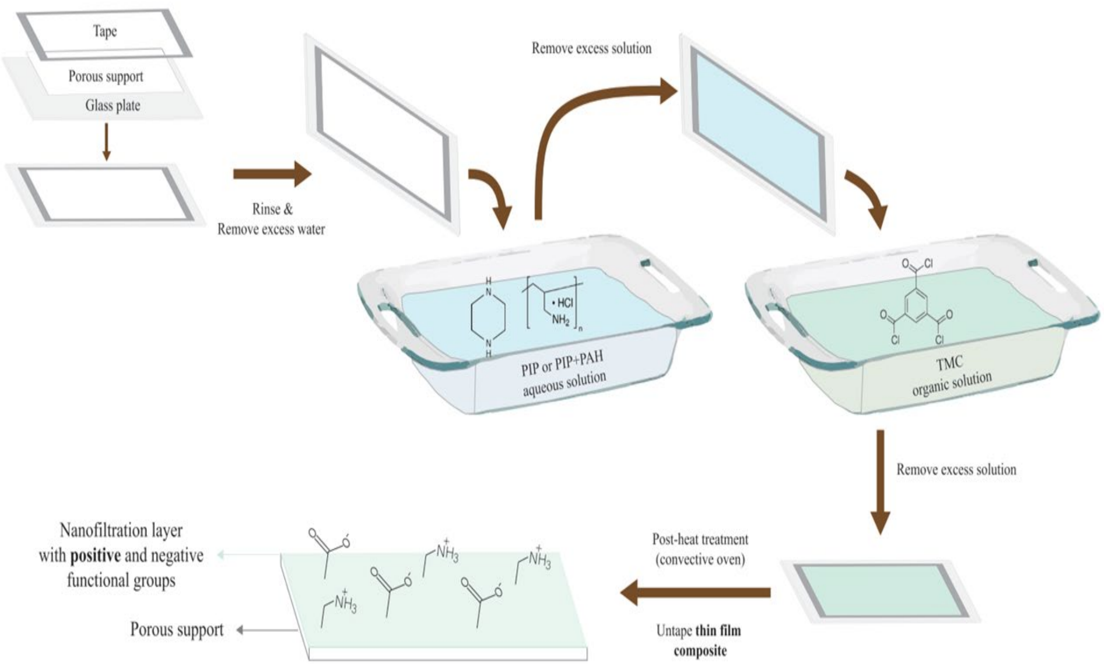
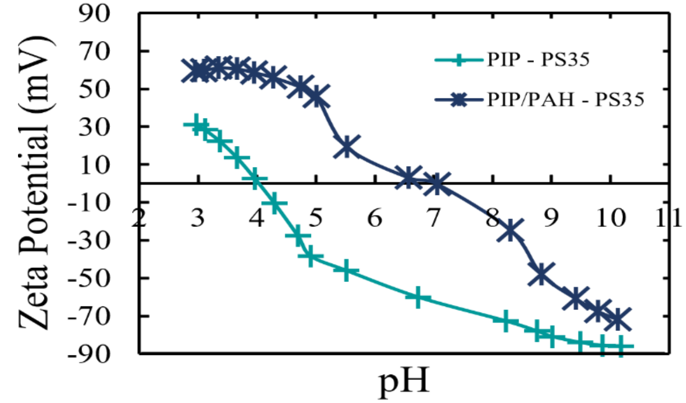


Figure 5. Schematic of interfacial polymerization process for synthesis of nanofiltration layer. This process was used for both PIP and PIP/PAH chemistries in the laboratory and simplified representation of final PIP/PAH – PS35 thin film composite functional groups is presented. ***[7]***



Chemical composition:

1) 1.4% PIP; 0.14% TMC

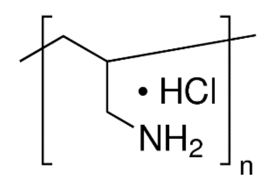
2) 1.0% PIP and **0.4% PAH**; 0.14% TMC

Porous Support:

Commercial PS35 (Solecta co)

PAH:

- MW~15,000 Da
- Calculated $< r^2 >_{fa}^{1/2}$= 4.8(nm)



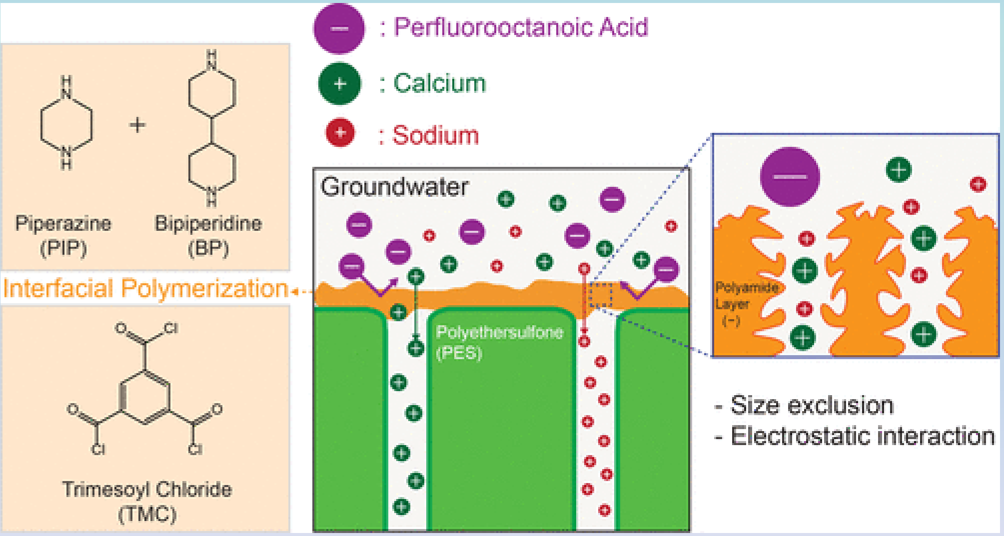
Leniz, Escobar, Liu, and Bhattacharyya, J. Memb. Sci. 620 (2021)

High Performance Nanofiltration Membrane for Effective Removal of Perfluoroalkyl Substances at High Water Recovery

Chanhee Boo, Yunkun Wang, Ines Zucker, Youngwoo Choo, Chinedum O. Osuji, and Menachem Elimelech

Environ. Sci. Technol., 2018, 52 (13), pp 7279–7288

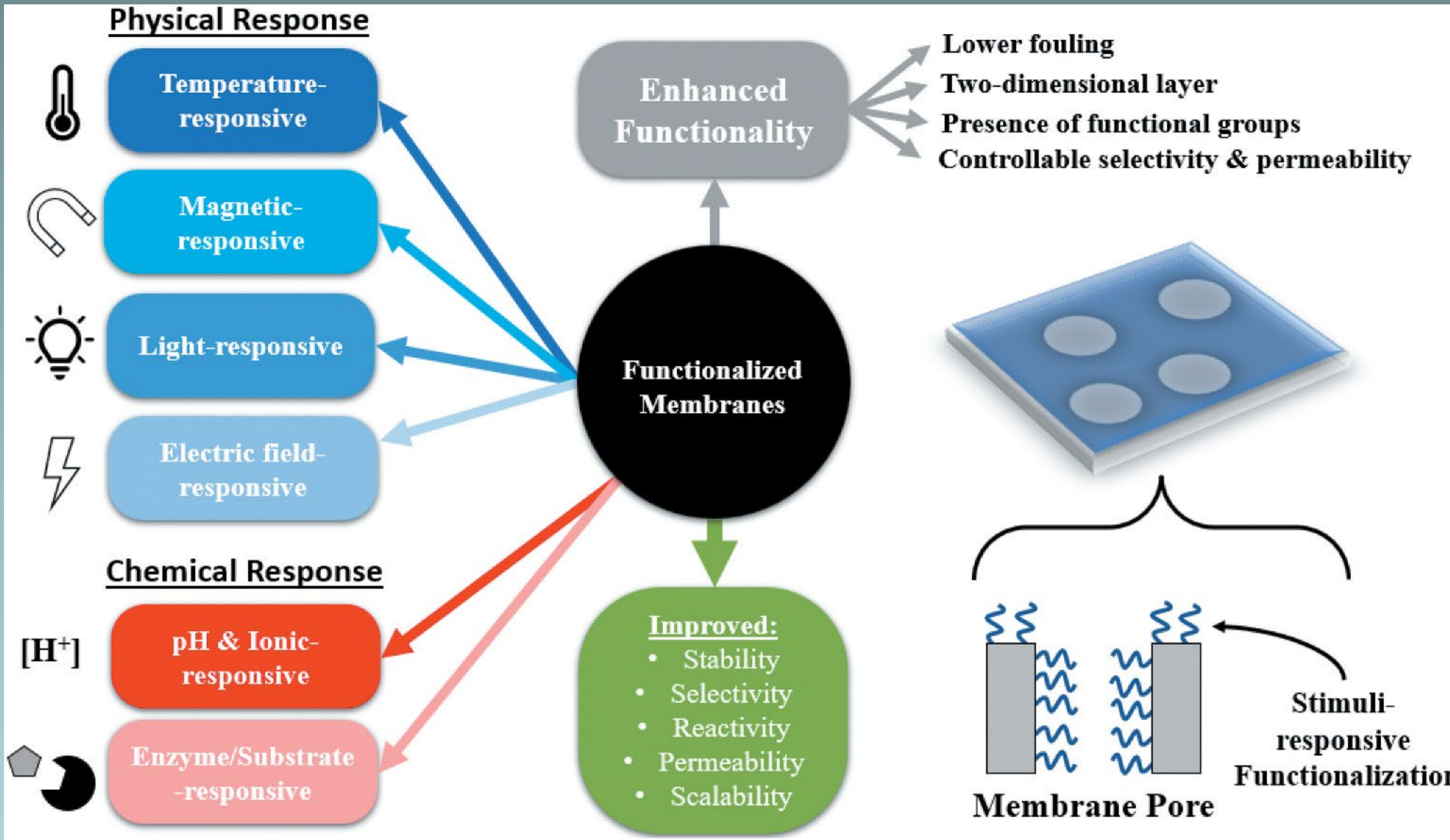
Demonstrated the fabrication of a loose, negatively charged nanofiltration (NF) membrane with tailored selectivity for the removal of perfluoroalkyl substances with reduced scaling potential.



The fabricated NF membrane possessed a negative surface charge and had a pore diameter of ~1.2 nm. exhibited a high retention of PFOA (~90%) while allowing high passage of scale-forming cations (i.e., calcium)

Pore and Fiber Functionalized membranes

- Temperature swing PFAS sorption/desorption
- Pore functionalized amine hydrogels for PFAS capture and concentration
- Nanofiber membrane co-valent quat amine functionalization

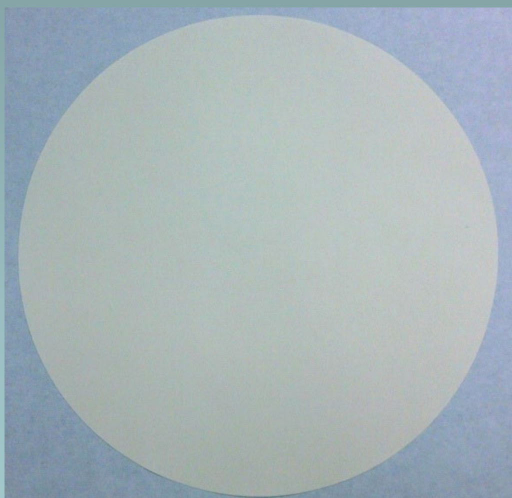


Summary of primary functionalized membranes, their responsive nature, and key improvements (Mills, Bhattacharyya, et al, Sep. Sci. and Technology (Dec 2022)

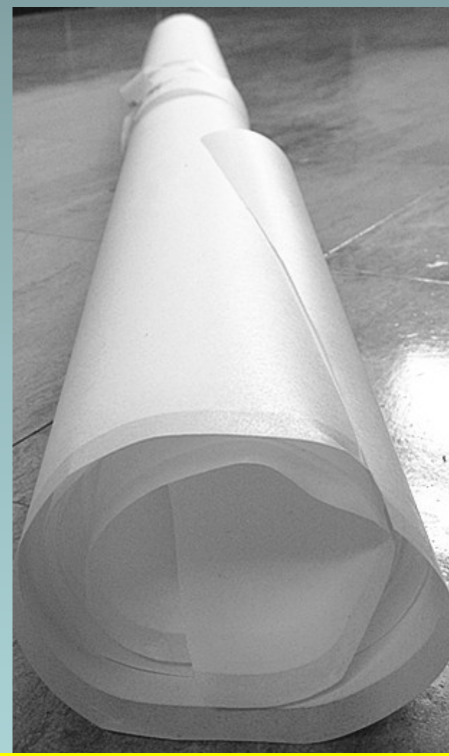
Lab-scale studies

Large-scale production

2514 Spiral-wound modules

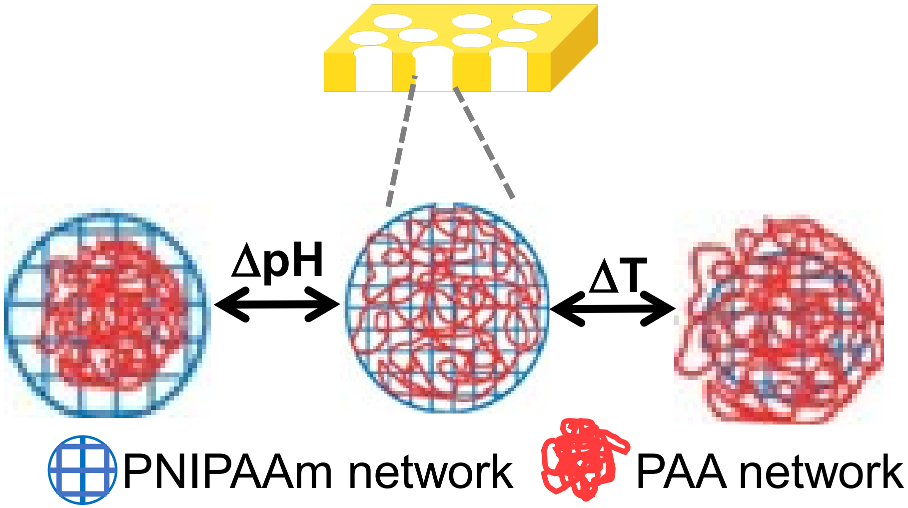


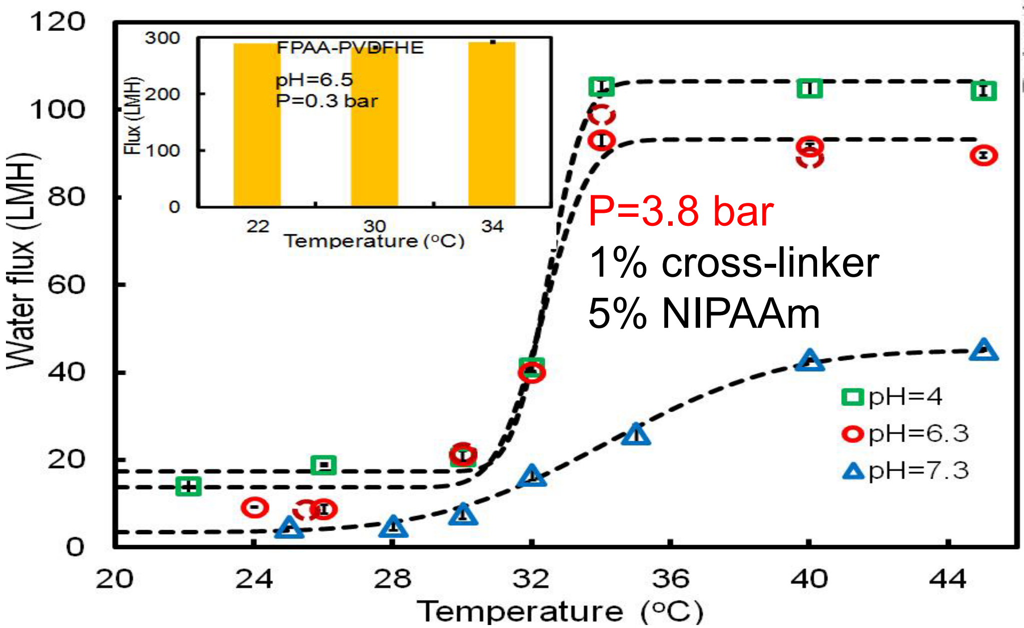
Small membrane

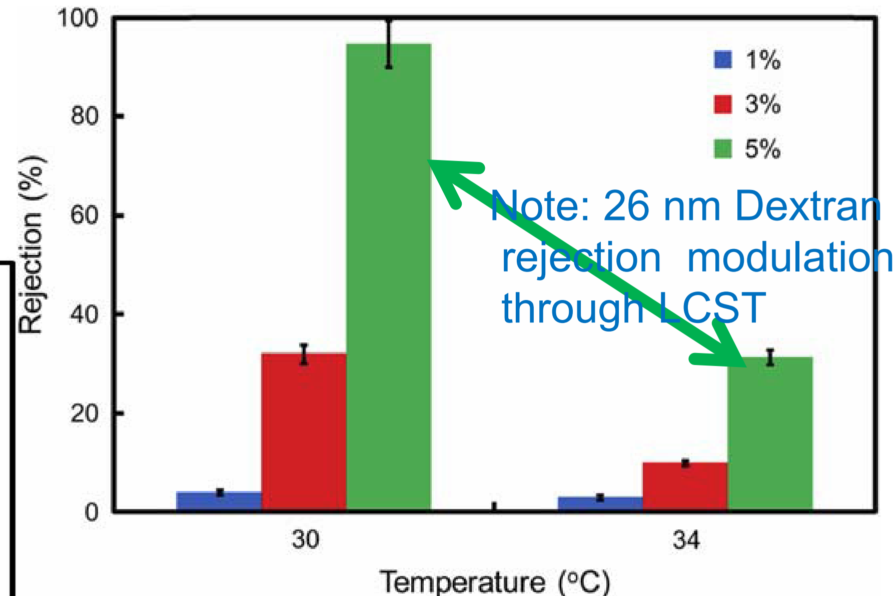


Large-scale flat sheet and modules
(collaborative work with Nanostone/Solecta Membranes, Oceanside, CA)

Temperature and pH Responsive (PNIPAAM and PAA) Full - Scale PNIPAAm-PAA-PVDF Membrane





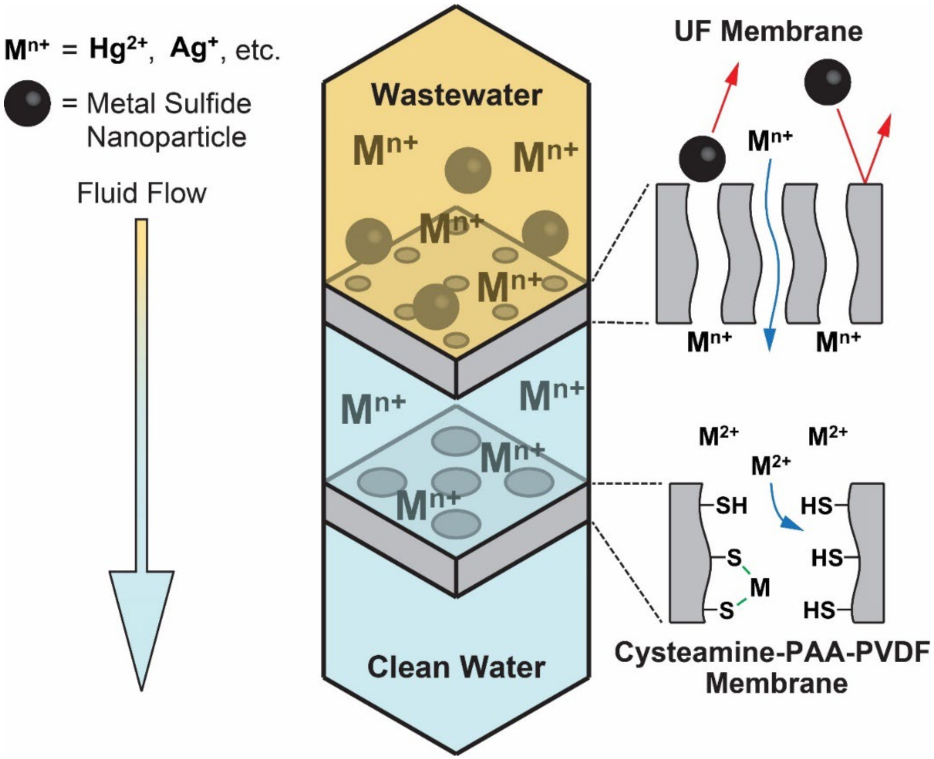


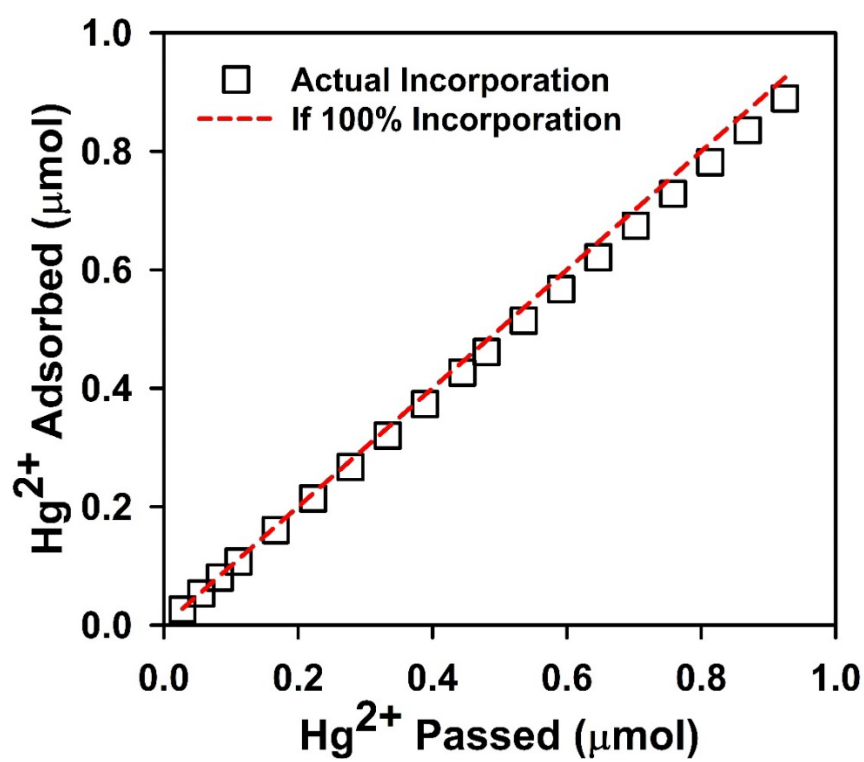
Note: UF Type tunable separations with pore Functionalized MF membranes

Xiao,Takigawa, Bhattacharyya, et al D., J. Membrane. Sci. 457, 39-49 (2014)

High value metal recovery (Ag) and toxic Metal (Hg) Sorption by Thiol Functionalized MF Membrane Pores

Membrane Adsorption Bed >> conventional ion exchange ; Joint develpment with industry





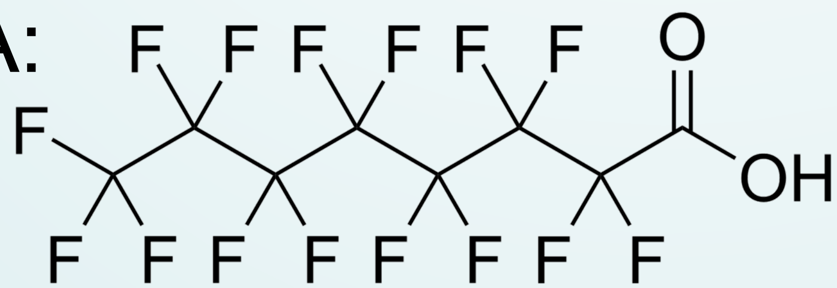
- No pore diffusion issues
- Convective flow
- High dynamic capacity
- > 90% sorption site utilization

Islam,, Hernandez, Hatakeyama (Chevron), Vogler, Bhattacharyya, et al, ACS Omega (2020)

Converting traditional MF membranes for emerging toxic halo organic separations

PNIPAm (Poly(N-isopropylacrylamide) Functionalized Responsive Membranes and hydrogels for temperature swing perfluoro-organics Sorption/desorption (Emerging Pollutants in water)

PFOA:

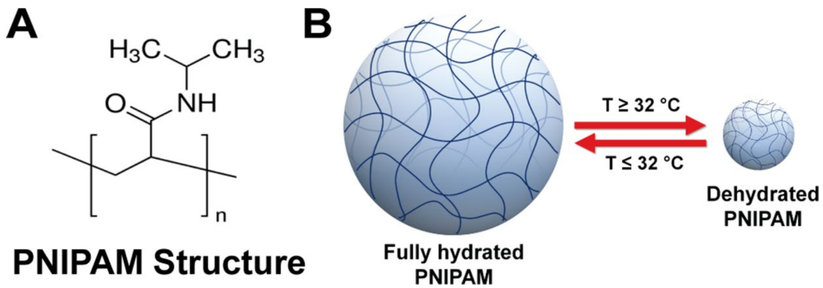


Why not carbon Adsorption?
High T regeneration and Corrosive gas potential

Saad, A., Mills, R., Wan, H., Mottaleb, MA., Ormsbee, L., & Bhattacharyya, D. J. Membrane Science (2020); Leniz, Zimmerman, Bhattacharyya, et al , ACS Appl Mat Interface (2023)

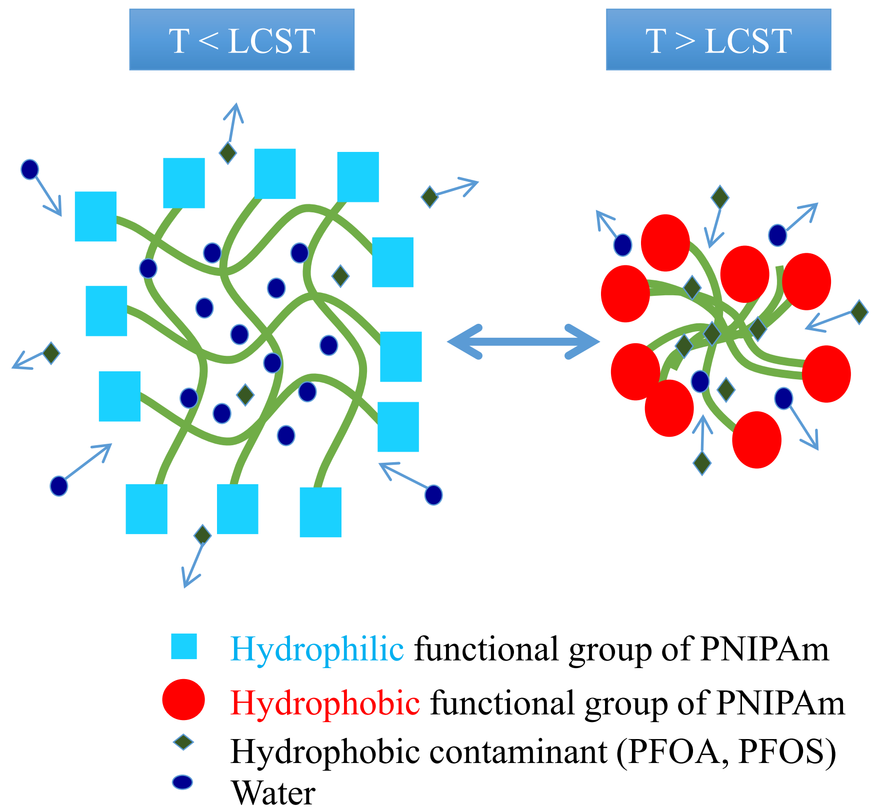
Bhattacharyya, Saad, Mills, Ormsbee, on PFOS technology with temp responsive Membranes and hydrogel, US Patent (*US 11,660,574 B2*), May 30, 2023

Temperature Responsive Polymer
Sorption/desorption applications

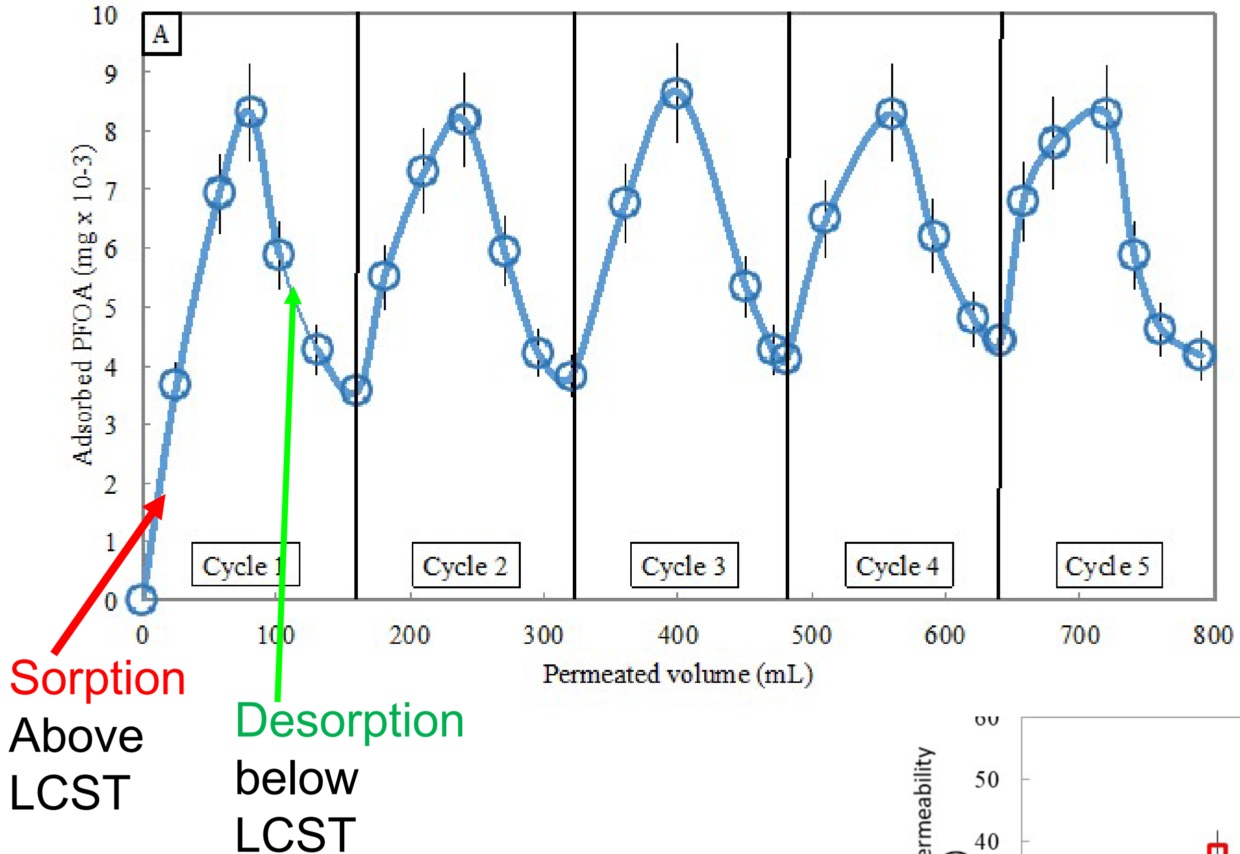


PNIPAm

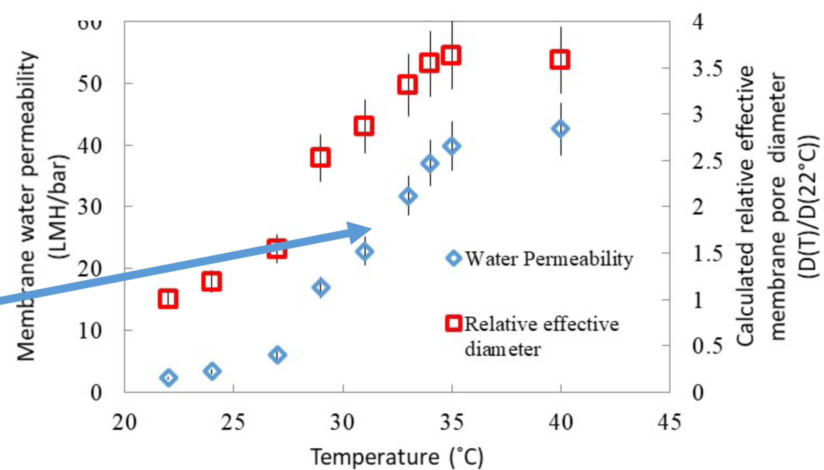
- LCST behavior
- Controllable LCST value
- Controlled flux
- Gating character
- Conformational changes



PFOA sorption-desorption from water over multiple cycles: Temp Responsive PVDF membranes Pressure= 3.5 bar

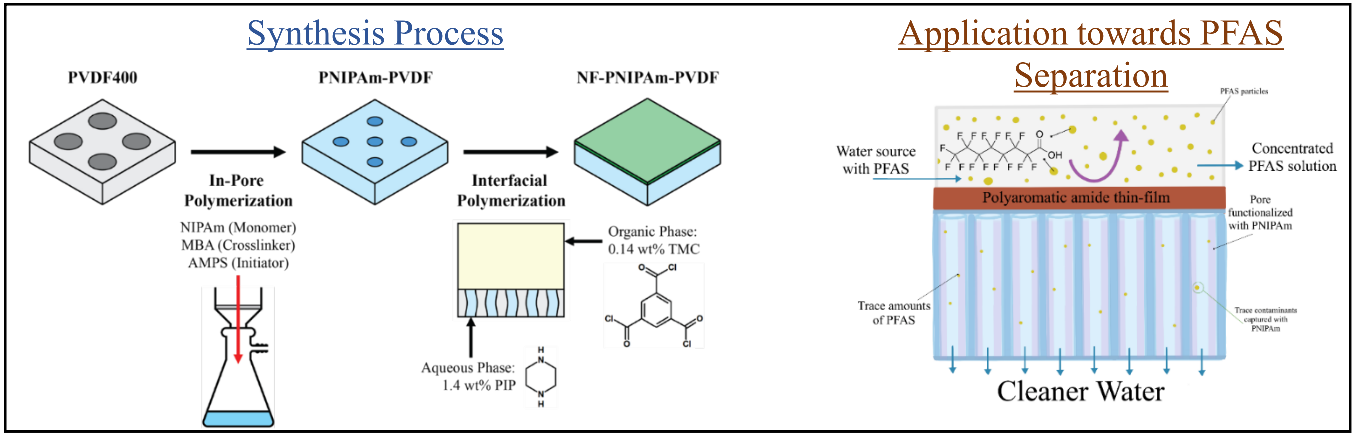


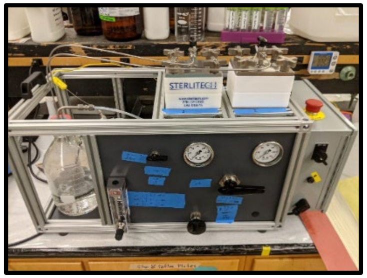
Membrane Water Permeability



Dual-Functional Responsive Membranes for PFAS and Organics Separation from Water

Dual-Functional Nanofiltration and Adsorptive Membranes





Crossflow membrane testing unit for halo-organic compounds separations
- Small volume for hazardous solutions.
- Easy to transport for on site runs.

Crossflow membrane testing unit for scaling up systems:
- Large processing volumes.
- 4 membranes simultaneously.
- Temperature, pump and other control functions, with recording and digital display functions

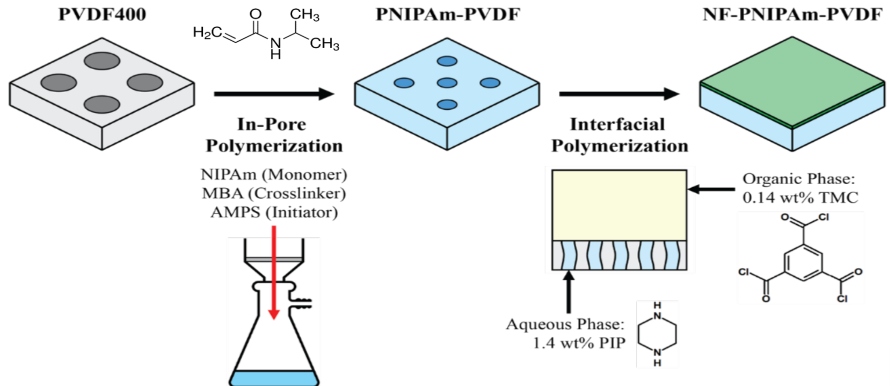
PermeGear Membrane Permeability Measurement System:
- Fast throughput membrane solute PERMEABILITY ANALYSIS
- Up to 7 membrane samples simultaneously Continuous flow

For positively charged NF membrane synthesis and application See Leniz, Liu, Bhattacharyya, et al, J. Membrane Sci (2021)

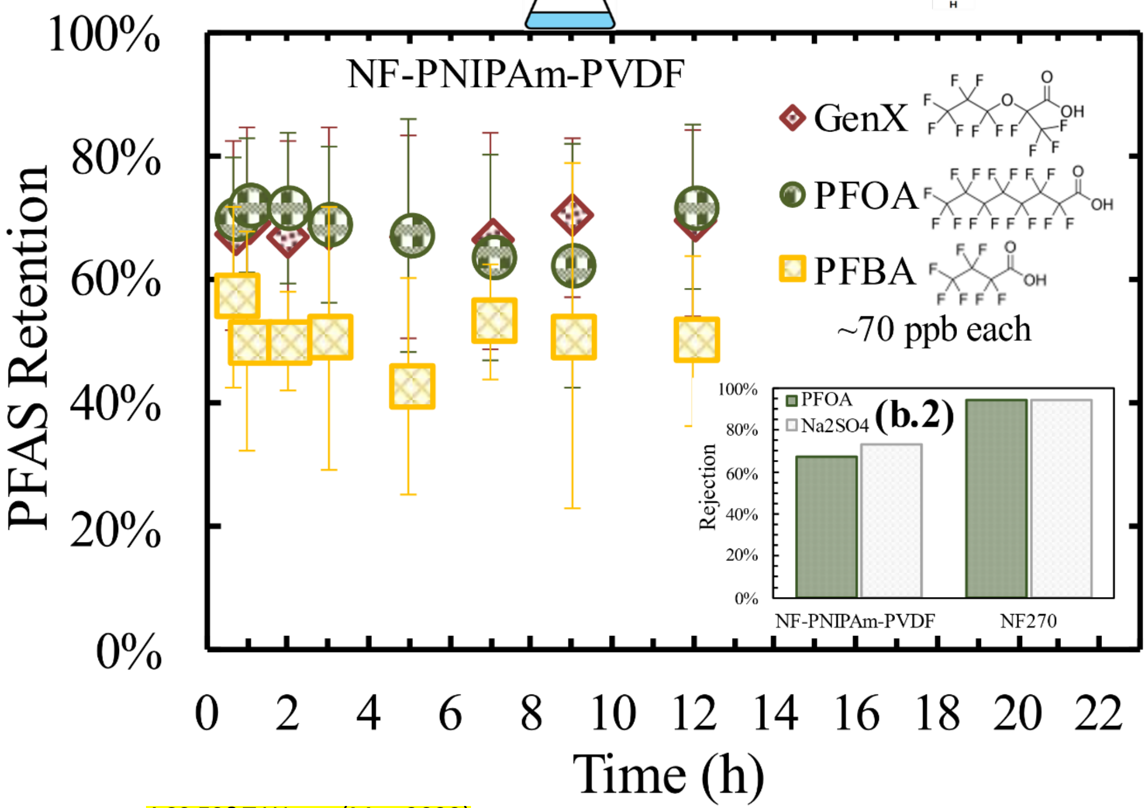
For PFAS and metal capture, see Leniz, Bhattacharyya, et al, ACS Appl Mat Interfaces (2023)

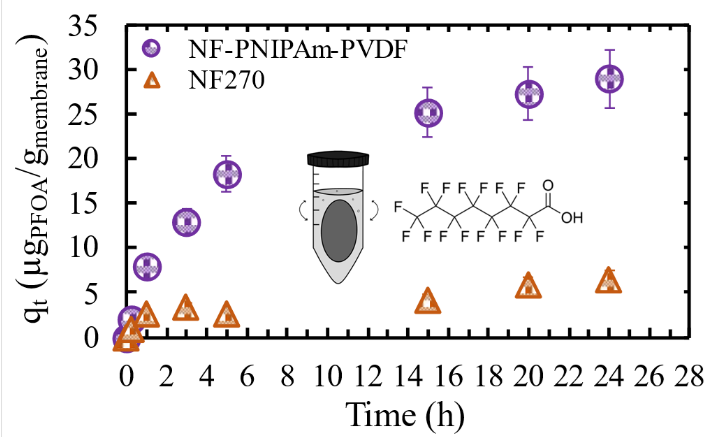
Challenges to make NF on MF support (**Dual Functional Temp responsive and Adsorptive Nanofiltration Membrane towards PFAS separation)**

Synthesis of NF layer on top of open porous PVDF400



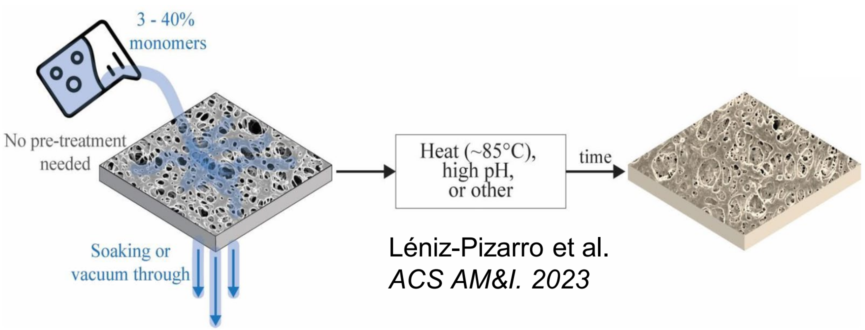
NF Cross flow unit (7 bar, flux 100 LMH)
to get high water recovery and minimize
waste generation



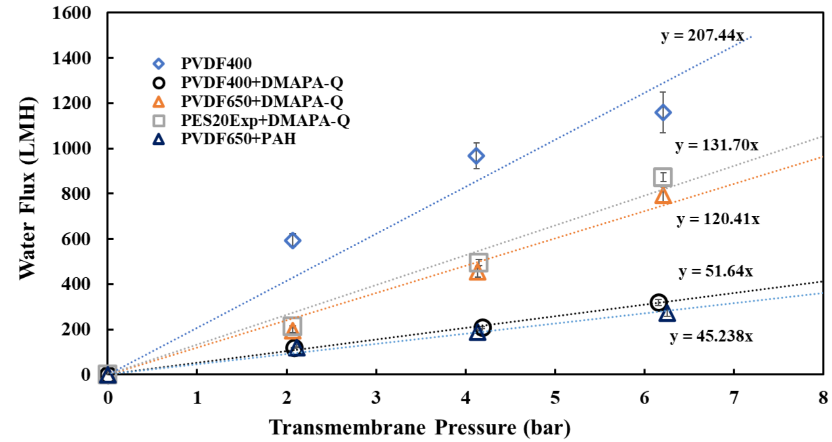


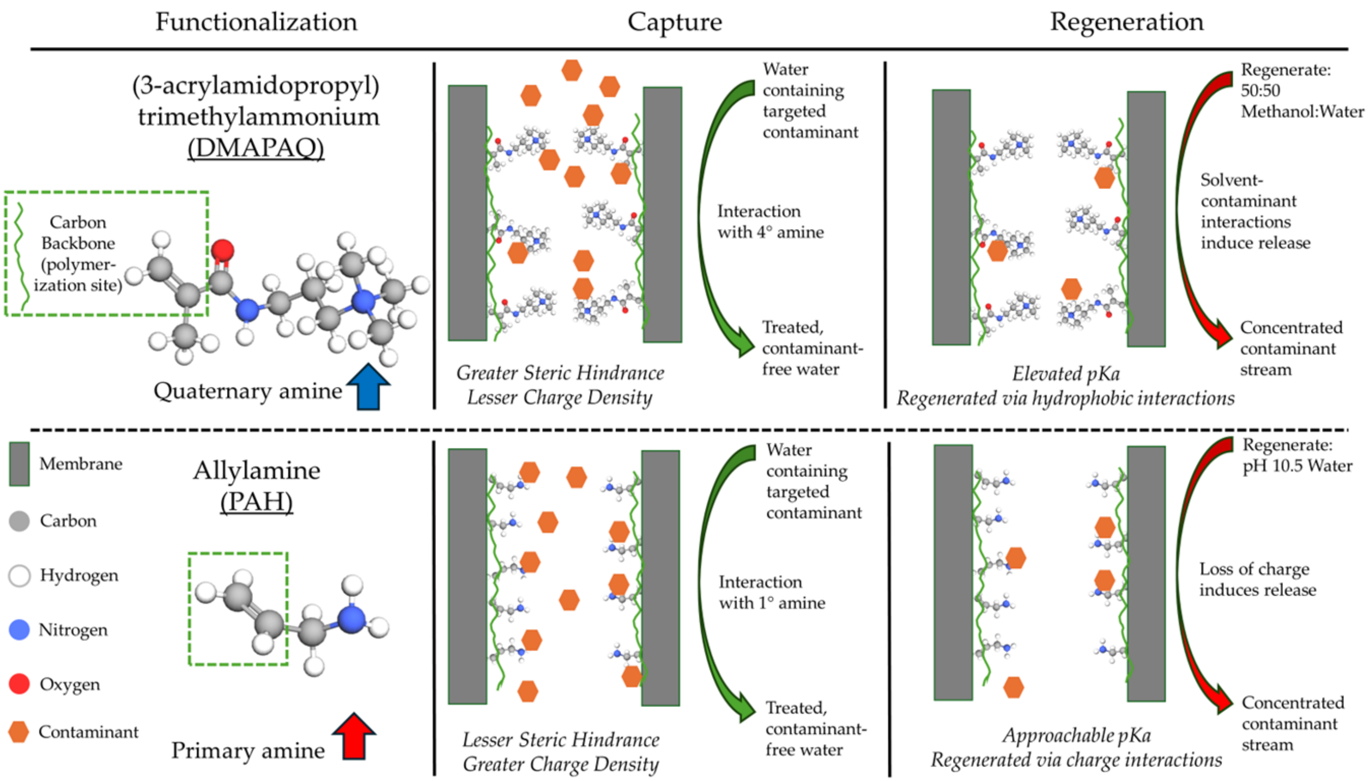
ACS ES&T Water (May 2022)

Procedure for MF Membrane Pore functionalized with hydrogels of Quat amine and Primary Amine



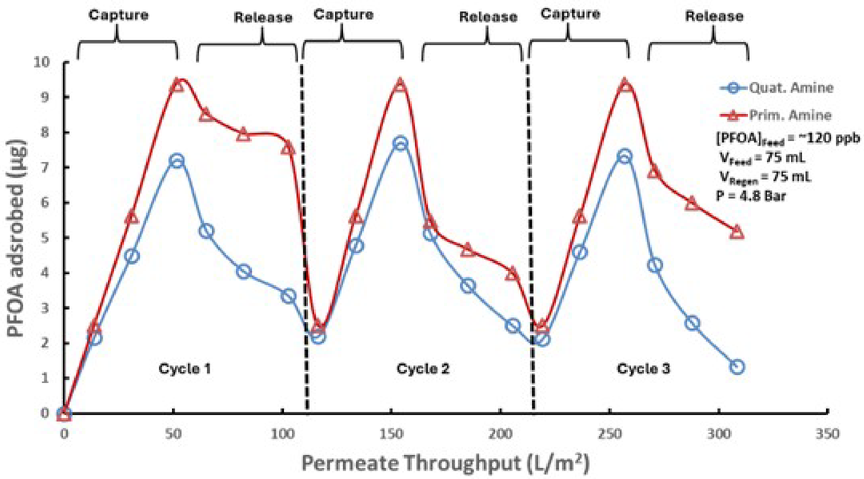
Léniz-Pizarro et al.
ACS AM&I. 2023



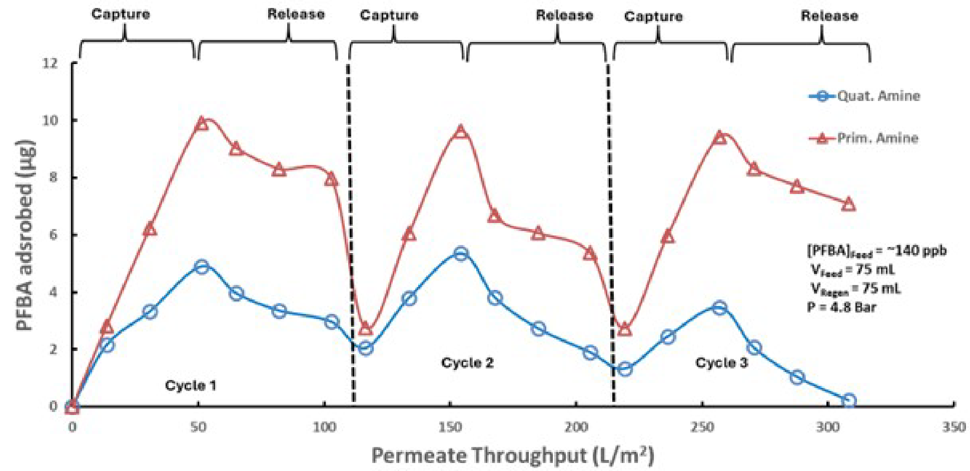


Ref: Thompson, Gutierrez, Bukowski, Bhattacharyya, Molecules (MDPI Journal) Sept 2024

MF Membrane Pore functionalized with hydrogels of Quat amine and Primary Amine (Sorption and desorption Cycles for PFOA and PFBA)



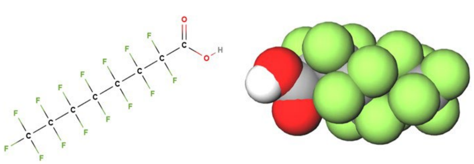
(a)



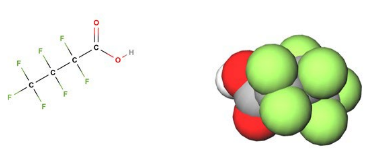
(b)

Capture and controlled release of **(a)** 120 ppb PFOA solution (at 1500 LMH) and **(b)** 140 ppb PFBA solution (at 900 LMH) in functionalized and pristine membranes. Quaternary amine-functionalized and primary amine-functionalized membranes were regenerated with 50:50 methanol:water mix and deionized water adjusted to pH 10.5 using NaOH, respectively. All permeations performed at 4.8 bar

PFOA



PFBA



$$R - N^{+}Cl^{-} + PFAS^{-} \Leftrightarrow R - N^{+}PFAS^{-} + Cl^{-}$$

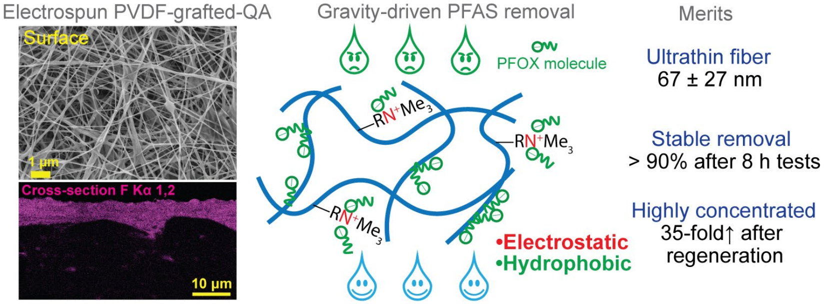
Thompson, Gutierrez, Bukowski, & Bhattacharyya. “Microfiltration Membrane Pore Functionalization with Primary and Quaternary Amines for PFAS Remediation: Capture, Regeneration, and Reuse”. *Molecules*. (Sept 2024)

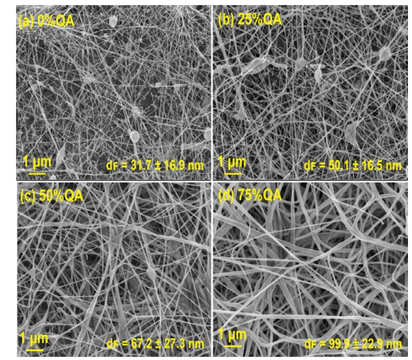
Gravity-driven electrospun membranes for effective removal of perfluoro-organics from synthetic groundwater

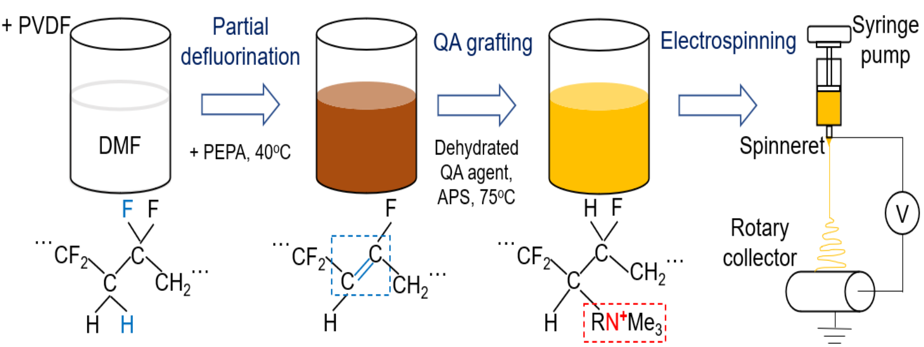
Hongyi Wan , Rollie Mills ,Yixing Wang ,Keyu Wang, Sunjie Xu, Dibakar Bhattacharyya , Zhi Xu
School of Chemical Engineering, **East China University of Science and Technology**, Shanghai, 200237, China Department of Chemical and Materials Engineering, **University of Kentucky**, Lexington, KY, 40506, USA

J. Membrane Sci (2022)

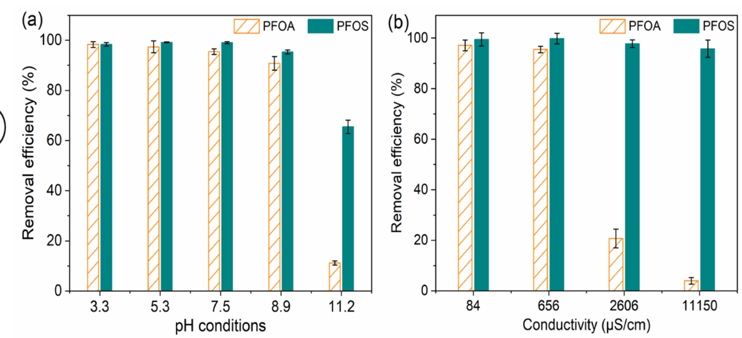
Here we show use of Quat amine cation functionalized Membrane (also with hydrophobic interactions) rather than temperature responsive p-Nipam







Membrane fabrication methods from the preparation of dope solution in the electrospinning process
QA:2-(methacryloyloxy)ethyl]trimethylammonium chloride



PFOX removal using the electrospun PVDF-g-QA membranes
Permeate flux=30.4 LMH
At h0 = 0.032 m; pressure = 313 Pa and T = 22 oC

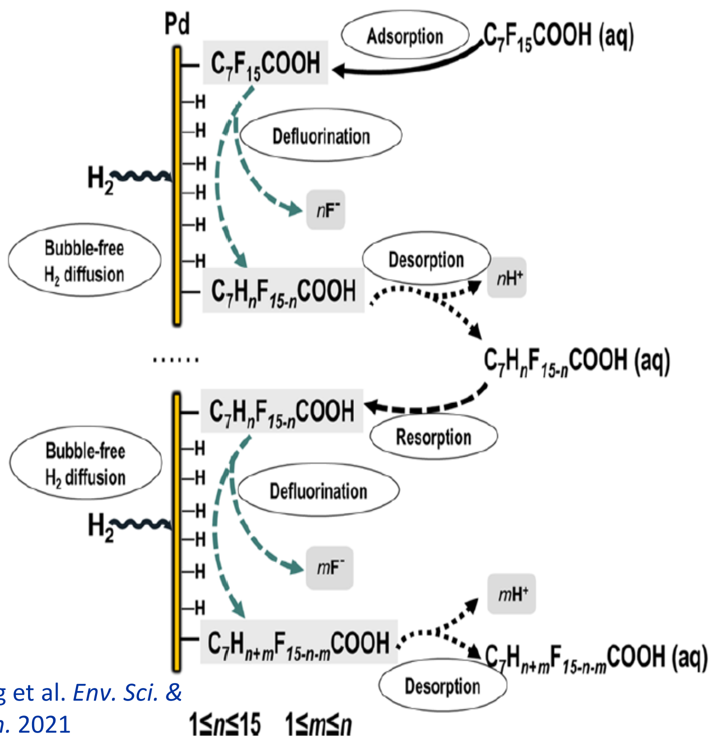
Dr. Hongyi Wan, currently Professor at Hunan Institute of Science and Technology

Direct nano structured metal catalyst synthesis on membranes:

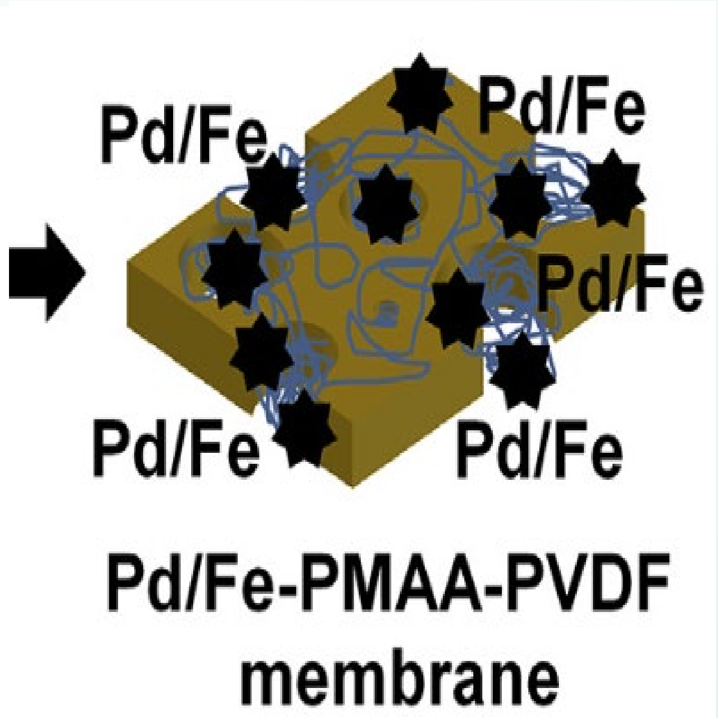
- Nano sized in-situ synthesis in MF membrane pores
- Thin Pd film (magnetron sputtering) on UF membrane surface

Some Environmental halogenation applications to reduce toxicity by hydrogenation

Detoxification



Long et al. *Env. Sci. & Tech.* 2021



Wan et al. *JMS.* 2020

Auto-Assembled Pd−Rh Nanoalloys Catalyzed Faster and Deeper Hydrodefluorination of Perfluorooctanoic Acid (PFOA) in Environmental Conditions

Min Long, Chen Zhou,* Welman C. Elias, Hunter P. Jacobs, Kimberly N. Heck, Michael S. Wong,
and Bruce E. Rittmann

ACS ES&T Eng (2024)

Evaluated auto-assembled palladium (Pd) plus rhodium (Rh) nanoalloys for H2-induced catalytic hydrodefluorination for one of the most prominent PFASs, perfluorooctanoic ... perature.

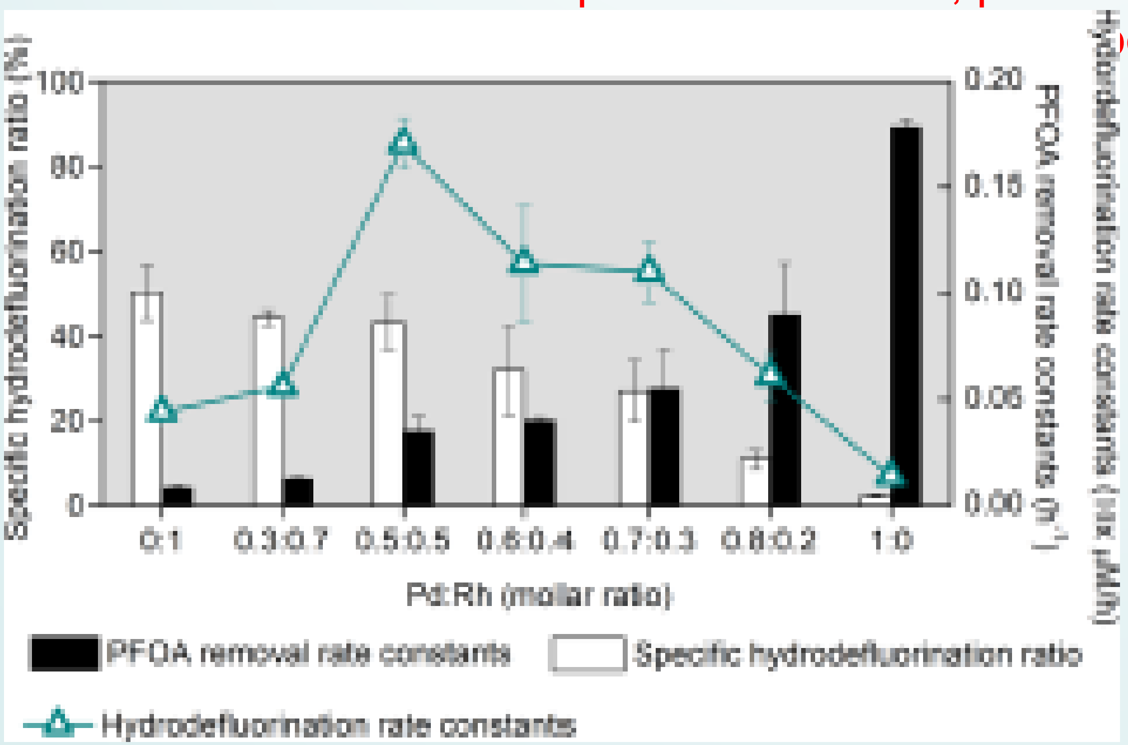
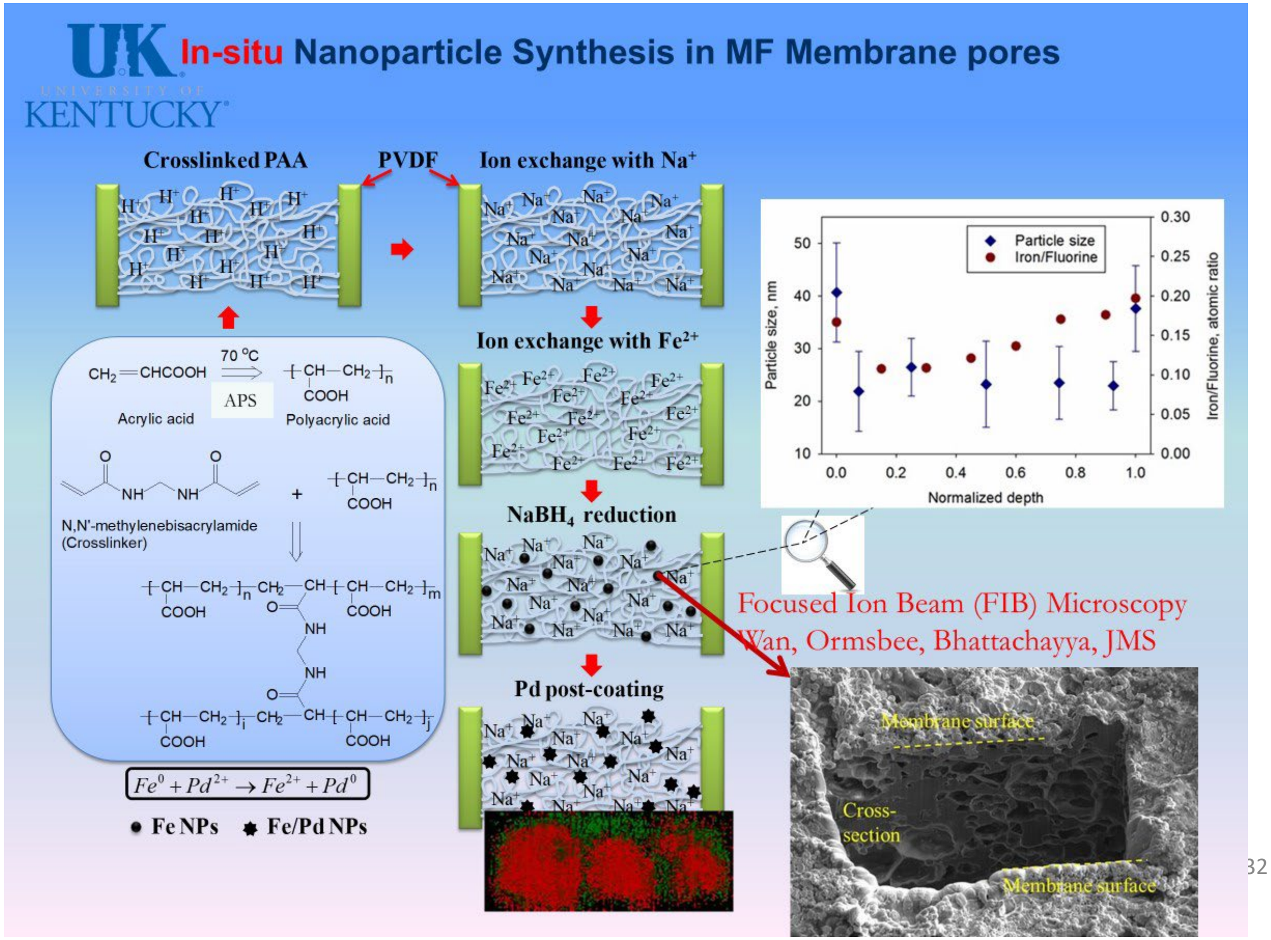
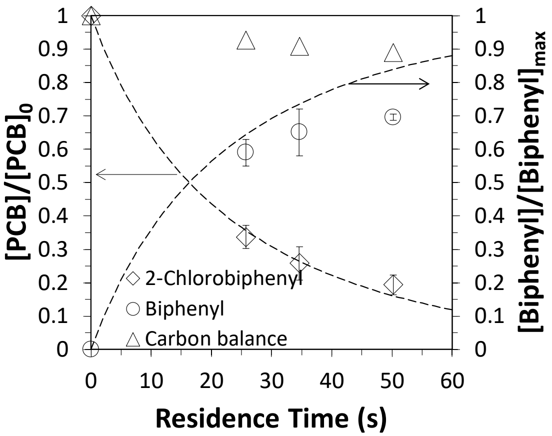


Figure 4. PFOA removal and hydrodefluorination rates catalyzed by monometallic Pd or Rh and by bimetallic Pd−Rh with different metal molar ratios at pH 7. Zero-order rate coefficients for hydro-defluorination rate are in units of μM/h. First-order rate coefficients for PFOA removal rate are in units of h−1. Specific hydro-defluorination ratios are in the unit of %.

One can use MF membrane pores to synthesize highly controlled size Nanocatalysts for halorganic hydrogenation





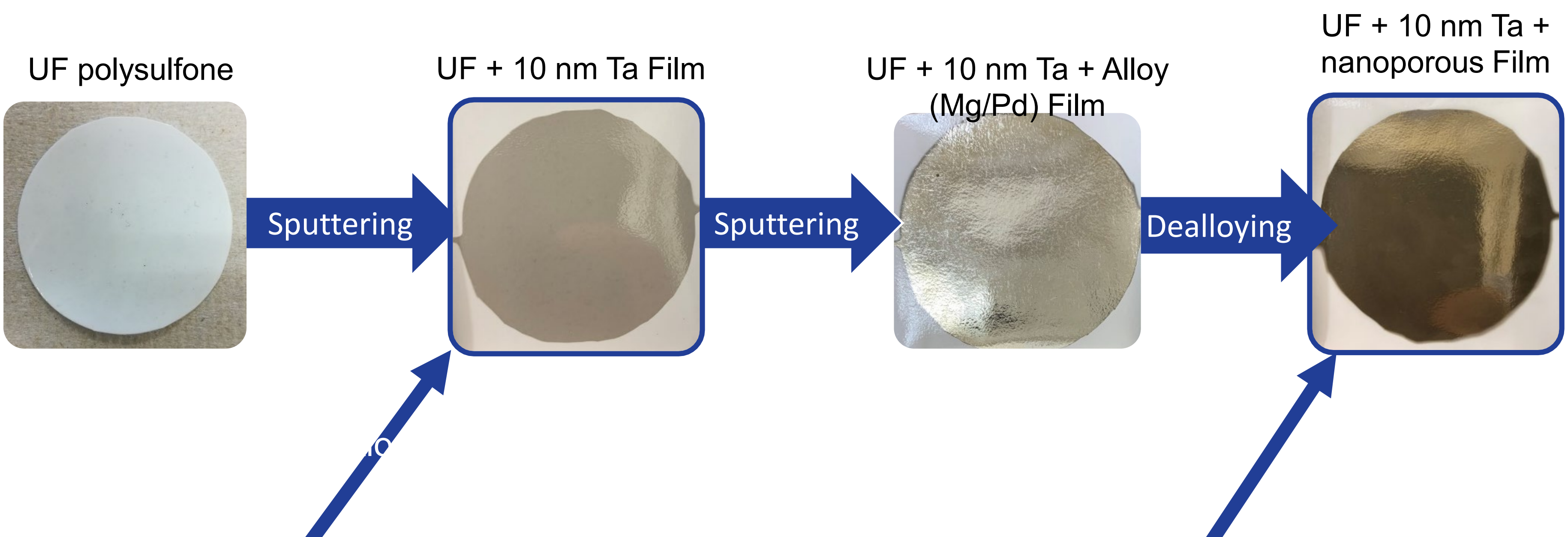
Gui, et al, JMS (2015); Hernandez, et al ACS journal on Sustainable Chemistry and Engineering (2016); Wan, et al, JMS (2020); Saad, et al, IEC Res (2020)

Magnetron Sputtered Nanostructured Metal Thin Films on UF membranes for Separations and Catalysis

Detisch, Bhattacharyya, et al ,
J. Materials Res (2021)

- addition of a thin metallic film top layer will modify separations capability of the resulting composite membranes, of value for separations in organic solvents or other harsh conditions.
- dealloying may be used to generate a nanoporous structured metal film for catalysis applications such as dechlorination in water treatment.

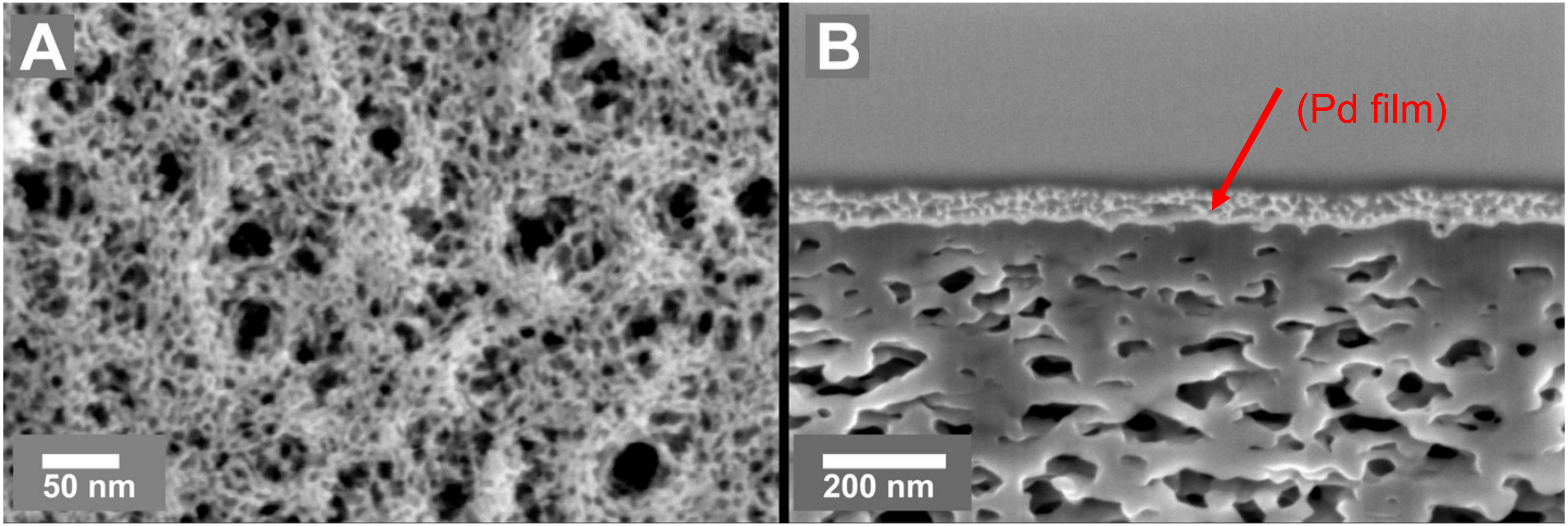
- UF PSf (Solecta PS 35) membrane used as substrate
- 10 nm Ta (about 1.5 min dep time) interlayer deposited
- Thickness can be controlled by deposition time
- 10 W RF bias applied during deposition
- 2.5 mtorr working pressure for deposition
- 100 nm deposited thickness 75/25 at. % Mg/Pd
- Post Mg leaching by water



Added separations properties

separations and catalytic properties

Nanoporous Pd Composite Catalytic Membrane



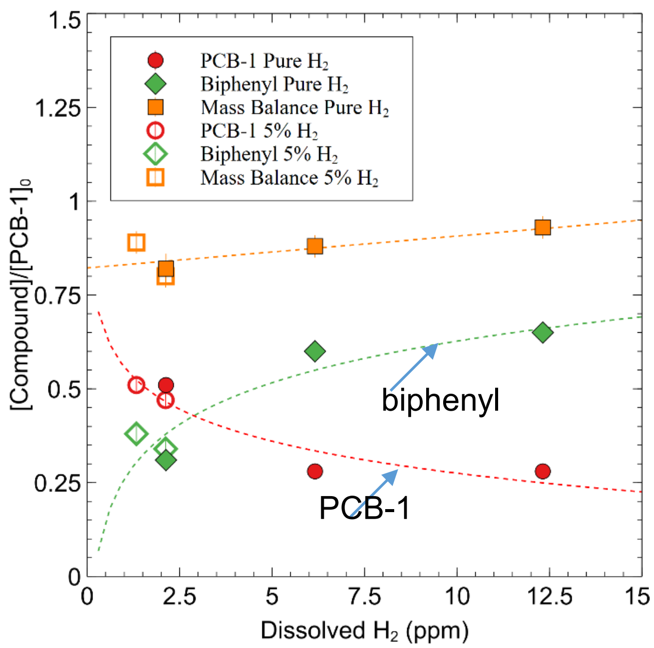
(A) Plan view of UF PSf + 10 nm Ta + 60 nm nanoporous Pd (npMTFC).
(B) Cross-section of npMTFC composite.

As-dealloyed Pd Composition: < 5 at. % Mg
Thickness reduced to 60 nm (bimodal pore distribution)
Average ligament size of 4.1 ± 0.9 nm

PCB-1 Dechlorination under convective flow using porous Pd film on UF Membrane

- npMTFC composite membranes were used in dead-end cells for dechlorination of PCB-1.
- The headspace was pressurized with H_2 at various pressures, resulting in various dissolved H_2 concentrations, and different residence times.
- A 95/5 Ar/H_2 mixture of gasses was also used for pressurization.
- H_2 concentration and residence time both depend on pressure and have opposite effects on PCB-1 dechlorination.

$$H^{cp}p = c_a$$



Some Key take away messages

- RO vs NF membrane, how to select
- Research needs in improving PFAS rejections
- Lower volume retentate for PFAS detoxification
- What about responsive and functionalized membranes? GAC won't do
- Both hydrophobic (possible temp responsive polymers) and Ion exchange domain in loose membranes
- Detoxify (Possible hydrogenation) the lower volume regenerant
- Role of other matrix in water (including other chloro-organics, such as TCE, PCB, NOM, etc.
- Need for hybrid technologies

Acknowledgement

- NIH-NIEHS –SRC program
- NSF- EPSCoR program; NSF-EAGER
- NSF RAPID
- Southern Co. ;ATMUS Corp; Chevron Corp
- **Dr. Scott Lewis, Dr. S. Hernandez, Dr. Doug Davenport, Dr. Xiao, Dr. Gui, Dr. Colburn, Dr. Sikdar (US EPA), Ben Weaver, Solecta Membranes, Dr. Evan Hatakyama, Chevron co, Dr. Chunqing Liu (Honeywell)**

NIH-NIEHS-SRC