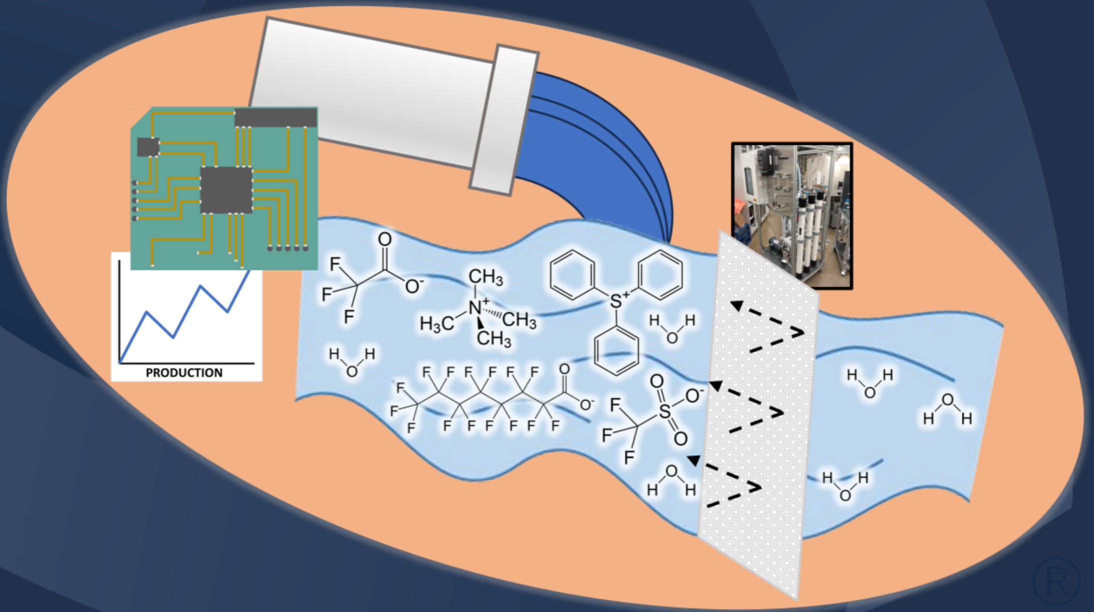
Use of High-Pressure Membranes for the Industrial Pretreatment of PFAS in Semiconductor Wastewater

6/6/24

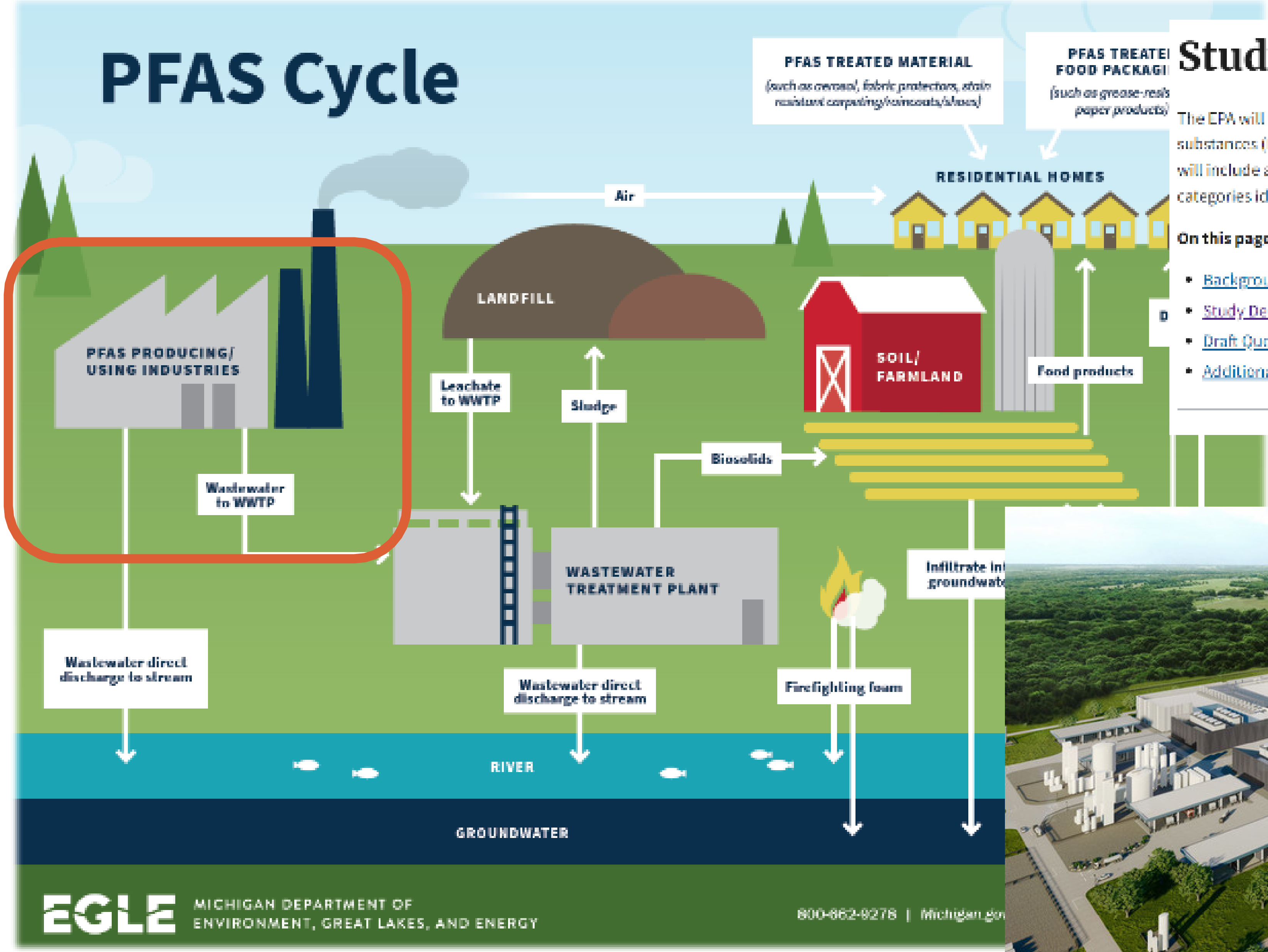
Aron Griffin, Chris Bellona, Timm Strathmann

Civil and Environmental Engineering



Outline

1. Semiconductor Manufacturing (FAB) Background
2. Membrane treatment of FAB Wastewater
3. Ultrashort PFAS Rejection Evaluation



Study of PFAS Influent to POTWs

The EPA will collect nationwide data on industrial discharges of per- and polyfluoralkyl substances (PFAS) to publicly owned treatment works (POTWs). The **POTW Influent PFAS Study** will include analysis of indirect discharges from categories recently reviewed by the agency and categories identified as discharging PFAS, but for which insufficient monitoring data exist.

On this page:

- Background
- Study Design
- Draft Questionnaire
- Additional Information

The New York Times

Micron Pledges Up to $100 Billion for Semiconductor Factory in New York

The company is planning a giant complex in Clay, N.Y., a sign that the government's investments in semiconductors are steering firms' decisions.

Administration Priorities The Record

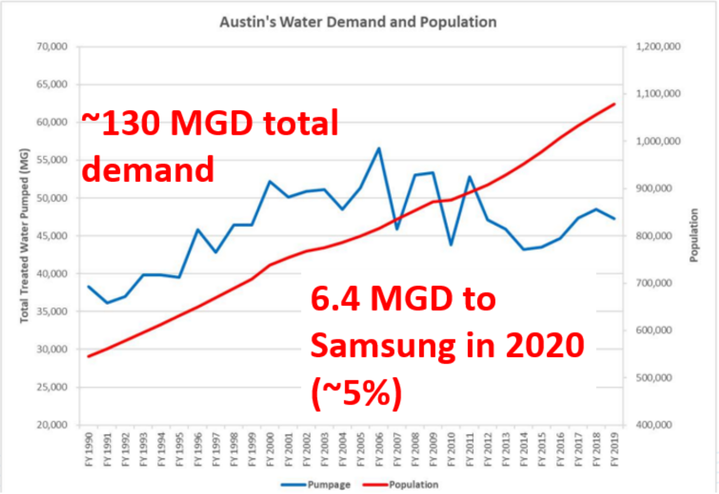
APRIL 25, 2024

FACT SHEET: President Biden Announces up to $6.1 Billion Preliminary Agreement with Micron under the CHIPS and Science Act

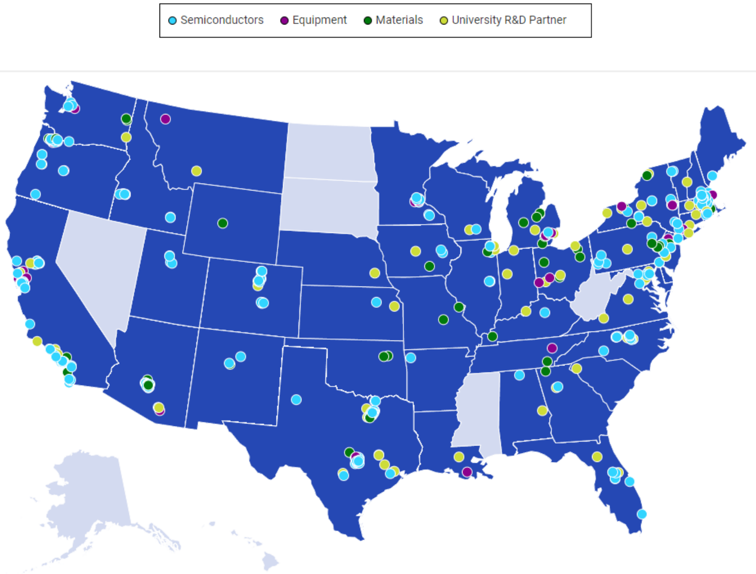
What does Micron's estimated 48 million gallons of water per day mean?

WRVO | By Ava Pukatch
Published August 17, 2023 at 5:17 AM EDT

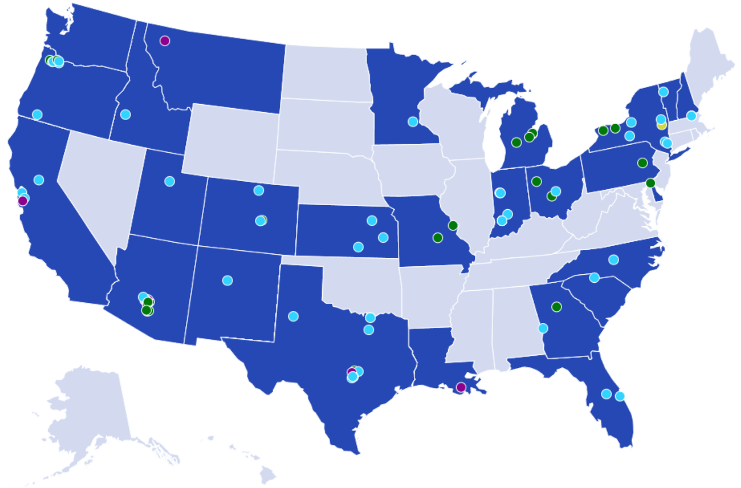
FABs require significant water resources



Current facilities



New or expanded



https://www.semiconductors.org/u-s-semiconductor-ecosystem-map/

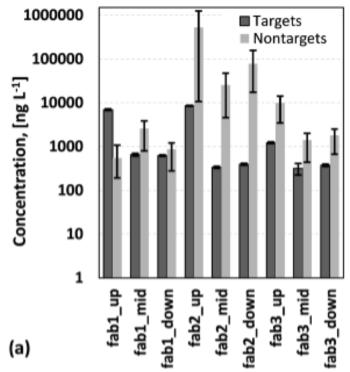
FAB wastewater contains a variety of PFAS

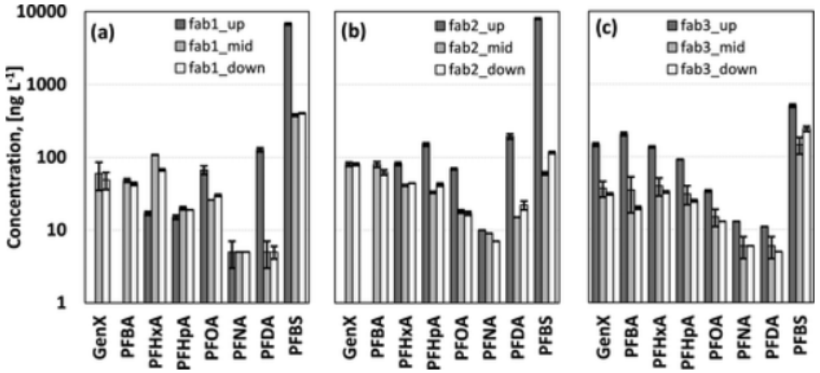
Environmental Science & Technology
pubs.acs.org/est Article

Target and Nontarget Analysis of Per- and Polyfluoroalkyl Substances in Wastewater from Electronics Fabrication Facilities

Paige Jacob, Krista A. Barzen-Hanson, and Damian E. Helbling*

Cite This: Environ. Sci. Technol. 2021, 55, 2346–2356 Read Online





ACS ES&T Water
pubs.acs.org/estwater Article

Rapid and Simultaneous Quantification of Short- and Ultrashort-Chain Perfluoroalkyl Substances in Water and Wastewater

Paige Jacob and Damian E. Helbling*

Cite This: ACS EST Water 2023, 3, 118–128 Read Online

Table 3. Average and Standard Deviations of PFAS Concentrations (ng L^{-1}) in Industrial and Commercial Water Samples

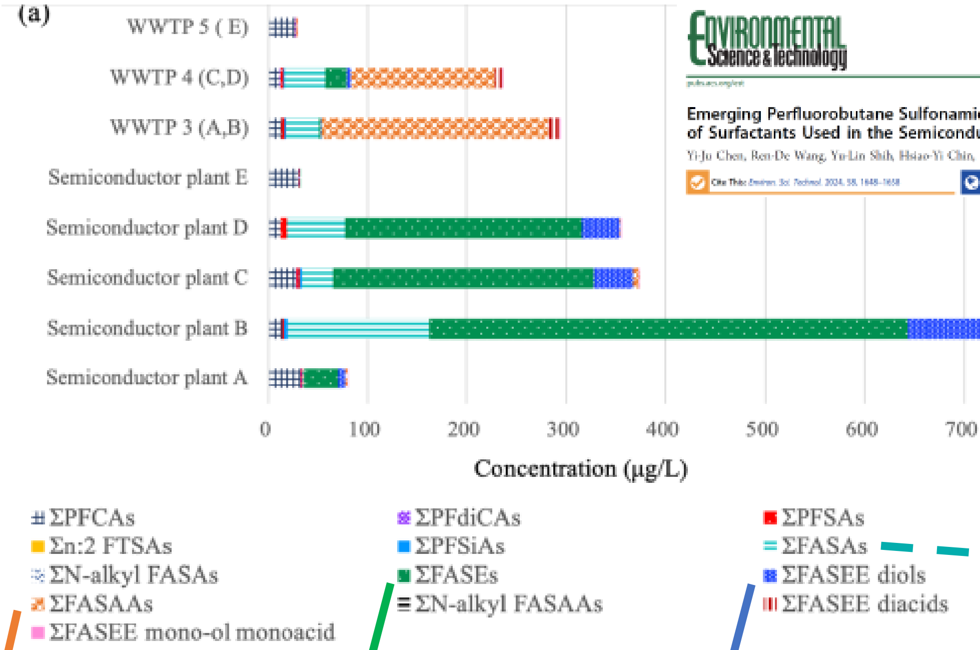
	TFA	PFPrA	PFBA	PFPeA	PFHxA	TFMS	PFEtS[c]	PFPrS	PFBS	PFPeS	PFHxS
Fab 1 WW	4133 ± 166	1125 ± 138	937 ± 58	124 ± 0	145 ± 4	173 ± 101	33 ± 2	ND	70 ± 15	ND	ND
Fab 2 WW	1571 ± 40	237 ± 34	214 ± 8	35 ± 1	46 ± 3	175 ± 9	0.4 ± 0.1	9 ± 0	108 ± 5	ND	ND
Fab 3 WW	15280 ± 78	4184 ± 183	2645 ± 261	394 ± 24	348 ± 25	121 ± 15	4 ± 1	ND	160 ± 9	ND	<LOQ

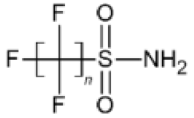
Environmental Science & Technology
pubs.acs.org/est Article

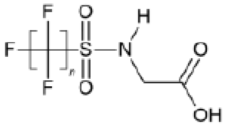
Emerging Perfluorobutane Sulfonamido Derivatives as a New Trend of Surfactants Used in the Semiconductor Industry

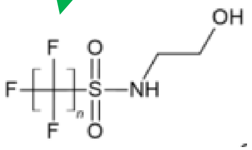
Yi-Ju Chen, Ren-De Wang, Yu-Lin Shih, Hsiao-Yi Chin, and Angela Yu-Chen Lin*

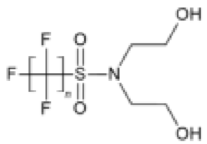
Cite This: Environ. Sci. Technol. 2024, 58, 1648–1658 Read Online





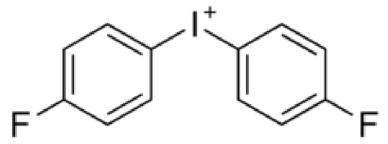




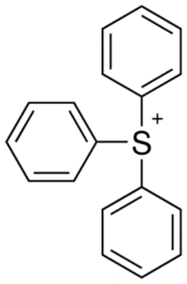


More than just PFAS is present!

Photoacid generating compounds (PAGs)

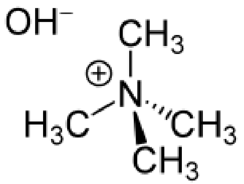


Diaryliodonium (DIA)



Triphenylsulfonium (TPS)

Organic Bases



Tetramethylammonium hydroxide (TMAH)

Also…

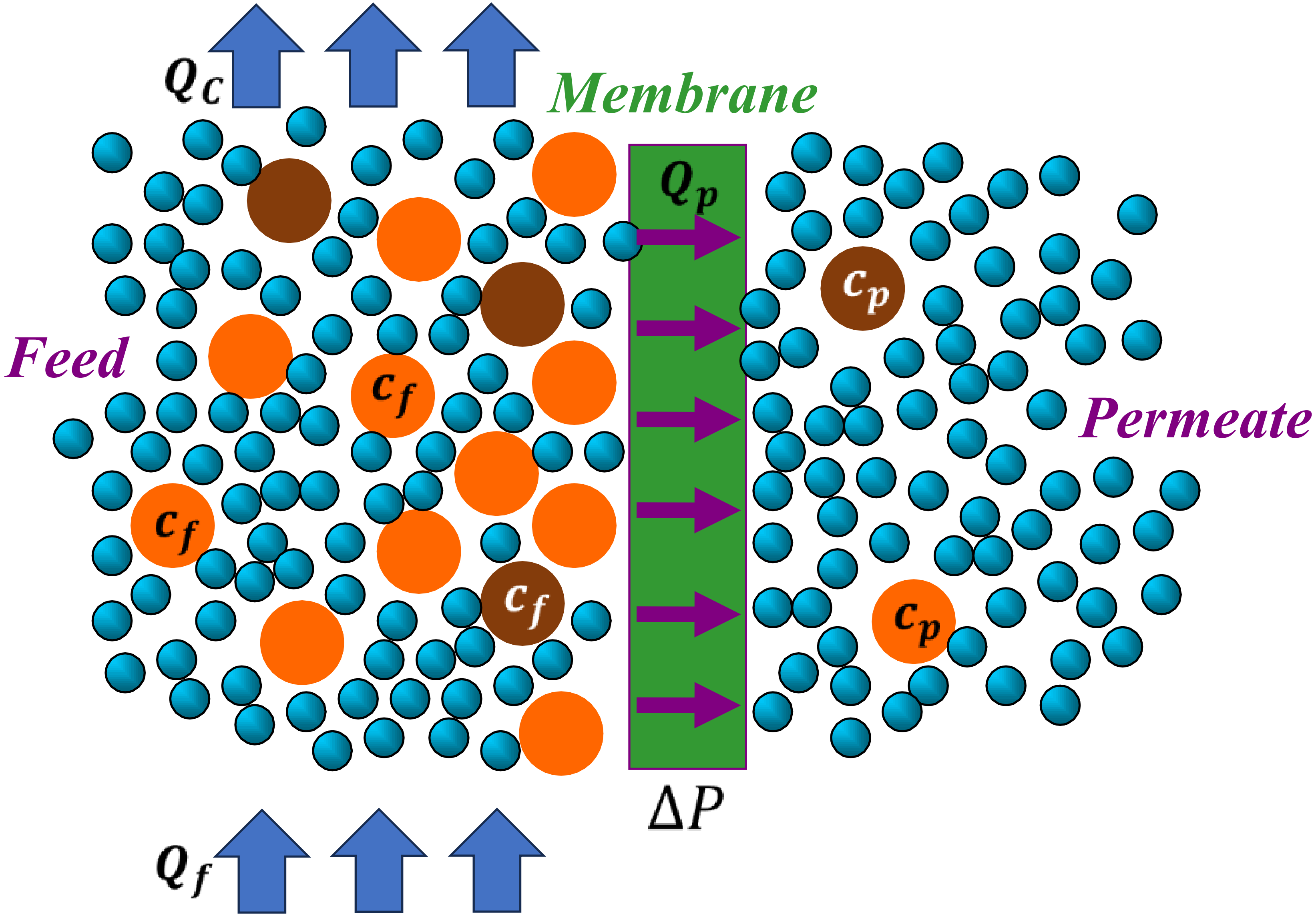
- High MW polymers
- Hydrogen peroxide
- Ammonium
- Metal nanoparticles
- Surface active organics
- Elevated TOC

Complicates treatment!!

1. Semiconductor Manufacturing (FAB) Wastewater

   FAB wastewater contains varied PFAS in a complex matrix

2. Membrane treatment of FAB Wastewater



Performance metrics

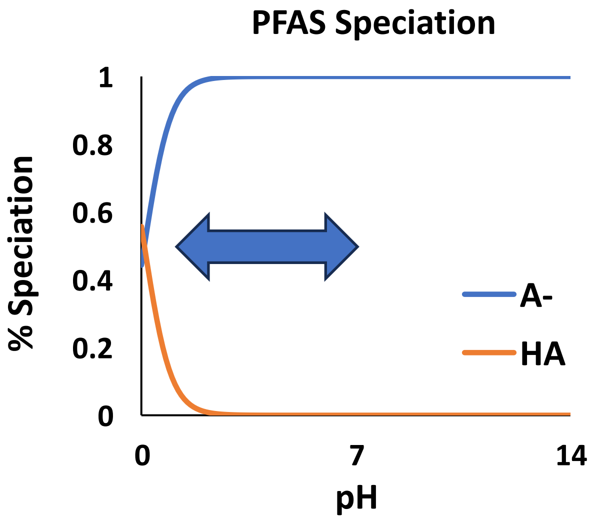
$$Rejection = \left(1 - \frac{c_p}{c_f}\right) * 100$$

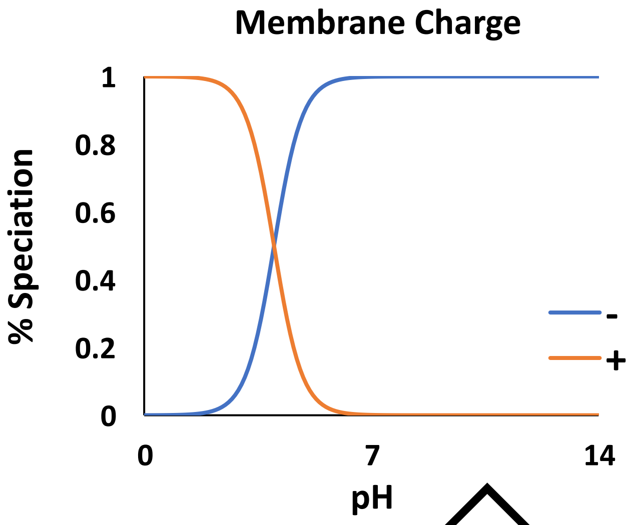
$$Recovery = \frac{Q_p}{Q_f} * 100$$

PFASs (solute) *Water (solvent)* *Co-contaminant (solute)*

Rejection Mechanisms

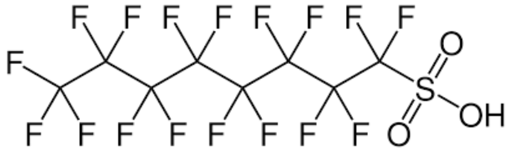
Electrostatic





Steric

Rs ≈ MW (g/mol)



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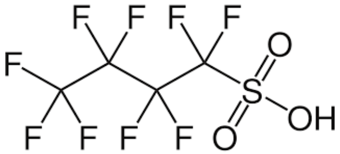

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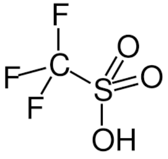

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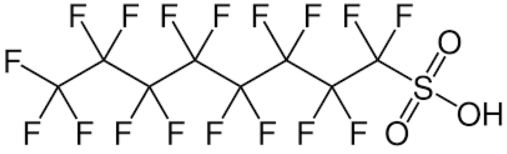
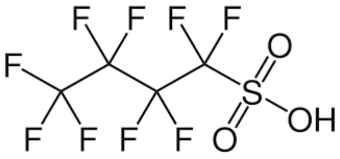
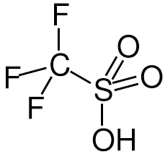
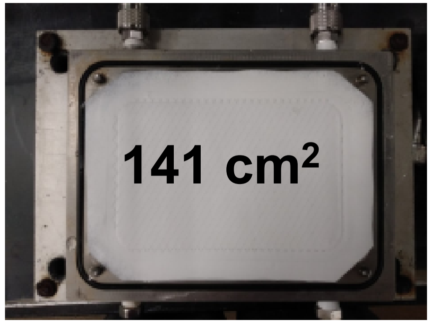
Compound-Membrane

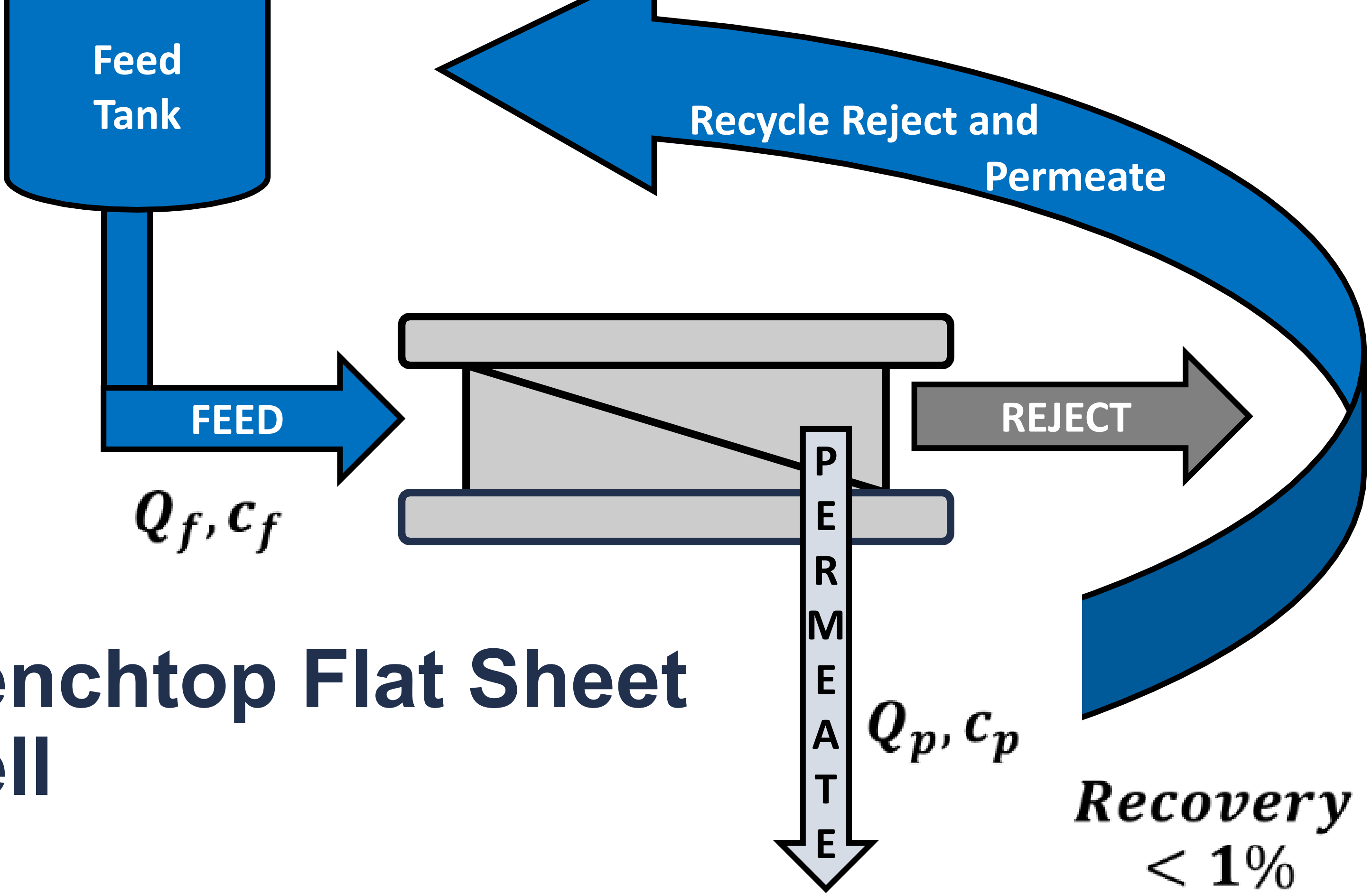






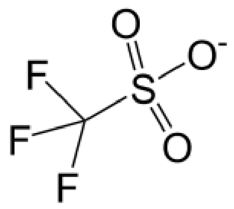
PARTITIONING



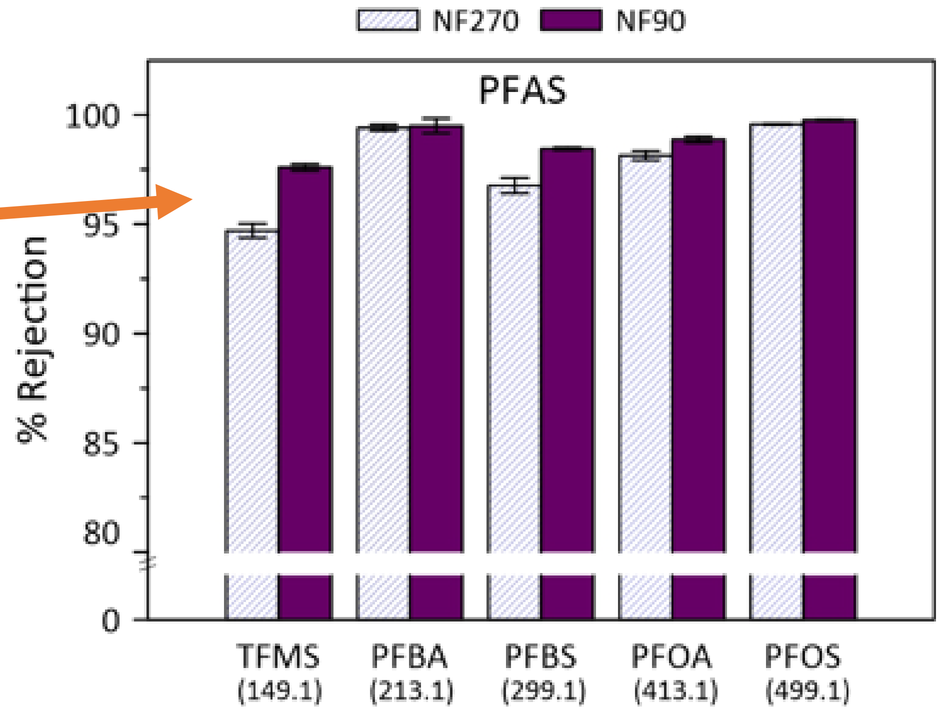


Benchtop Flat Sheet Cell

“Tight” NF membrane performed well for all PFAS compounds evaluated on bench system



Ultrashort trifluoromethane sulfonic acid (TFMS)

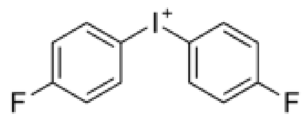


- Increasing rejection with chain length
- Anionic compounds → repulsion

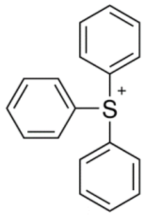
Electrostatic and compound-membrane interactions important for organic co-contaminant rejection

Fab Contaminants
(cations)

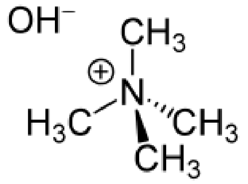
DIA

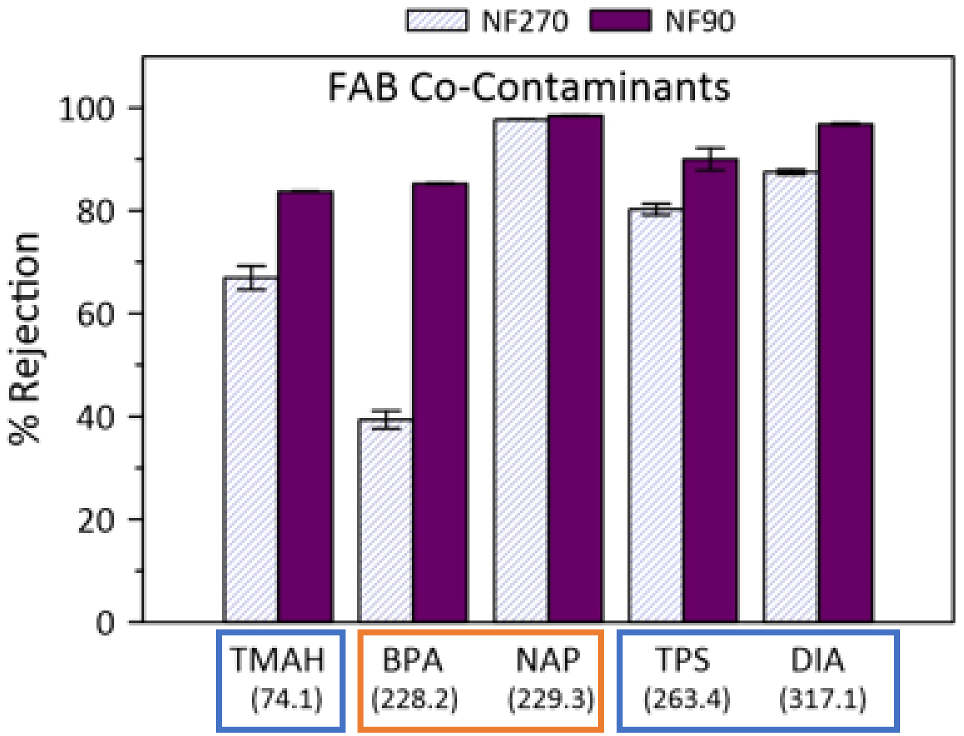


TPS



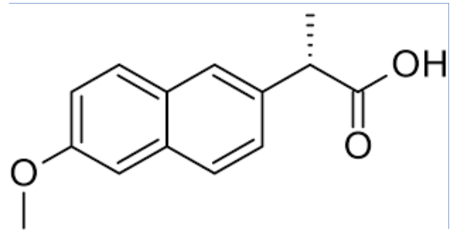
TMAH



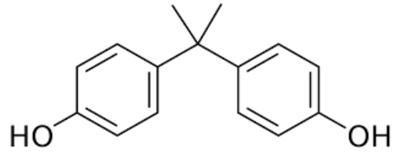


Charge Investigation (surrogates)

Naproxen (NAP)
Anion

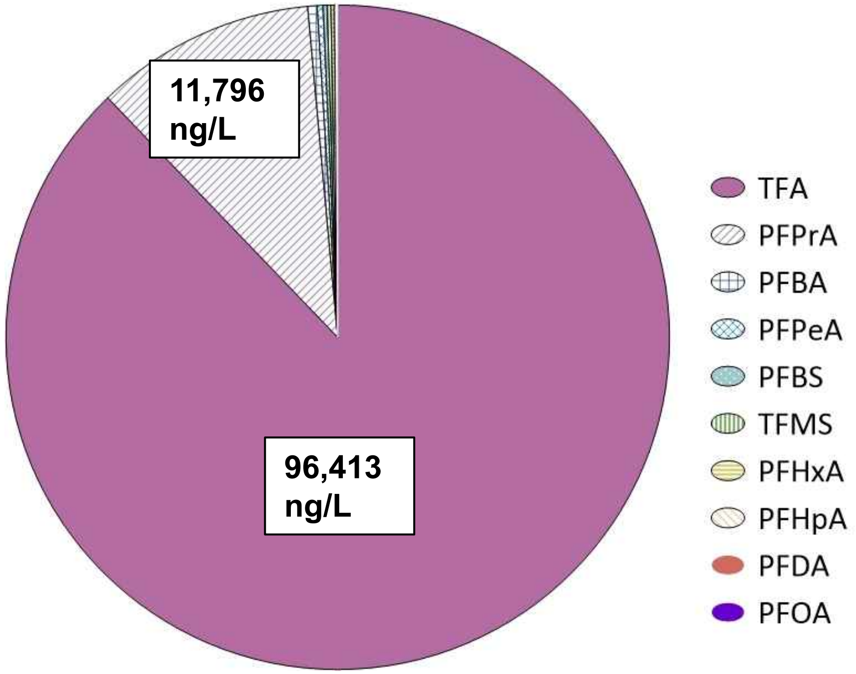


Bisphenol-A (BPA)
neutral



Collected FAB wastewater contained high concentrations of ultrashort PFCAs

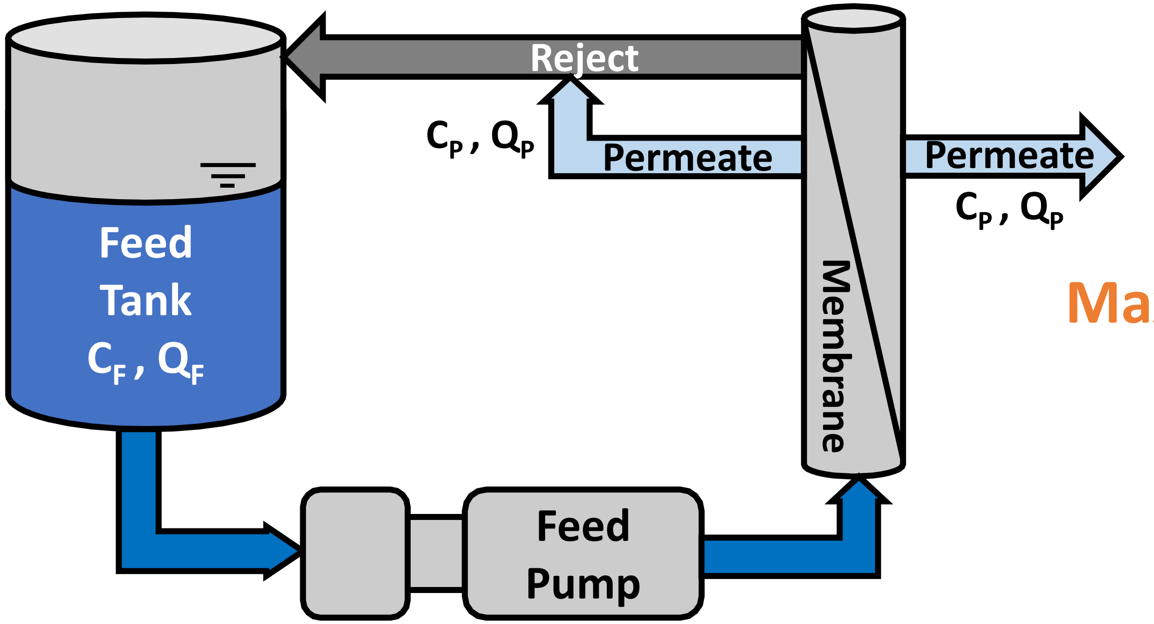
Category	Compound	Concentration
PFAS	TFMS	202 ng/L
	TFA	96,413 ng/L
	PFPrA	11,796 ng/L
	PFBA	504 ng/L
	PFBS	**213 ng/L**
	PFPeA	310 ng/L
	PFHxA	178 ng/L
	PFHpA	85 ng/L
	PFOA	**38.0 ng/L**
	PFNA	**17.2 ng/L**
	PFDA	57.3 ng/L
Water Quality	pH	6.9
	Conductivity	2,000 mS/cm
	Fl^-	121 mg/L
	Cl^-	24.5 mg/L
	NO_3^-	15.9 mg/L
	PO_4^{3-}	19.2 mg/L
	SO_4^{2-}	766 mg/L
	TOC	8.7 mg/L
	TN	93.4 mg/L



NF90 pilot system used in batch configuration to achieve 90% recovery

“Full Recycle”

“Semi Batch”



Maximize Water Recovery

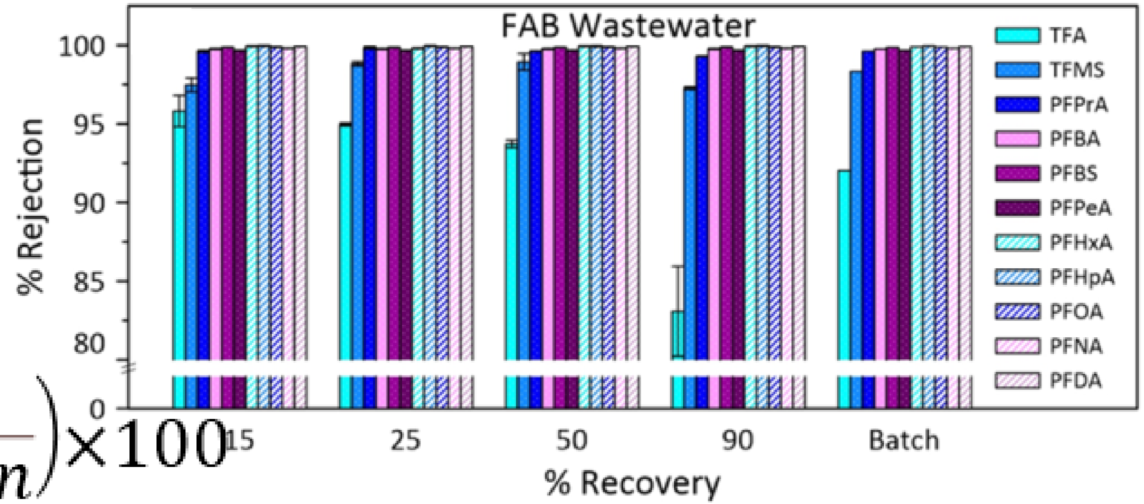
Constant Feed Conditions

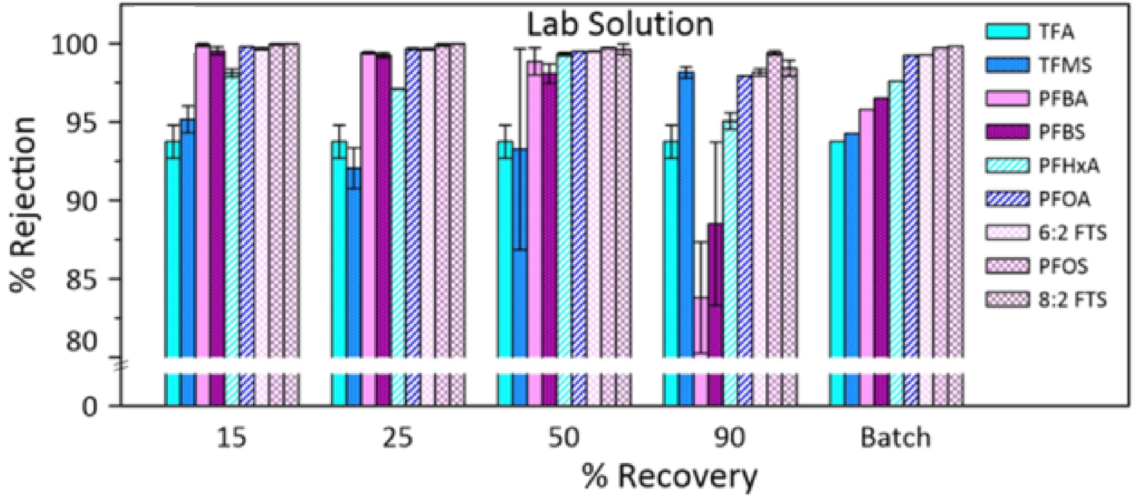
High rejection of PFAS at 90% recovery

- 92% and 98% batch rejection of ultrashort TFA and TFMS
- >99% rejection of all other compounds

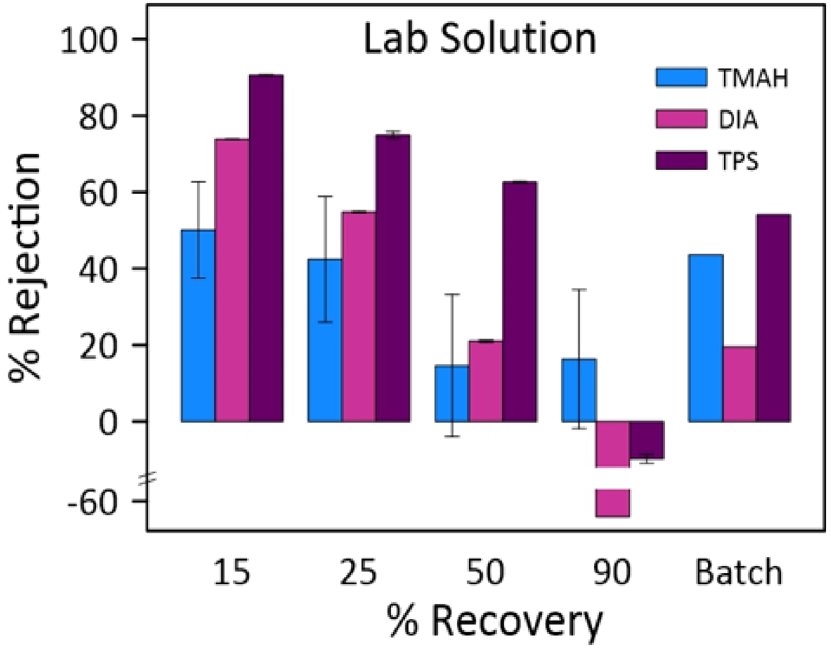
$$ction = \left(1 - \frac{permeate\,concentration}{original\,feed\,concentration}\right) \times 100$$

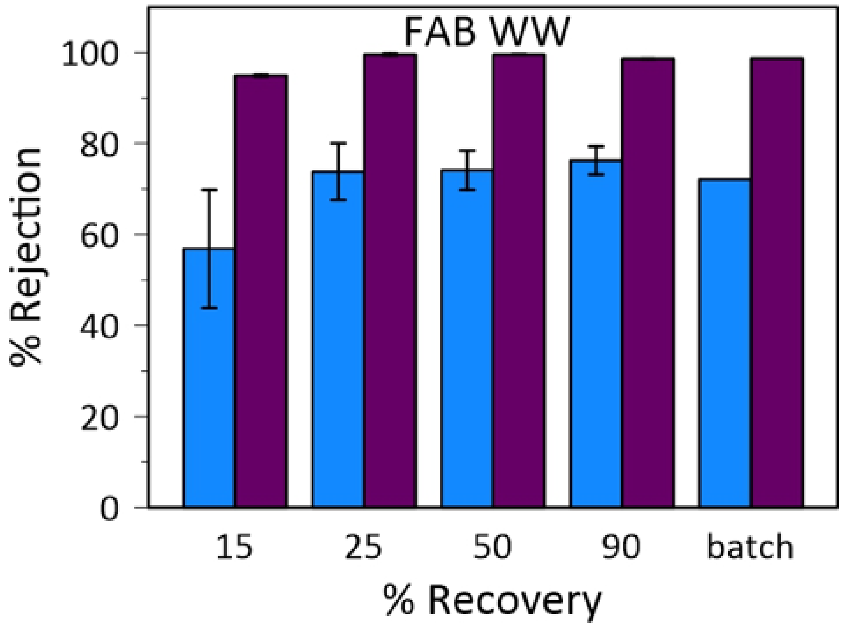
- Lower rejection in spiked DI water
- PFAS coordination with matrix constituents





Improved rejection of co-contaminants also observed





- "Negative" rejection observed in spiked DI water

- Decreased electrostatic attraction and compound-membrane interaction

1. Semiconductor Manufacturing (FAB) Wastewater
   FAB wastewater contains varied PFAS in a complex matrix

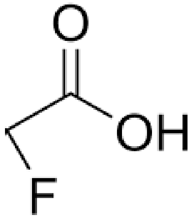
2. Membrane treatment of FAB Wastewater
   Membranes effective for removal of PFAS and co-contaminants

3. Ultrashort PFAS Rejection Evaluation

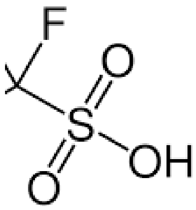
Flat sheet experimental conditions

Class	# Carbons	MW g/mol	pKa
Perfluorocarboxylic acids (PFCAs)	2, 3, 4, 8	113 - 413	<2
Perfluorosulfonic acids (PFSAs)	1, 2, 3, 4, 8	149 - 499	<1
Perfluorosulfonamides (FOSAs)	4	298	~6

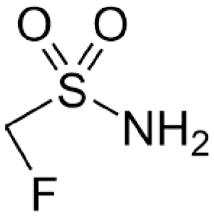
- As MW ↓, will rejection ↓?
- As pKa ↑, will rejection ↓?



PFCAs



PFSAs



FOSAs

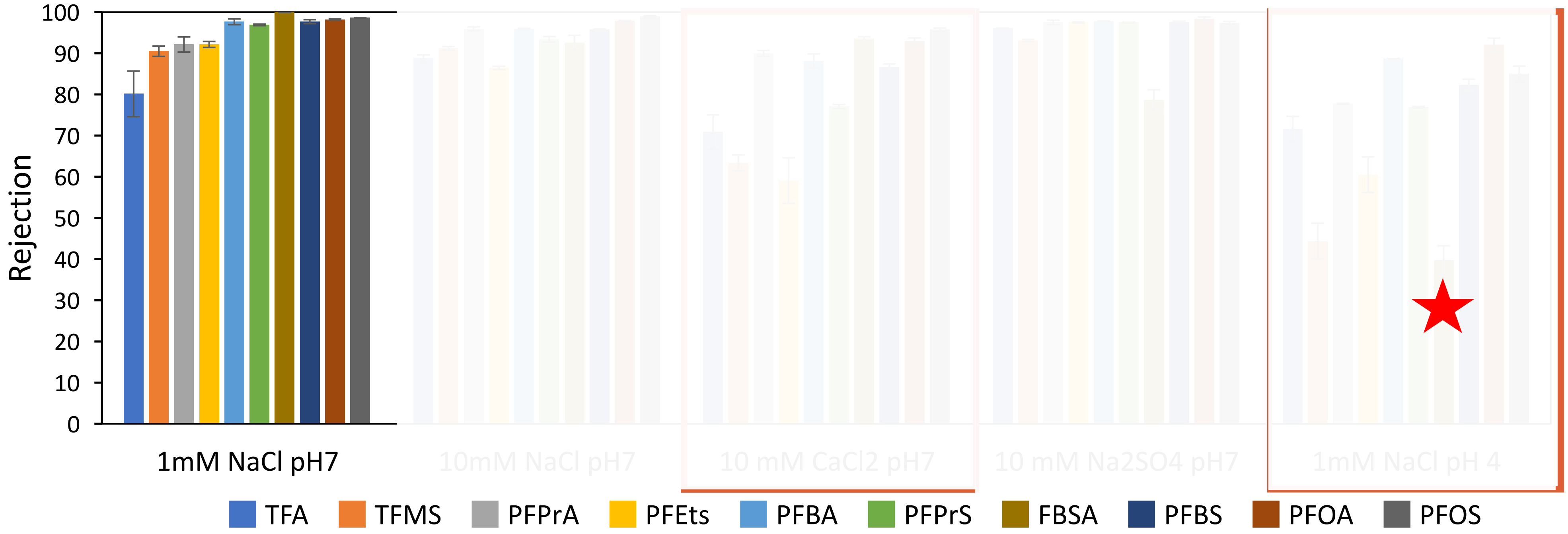
Background Electrolyte	pH	Ionic Strength mM
NaCl	4	1
	7	1
		10
$NaSO_4$	7	10
$CaCl_2$	7	10

- As pH ↓ will rejection ↓?
- Does ionic composition impact rejection?

Membranes Evaluated	Pore Size nm
NF270	0.36-0.44
NF90	0.29-0.39
BW30	NA?

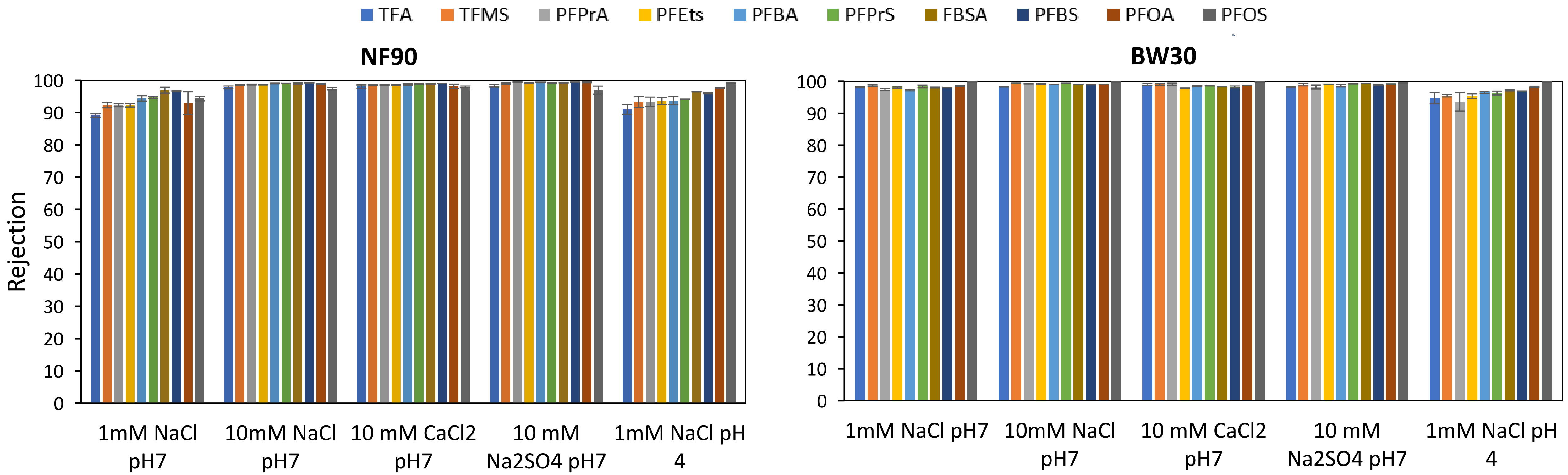
- Electrostatic vs steric interactions as pore size ↓

NF270 performance variable in different matrices



- Ca^{2+} and pH=4 may neutralize or reverse membrane charge and decrease electrostatic repulsion of anionic PFAS
- FBSA rejection impacted at low pH due to protonation of sulfonamide

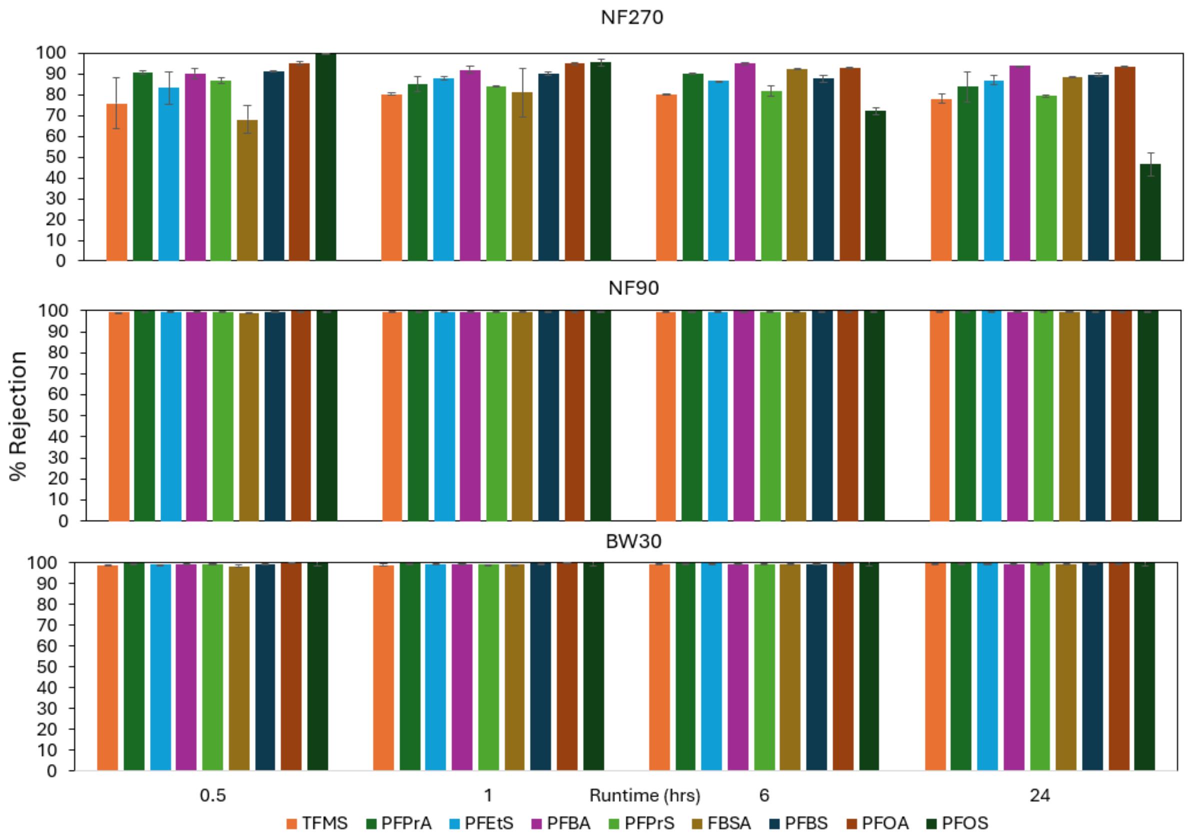
NF90 and BW30 provide more consistent rejection

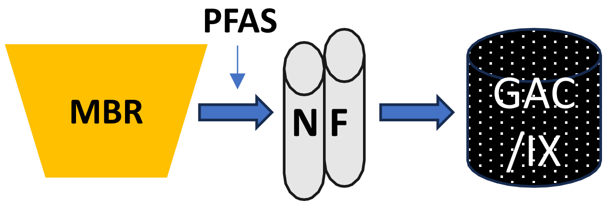


- Elevated rejection at higher ionic strengths
- Potential evidence of PFOS adsorption

- Chain length dependence only evident at pH 4 where electrostatic repulsion decreased

Similar rejection in spiked campus wastewater





- Prepping for long term demonstration at campus WWTP

Comparing multiple transport models

Pore Flow

$$J_i = -K_{i,d} D_{i,\infty} \frac{dc_i}{dx} + K_{i,a} c_i J_v + \frac{z_i c_i K_{i,d} D_{i,\infty} F}{RT} \frac{d\Phi(x)}{dx}$$

$$= \boldsymbol{Diffusion + Advection + Electromigration}$$

- Can account for PFAS charge
- Not suitable for complex matrices
- Using for flat sheet amended DI experiments

Phenomenological

$$J_s = -P \cdot \left(\frac{dc_s}{dx}\right) + J_v(1-\sigma)c_s$$

$$= \boldsymbol{Diffusion + Advection}$$

Solution Diffusion

$$J_s = \frac{D_s K_s}{l}\left(c_{i,0} - c_{i,\Delta x}\right)$$

$$= \boldsymbol{Diffusion}$$

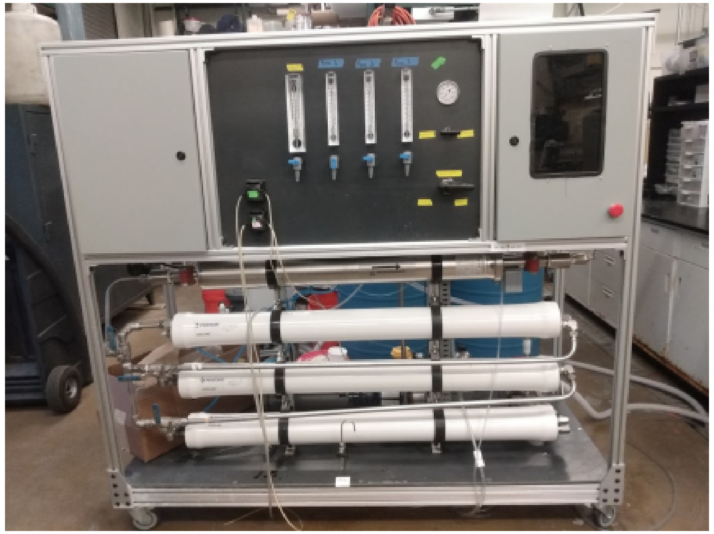
- No electromigration component
- Could also be applied to field studies

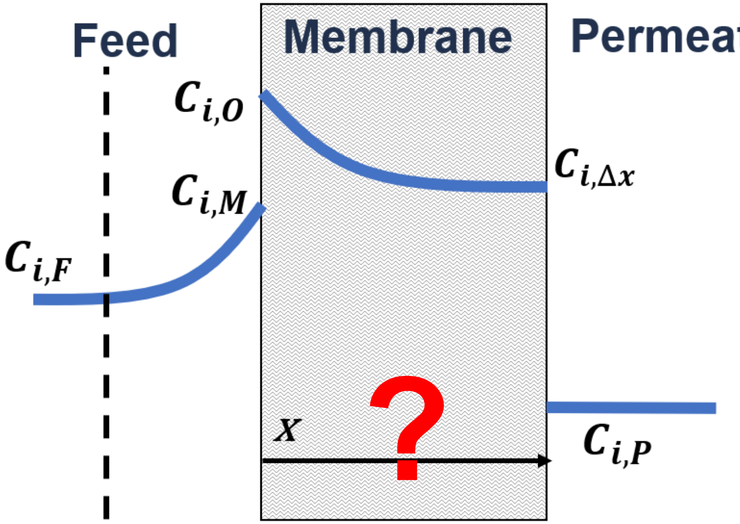
- Past organic micropollutant studies incorporated adsorption terms

Conclusions

- Membranes effective for industrial pre-treatment of FAB wastewater
- Able to remove of long, short, and ultrashort PFAS
- Electrostatic impacts important for loose NF membranes

Next Steps





Thank you!

Timm Strathmann

arongriffin@mines.edu

Chris Bellona

The Edna Bailey Sussman Fund

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American Membrane Technology Association
1973–2023 | 50 YEARS

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NATIONAL WATER RESEARCH INSTITUTE

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