Not-So-Forever Chemicals: Field Demonstration of PFAS Destruction by a Pilot-Scale Nanofiltration and UV-Sulfite Treatment Train

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Funding: Air Force Civil Engineering Center (AFCEC)

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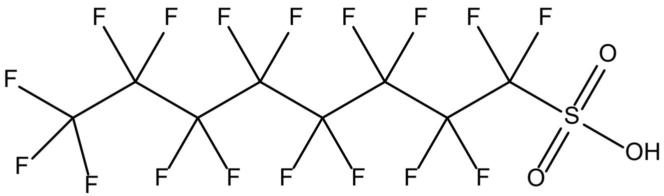
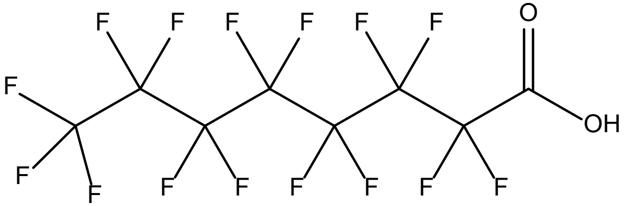
PFAS in the Water Cycle



PFOS

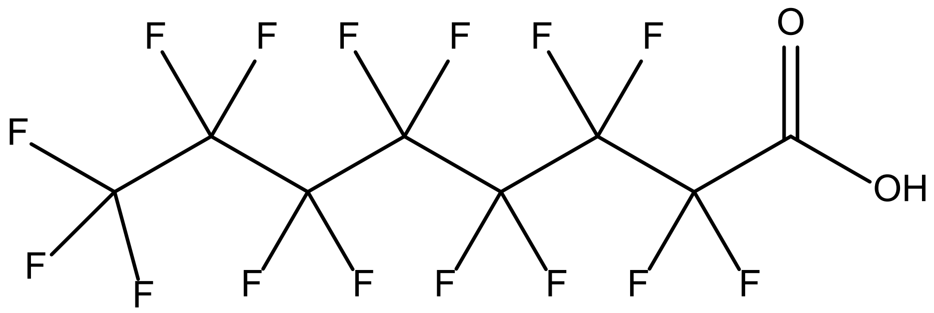
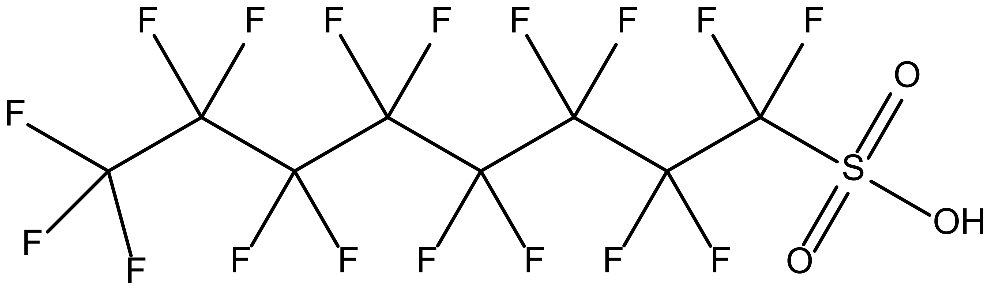


PFOA

Natural Degradation

Treatment Options for PFAS?

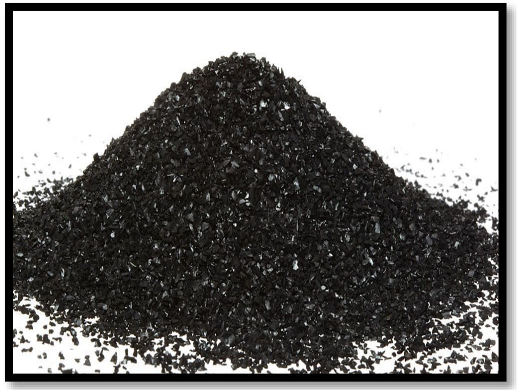
PFCAs versus PFSAs

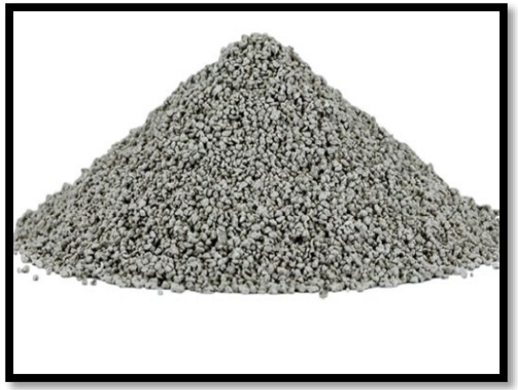
Perfluorocarboxylic Acids (PFCAs)	Perfluorosulfonic Acids (PFSAs)
	
PFOA (8)	PFOS (8)
+ other chain length PFCAs (e.g., PFHxA (6), PFBA (4))	+ other chain length PFSAs (e.g., PFHxS (6), PFBS (4))

Current PFAS Treatment Technologies

Adsorbents

GAC, IX, Emerging Adsorbents





Membranes

Reverse Osmosis (RO), Nanofiltration (NF)

Separation only, no destruction

Emerging PFAS Destruction Technologies

Reductive defluorination with hydrated electrons

UV_{254} + Sulfite → e_{aq}^{-}

Other treatment technologies undergoing research…

Supercritical Water Oxidation	Hydrothermal Liquefaction	Electrochemical Oxidation	Plasma

Treatment Conditions and Challenges For UV/Sulfite

- Existing UV reactors and lamps used for treatment; sodium sulfite easily accessible
- High energy requirements and long reaction time
- Requires a concentrated PFAS feed stream for more cost-effective degradation

Leveraging Technology Drawbacks in a Treatment Train

NF and RO Membranes

\+ Effective PFASs Rejection

− Disposal of PFAS in Brine Stream

UV – Sulfite

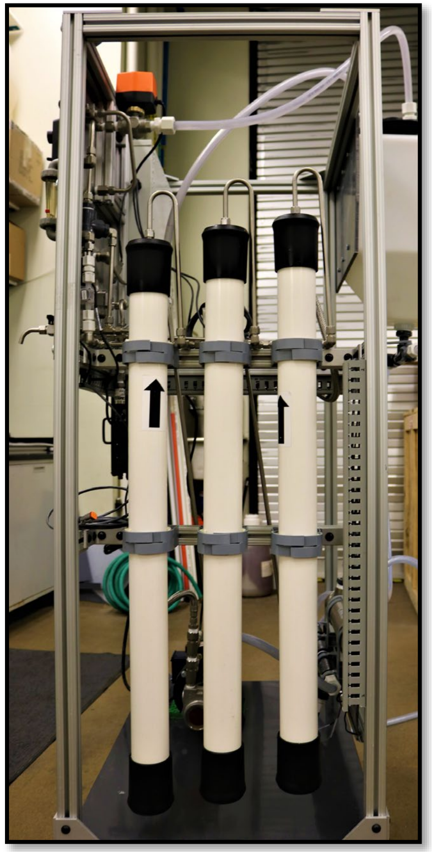
\+ PFAS Degradation, Accessible Implementation

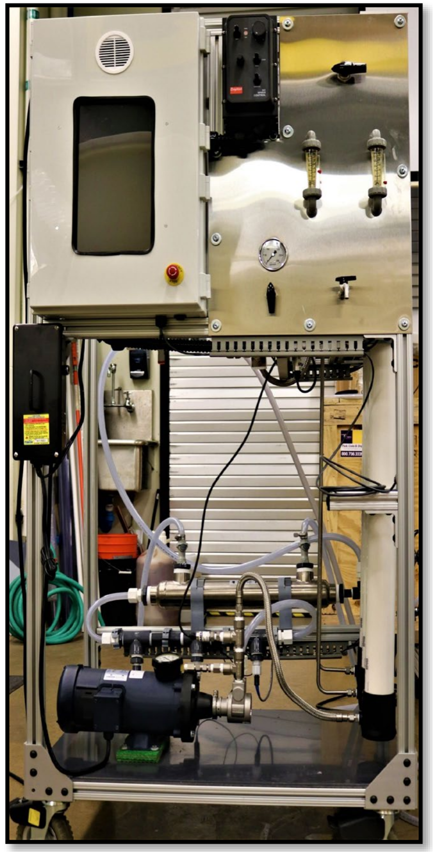
− Energy Intensive; Requires Concentrated PFAS Solution

Combined in a Treatment Train?

Combining Two Pilot-Scale Systems

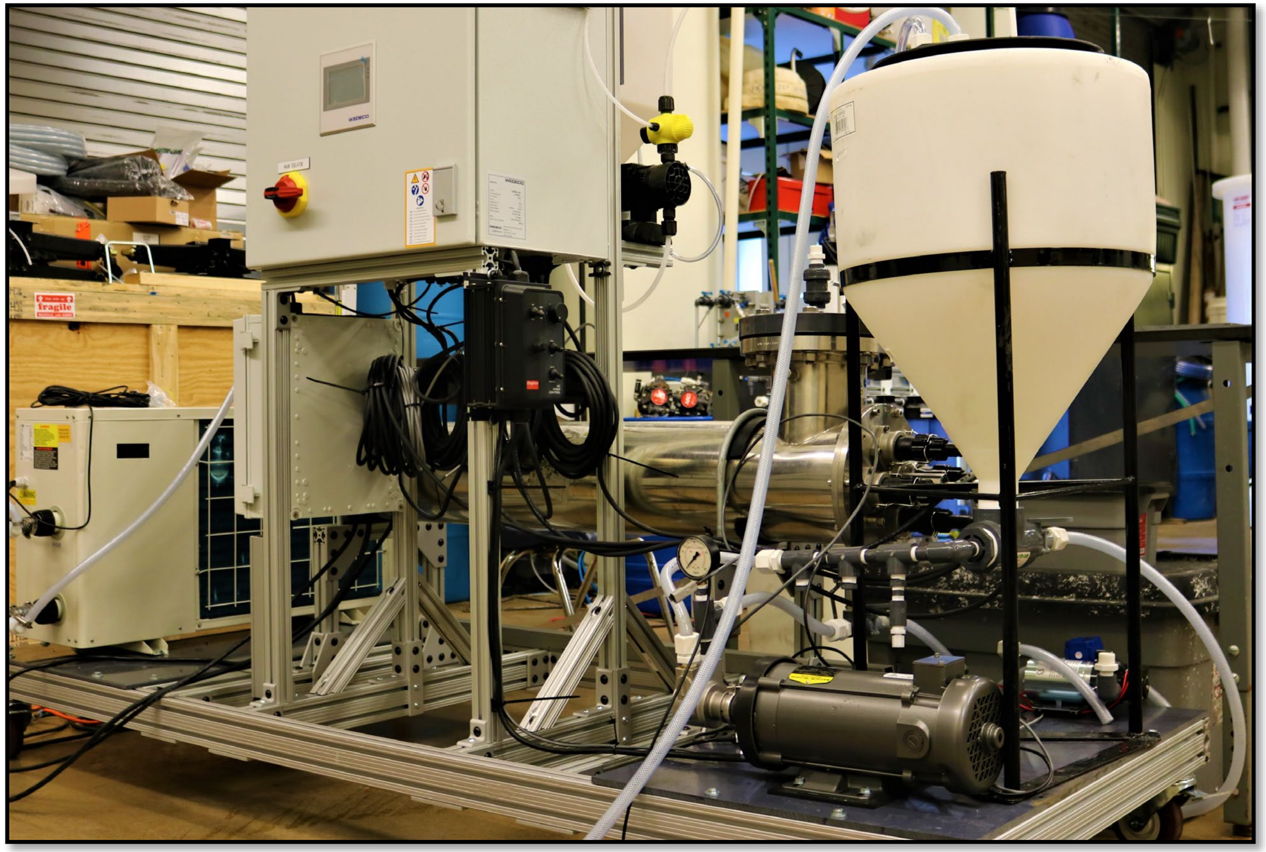
Membrane Pilot System





RO: Hydranautics ESPA
NF: DOW NF270 Membrane

UV Pilot System



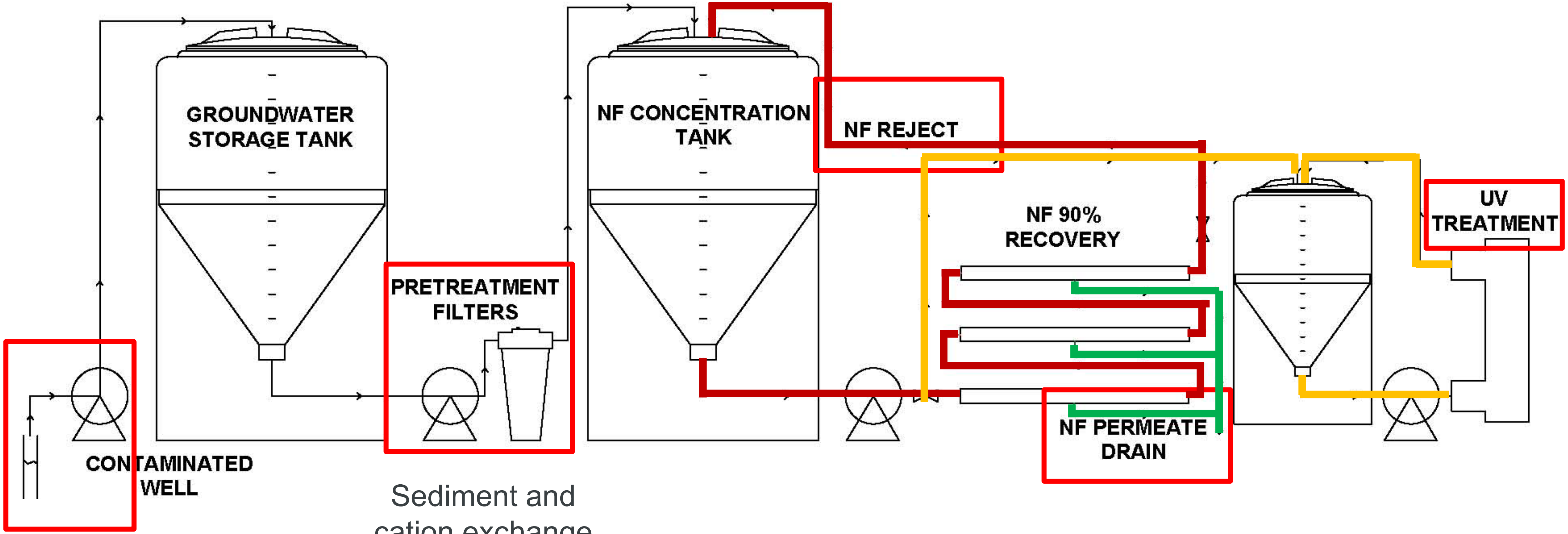
Xylem LBX90e
4x 330W LP hg lamps

Pilot System Deployment

Field deployment at a contaminated wellhead on a DoD site

Treatment Train Operation

~6 month field demonstration

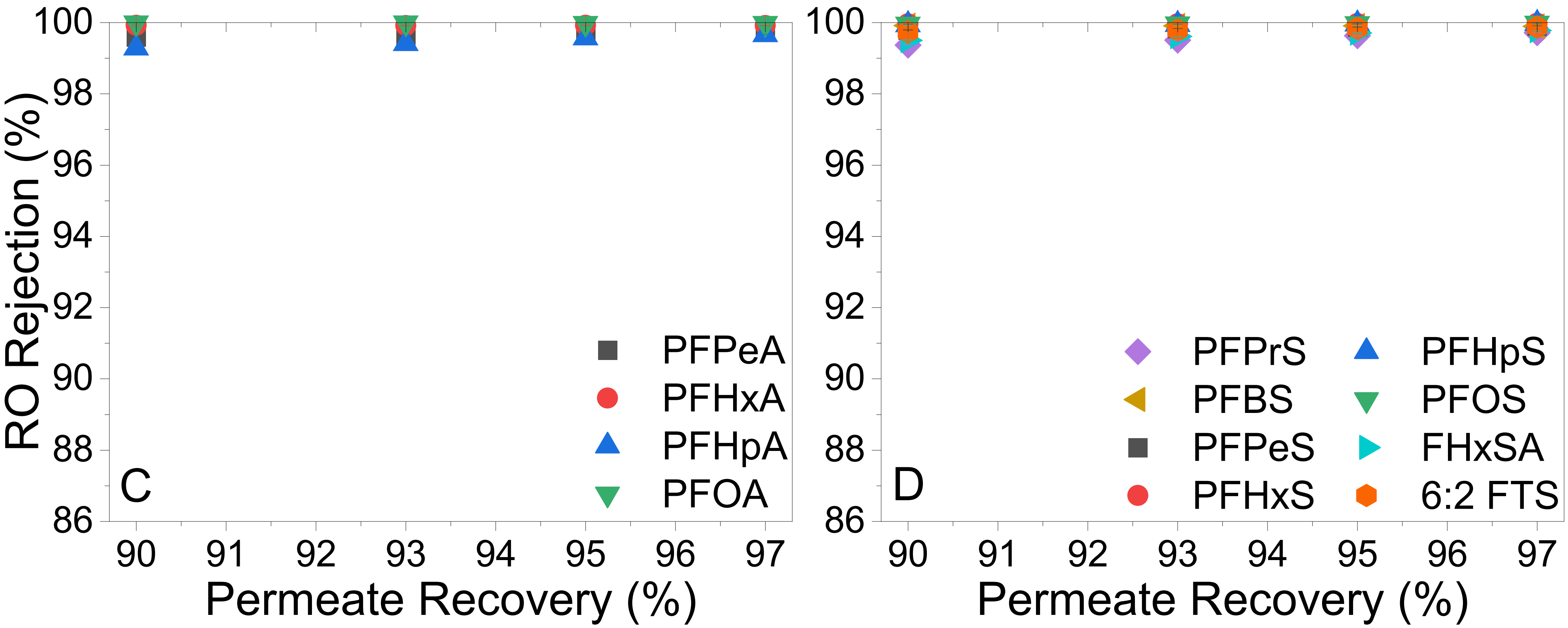


Sediment and cation exchange

Experimental Goals and Testing

1. Evaluate rejection of PFAS by NF and RO membranes
2. Assess destruction of PFAS by UV-sulfite in the membrane concentrate
3. Confirm long-term operation process stability

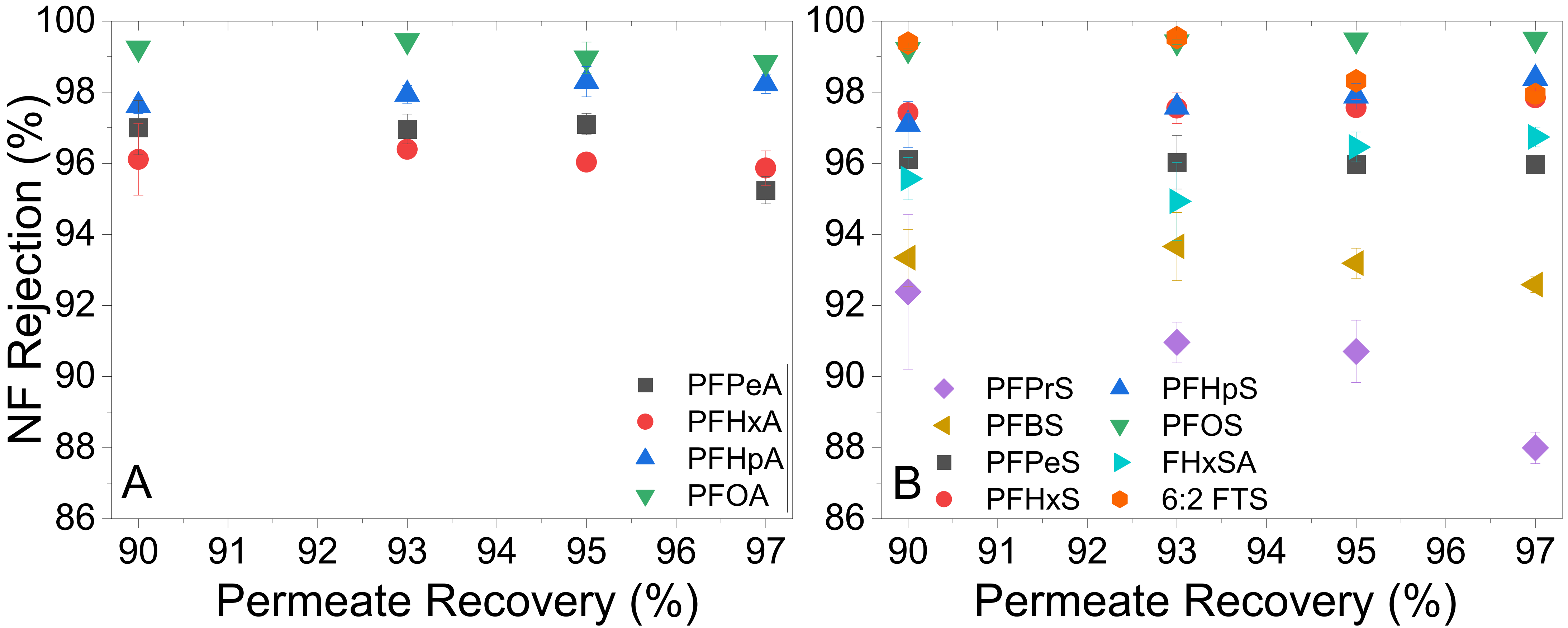
PFAS Rejection by RO Membranes



✓ RO rejected all PFAS to > 99%

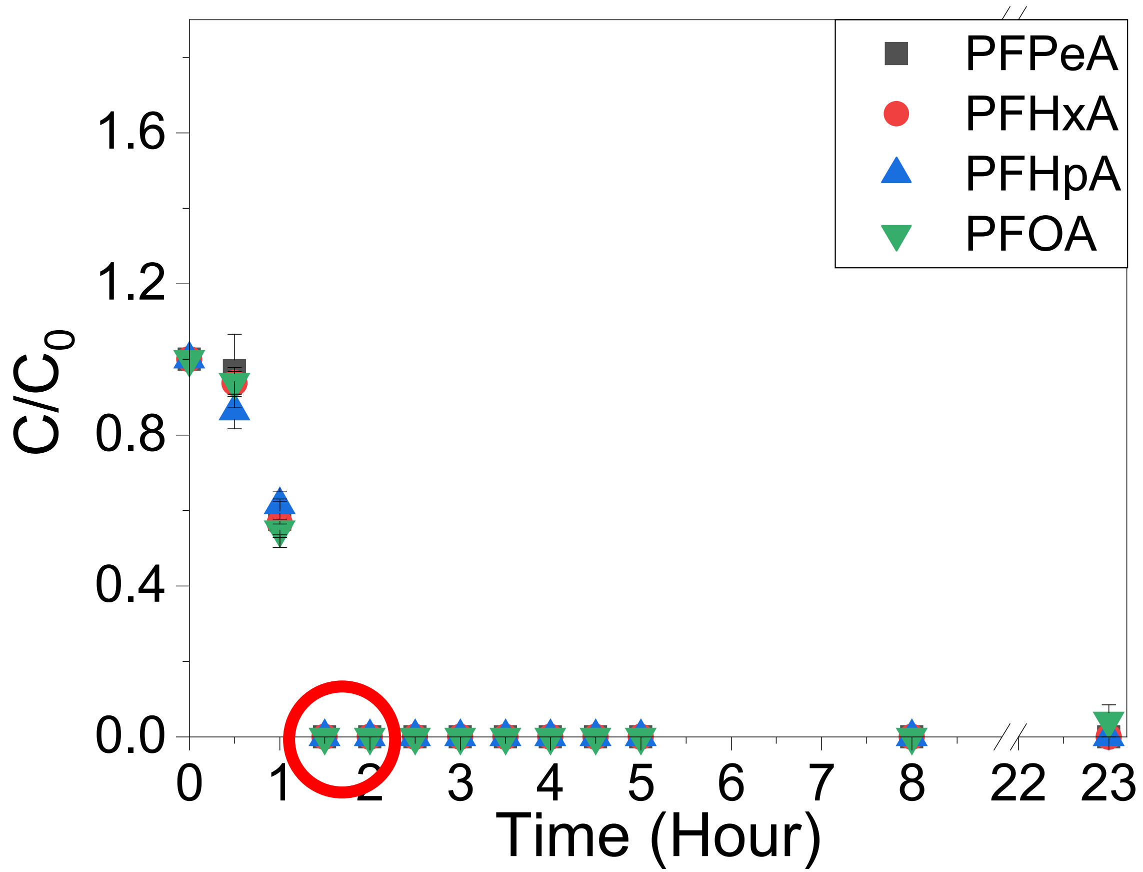
✓ No discernable influence of chain length and recovery on rejection

PFAS Rejection by NF Membranes



✓ Better rejection of longer chain PFAS
✓ Lower rejection at higher recovery

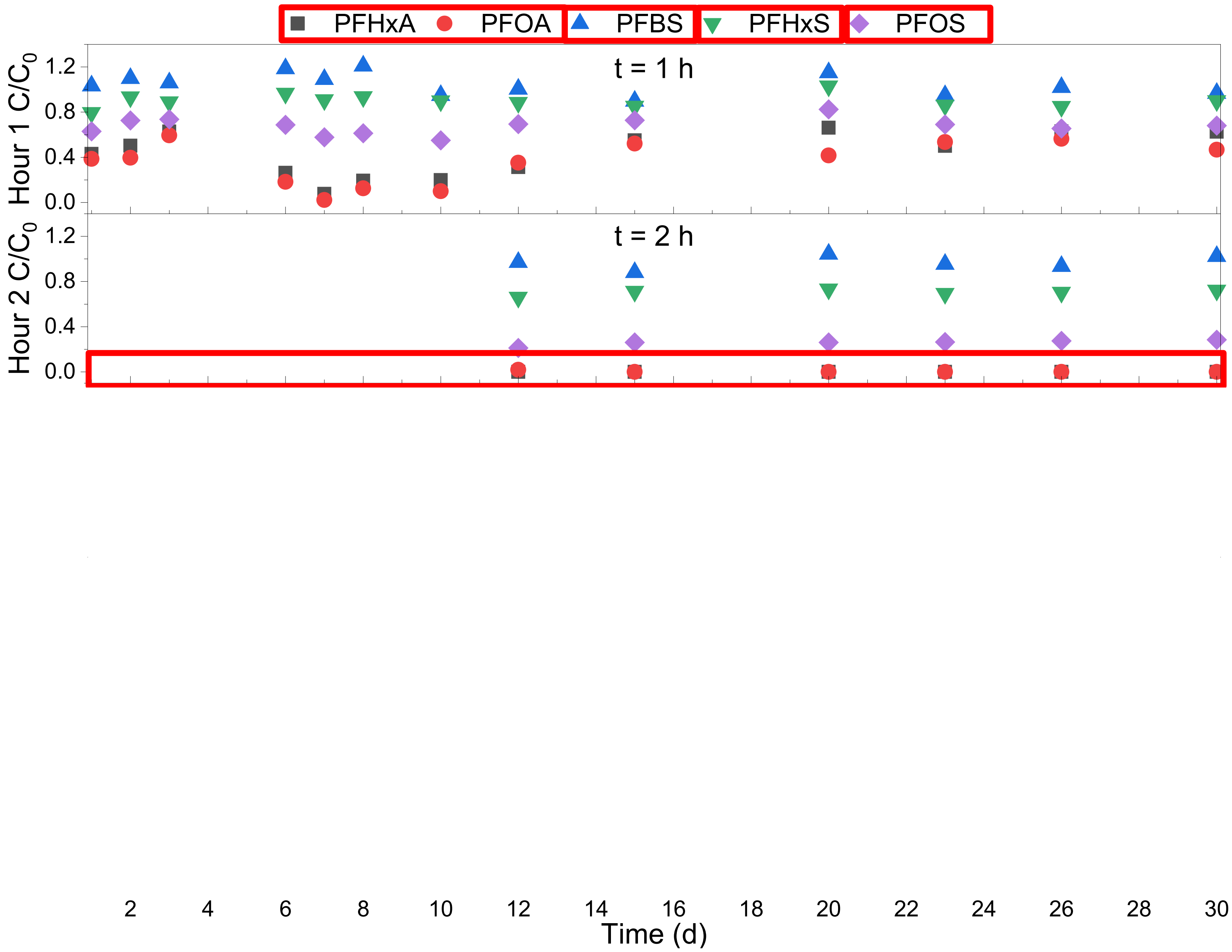
PFAS Destruction in Membrane Concentrate



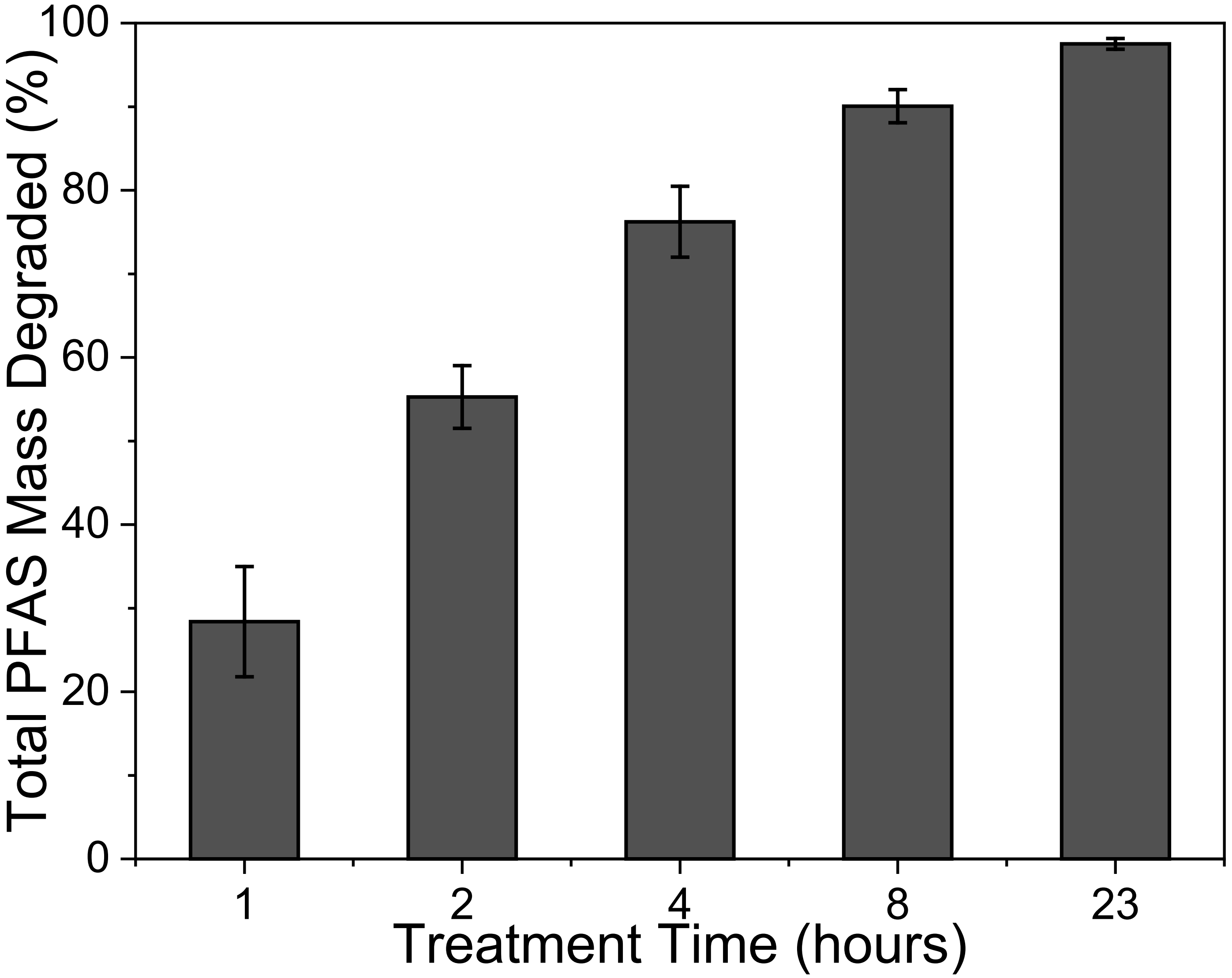
- ✓ No impact of chain length on PFCA degradation
- ✓ All degraded in <2 hours

- ✓ Clear impact of chain length on PFSA degradation
- ✓ PFOS degraded in <4 hours

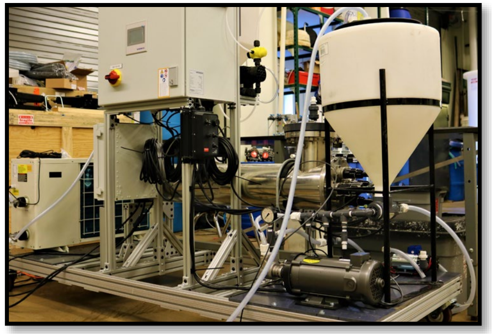
PFAS Degradation is Stable Over 30 Days



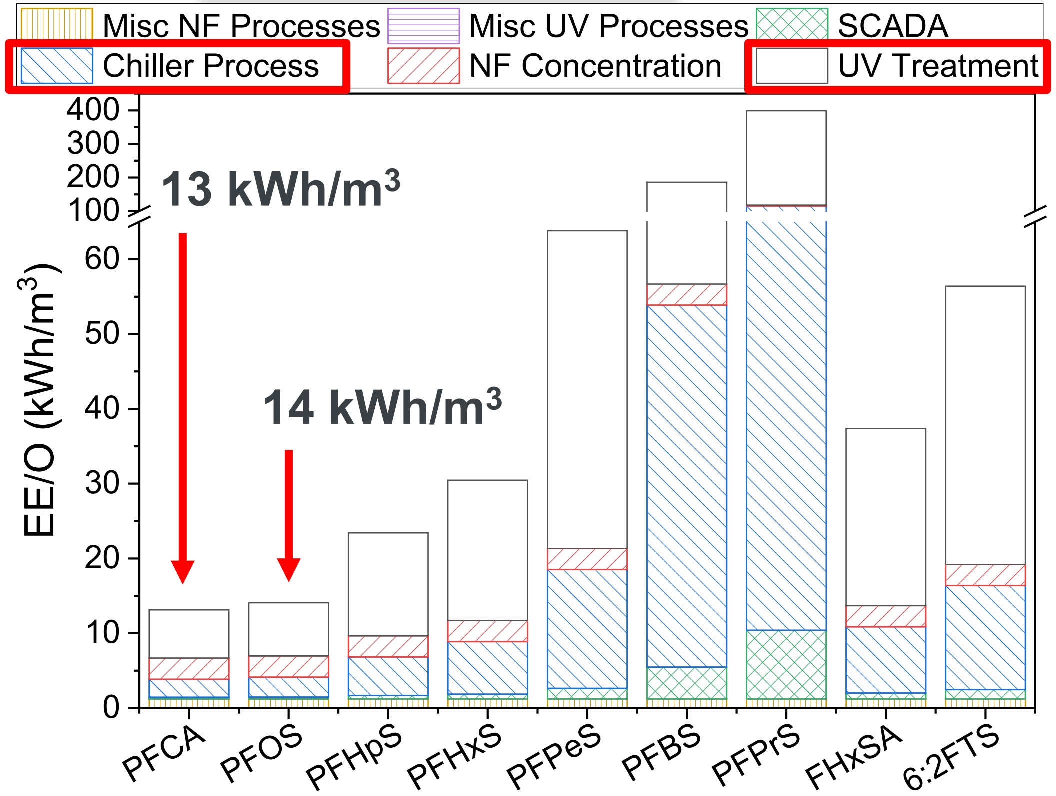
Detectable PFAS Mass Removal vs. Treatment Time



Okay, So What Are the Caveats?



- ✓ HIGH pH for operation, pH =11.2
- ✓ HIGH chemical use; sodium sulfite = 10 mM = 1.26 g/L
- ✓ HIGH energy use



Energy Per Order Magnitude (EE/O)
13.1 kWh/m^3 for PFCAs
14.1 kWh/m^3 for PFOS

Plasma ~16 kWh/m^3 (Nau-Hix 2021)
Photocatalysis ~51 kWh/m^3 (Qanbarzadeh 2020)
Electrochemical ~6 kWh/m^3 (Le 2019)

Seawater Desal ~ 2.54 kWh/m^3 (Zarzo and Prats 2018)

Conclusions and Practical Implications

✓ Effective PFAS rejection by RO membranes

Removal of PFAS in RO concentrate?

Adsorbents

PFAS Destruction

Continuous-flow destruction

More research / validation testing needed

Non-continuous-flow destruction

UV_{254} + Sulfite → e_{aq}^{-}

Additional treatment for PFAS in RO concentrate stream needed

Q & A

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https://doi.org/10.1016/j.watres.2021.117677 (UV-Sulfite)
https://doi.org/10.1016/j.watres.2020.116546 (NF/RO)

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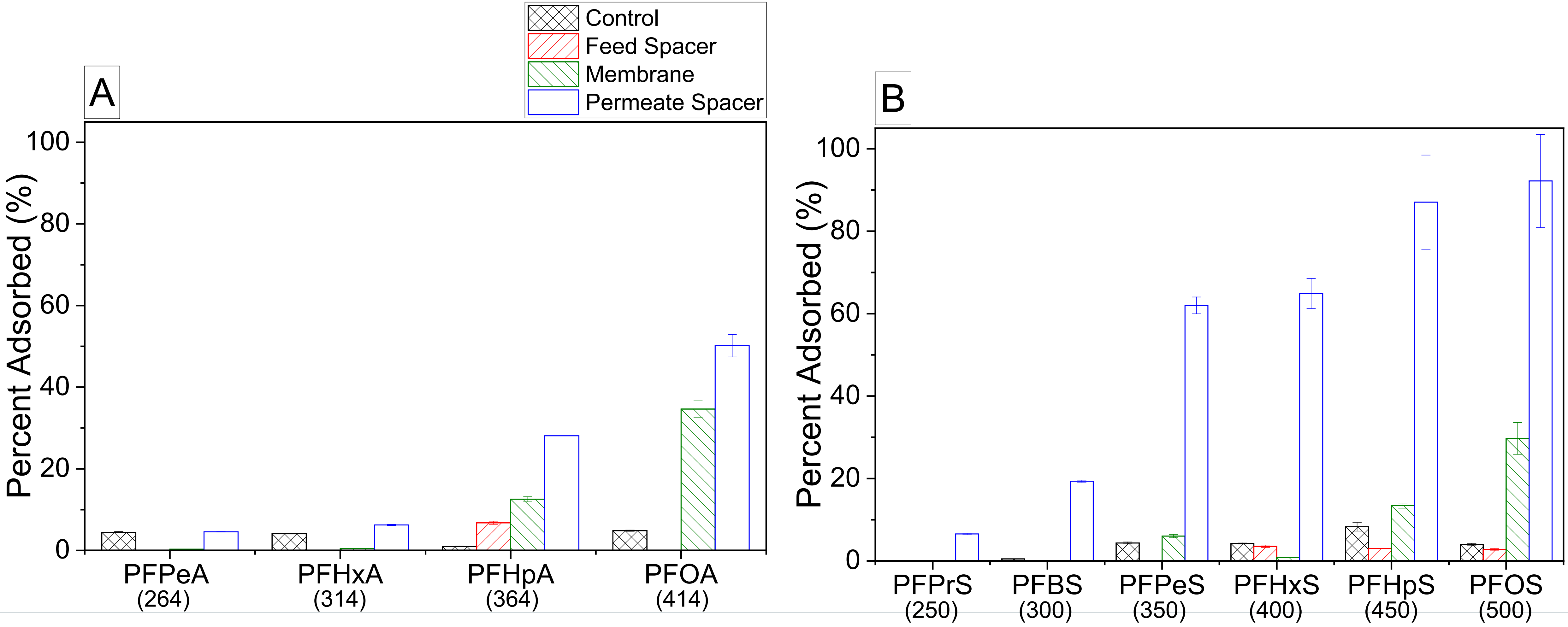
PFAS Adsorption to Membrane Elements and Spacers

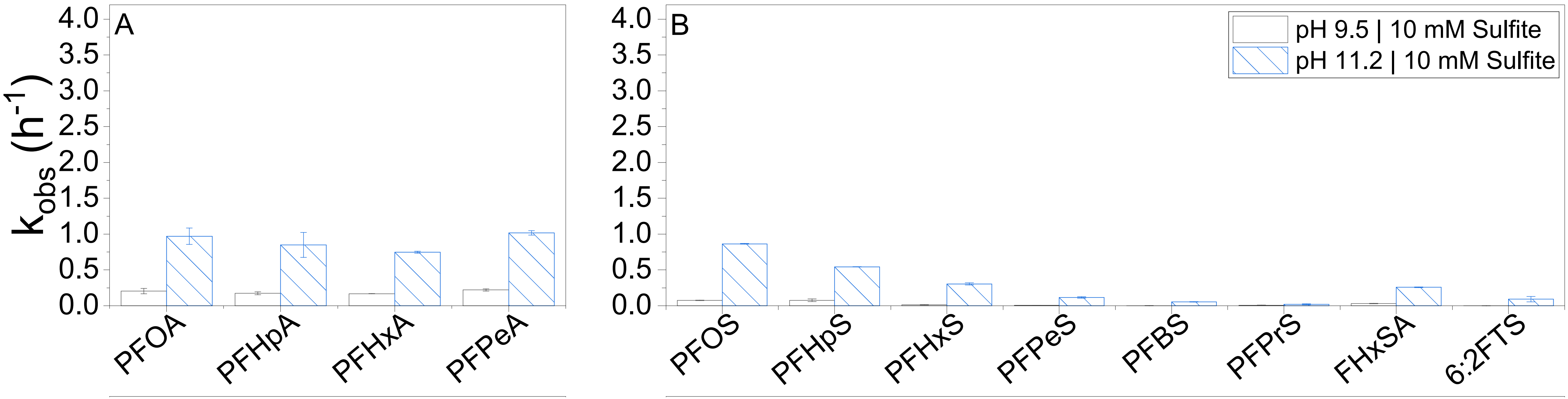
PFAS concentration ~ 60 ug/L | deionized water matrix | batch adsorption | NF270



Groundwater Quality

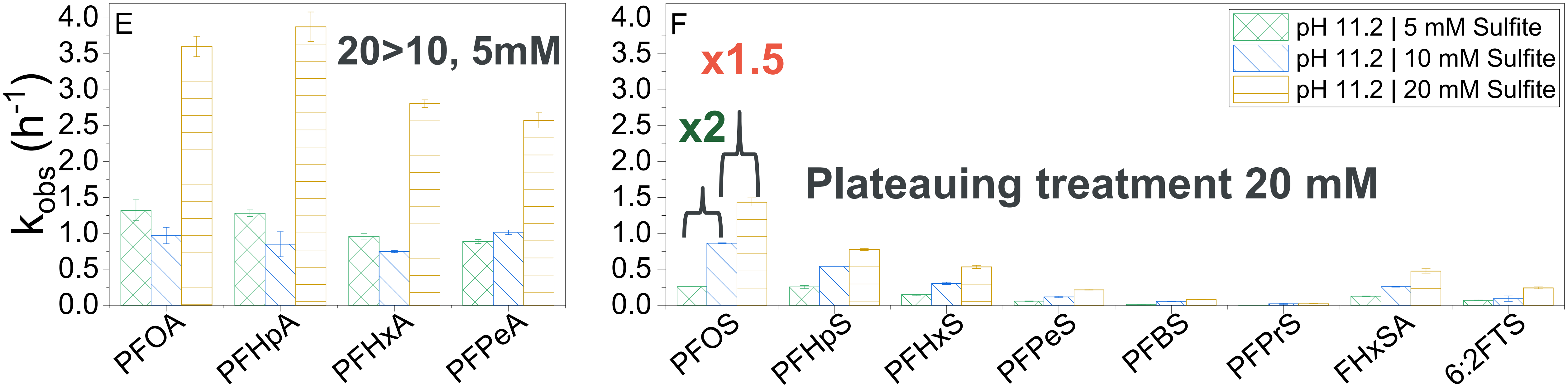
Day	1	6	10	15	30	Average
DOC (mg/L)	2.5	2.6	2.1	2.3	2.5	2.4 ± 0.2
Total Nitrogen (mg/L)	4.7	4.7	4.6	5.4	5.3	4.9 ± 0.4
pH	7.5	7.4	7.3	7.3	7.2	7.3 ± 0.1
UV254 (%T)	96.9	96.6	96.3	96.5	97.4	96.7 ± 0.4
Fluoride (mg/L)	0.4	0.4	0.4	0.4	0.5	0.4 ± 0.0
Chloride (mg/L)	37.9	36.0	35.5	35.2	33.5	35.6 ± 1.6
Nitrate (mg/L)	24.9	25.6	25.7	27.4	26.6	26.0 ± 1.0
Sulfate (mg/L)	80.0	77.4	77.9	78.6	77.7	78.3 ± 1.0
Calcium (mg/L)	BDL	0.8	BDL	BDL	BDL	-
Potassium (mg/L)	BDL	22.4	BDL	BDL	BDL	-
Magnesium (mg/L)	BDL	9.7	BDL	BDL	BDL	-
Sodium (mg/L)	118.1	87.7	116.4	129.3	133.2	116.9 ± 17.8
Sulfur (mg/L)	32.5	29.4	31.3	28.5	29.5	30.2 ± 1.6
Silica (mg/L)	9.7	8.9	9.8	10.8	11.4	10.1 ± 1.0

Impact of pH on UV-Sulfite Treatment



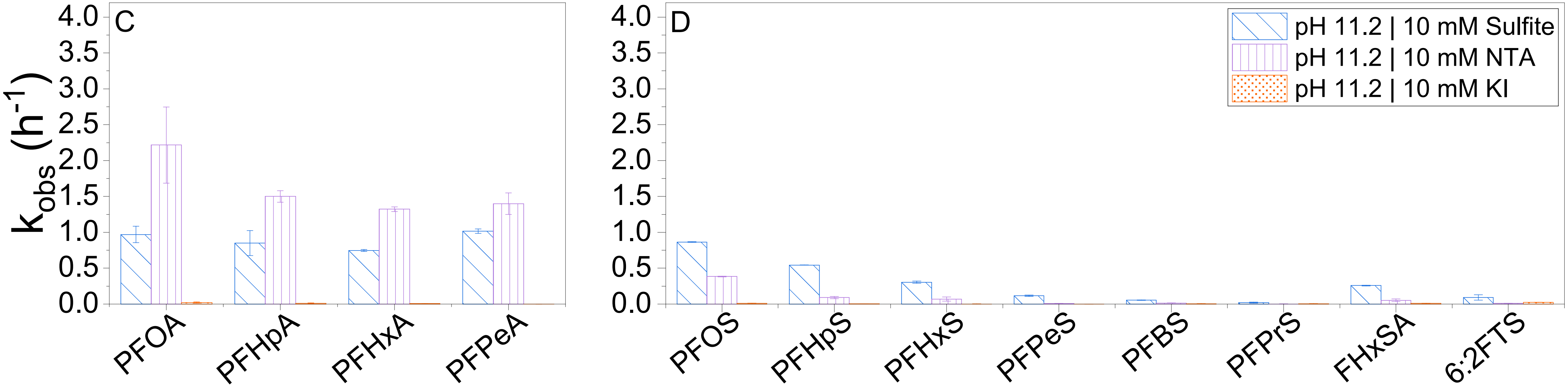
pH 11.2 > pH 9.5

Impact of Sulfite Dose on UV-Sulfite Treatment



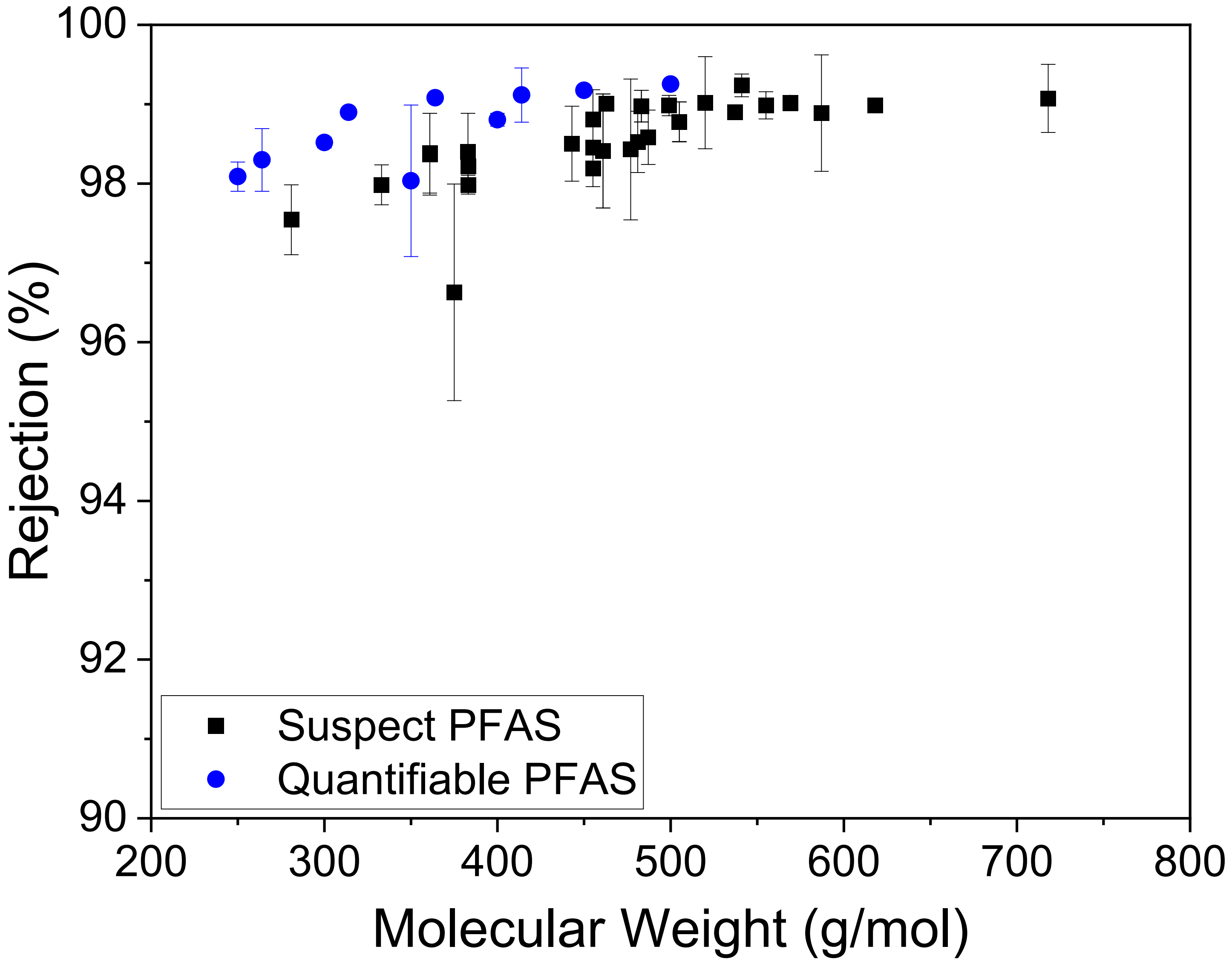
20 mM > 10 mM > 5 mM

Impact of Photosensitizer on UV-Sulfite Treatment

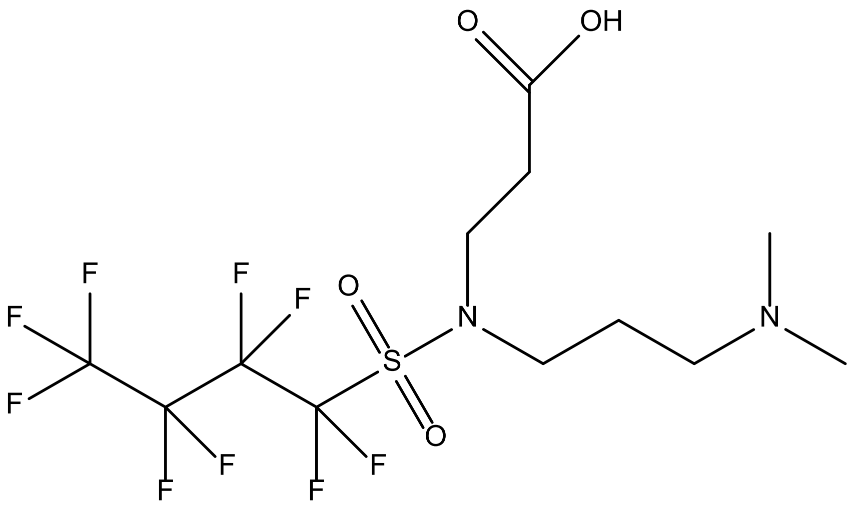


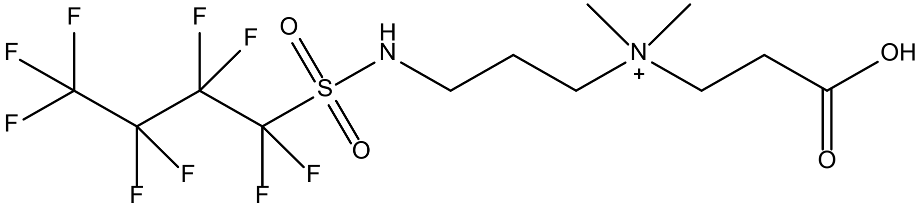
Sulfite > NTA > KI

Rejection of Suspect Screened PFASs by NF

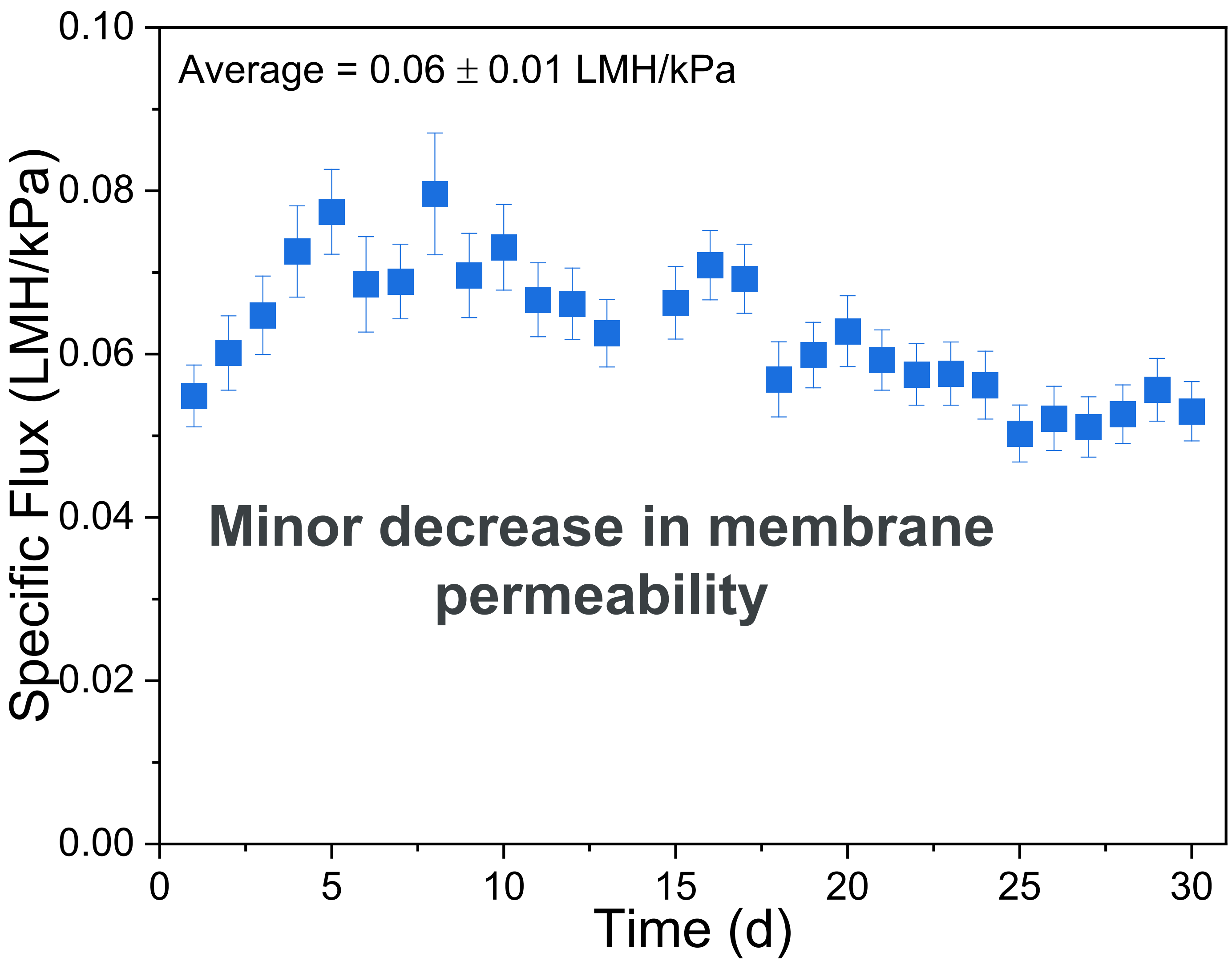


Deionized water matrix

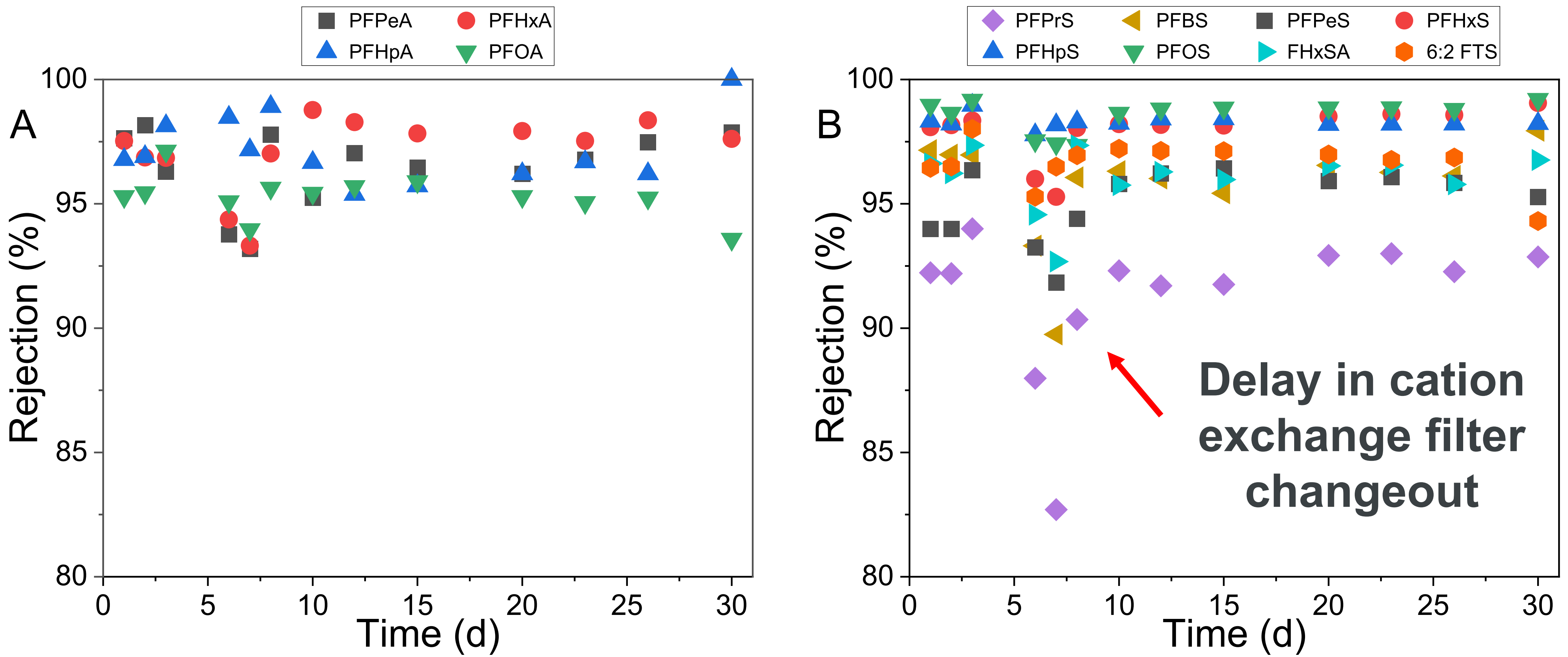




Minor Decreases in Membrane Permeability over 30 Days



PFAS Rejection by NF Over 30 Days @90% Recovery



Practical Implications

- ✓ Effective PFAS rejection by RO membranes
- ✓ Membranes to aid in destructive technologies
    - Other concentration technologies?
- Destruction of existing PFAS stockpiles
- Need to reduce time and cost of treatment

$$UV_{254} + \text{Sulfite} \rightarrow e_{aq}^{-}$$