Treatment of PFAS Residuals Using a Membrane Distillation Crystallizer

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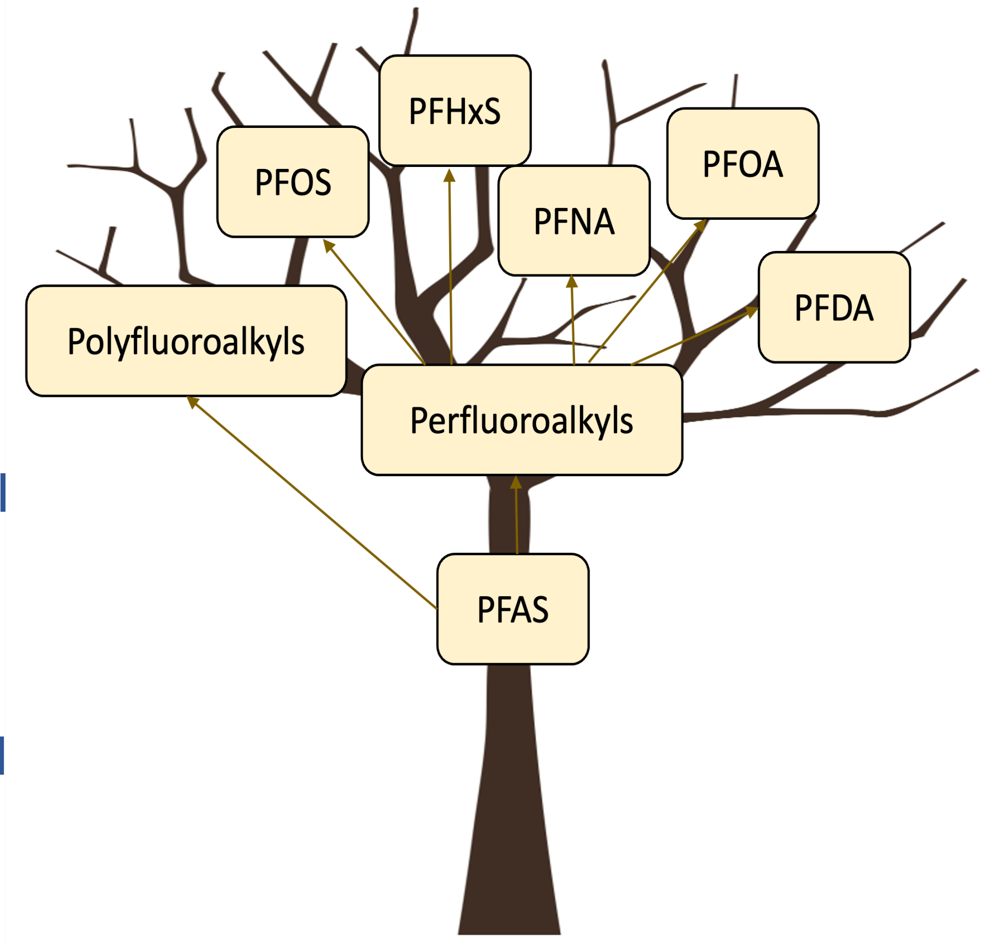
What are PFAS Compounds?

Per- and Polyfluoroalkyl Substances (PFAS) are synthetic compounds containing thousands of chemicals formed from carbon chains with fluorine attached to these chains.

- Resistant to heat, water, and oil
- Widely used since the 1950s in household and industrial products such as carpeting, waterproof clothing, upholstery, food paper wrappings, fire-fighting foams, and metal plating
- U.S. Environmental Protection Agency (EPA) has issued an Action Plan to document steps that the agency is taking to address challenges with PFAS in the environment



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PFAS Exposure Pathways

Reproduced from: J. Expo. Sci. Environ. Epidemiol. 2019; 29 (2): 131-147.

PFAS Removal Technologies

Compound	M.W. (g/mol)	Aeration	Coagulation Dissolved Air Floatation	Coagulation Flocculation Sedimentation Filtration	Conventional Oxidation (MnO_4, O_3, ClO_2, CLM, UV-AOP)	Anion Exchange	Granular Activated Carbon	Nano Filtration	Reverse Osmosis
PFBA	214	assumed	assumed						
PFPeA	264								
PFHxA	314								
PFHpA	364								
PFOA	**414**								
PFNA	464					assumed	assumed		
PFDA	514					assumed	assumed		
PFBS	300								
PFHxS	400								
PFOS	**500**								
FOSA	499						assumed		assumed
N-MeFOSAA	571	assumed				assumed	assumed	assumed	
N-EtFOSAA	585					assumed	assumed	assumed	

< 10% removal
unknown
> 90% removal
> 10%, < 90% removal

Source: Dickenson and Higgins, 2016.

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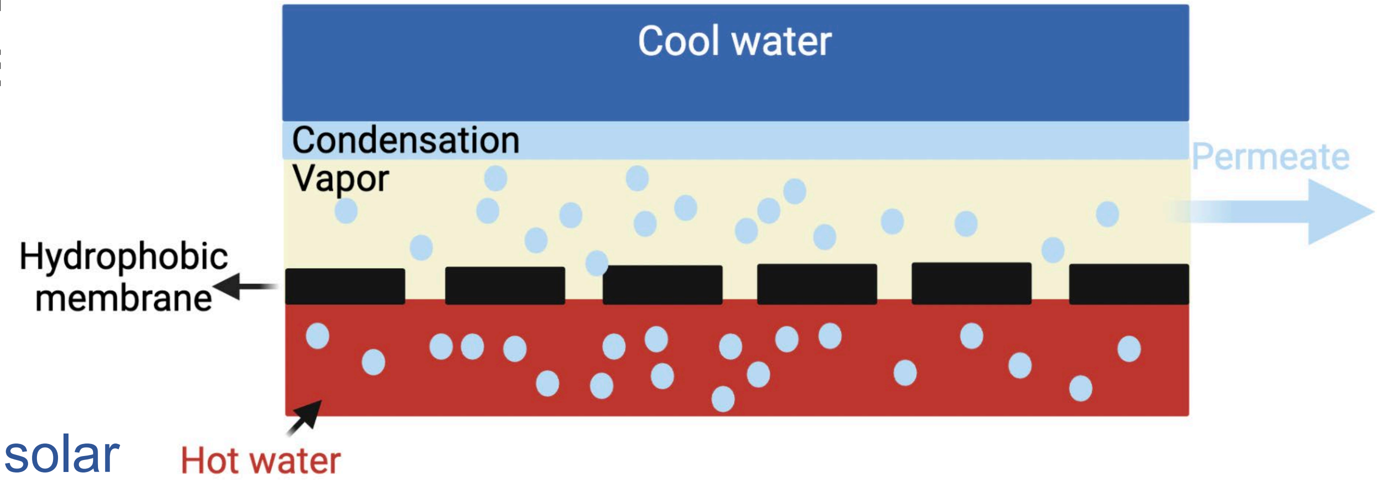
Why use Membrane Distillation (MD)?

MD is a thermally driven separati
process governed by vapor press
difference across a hydrophobic
membrane

- Suitable for hypersaline solutions
- Can utilize low-value heat sources (e.g., solar or waste heat from flue gases with temperature <100 °C)
- Can be coupled with crystallization to remove water and promote crystal formation and growth.



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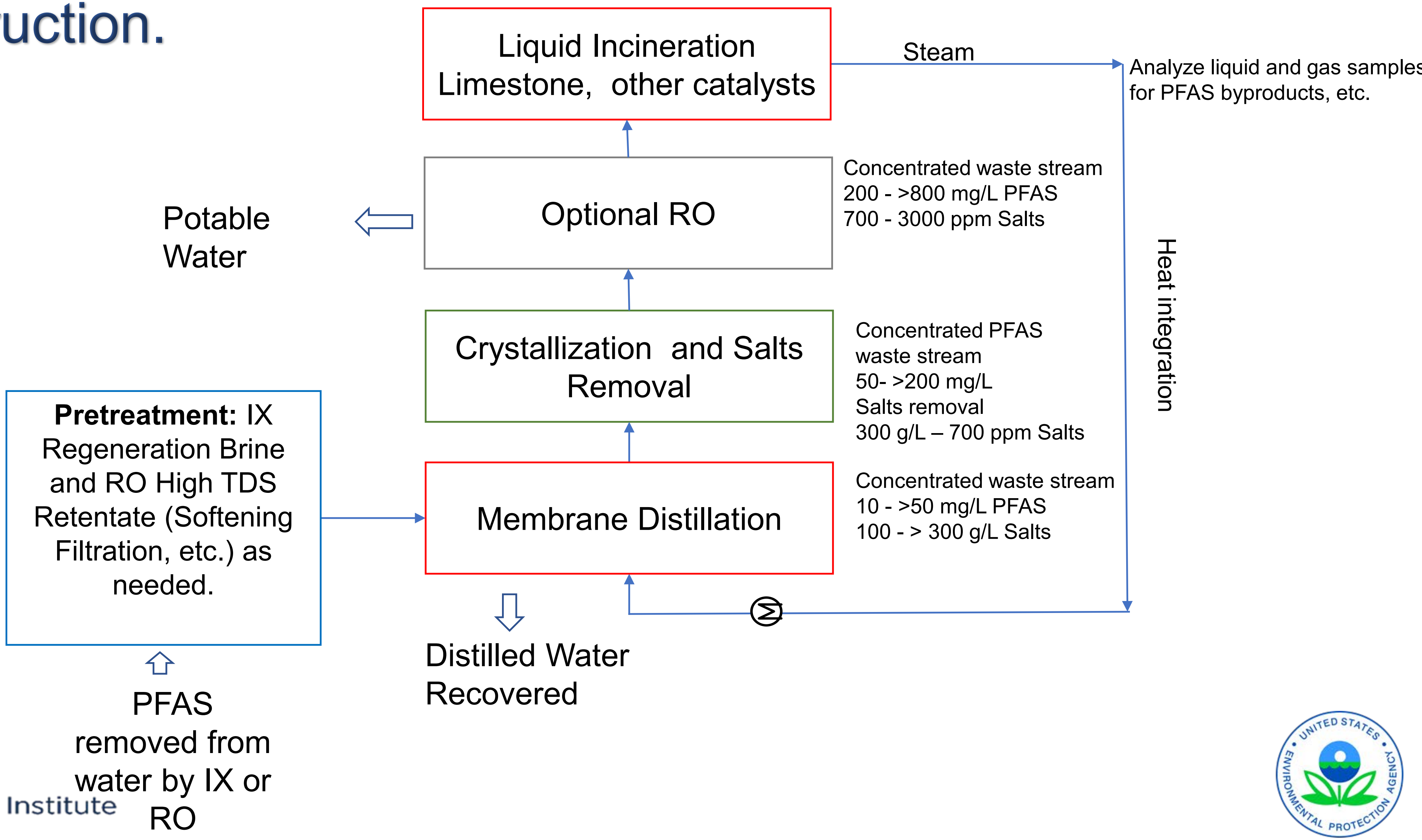
PFAS removal from hypersaline wastewater and safe end-of-life destruction.



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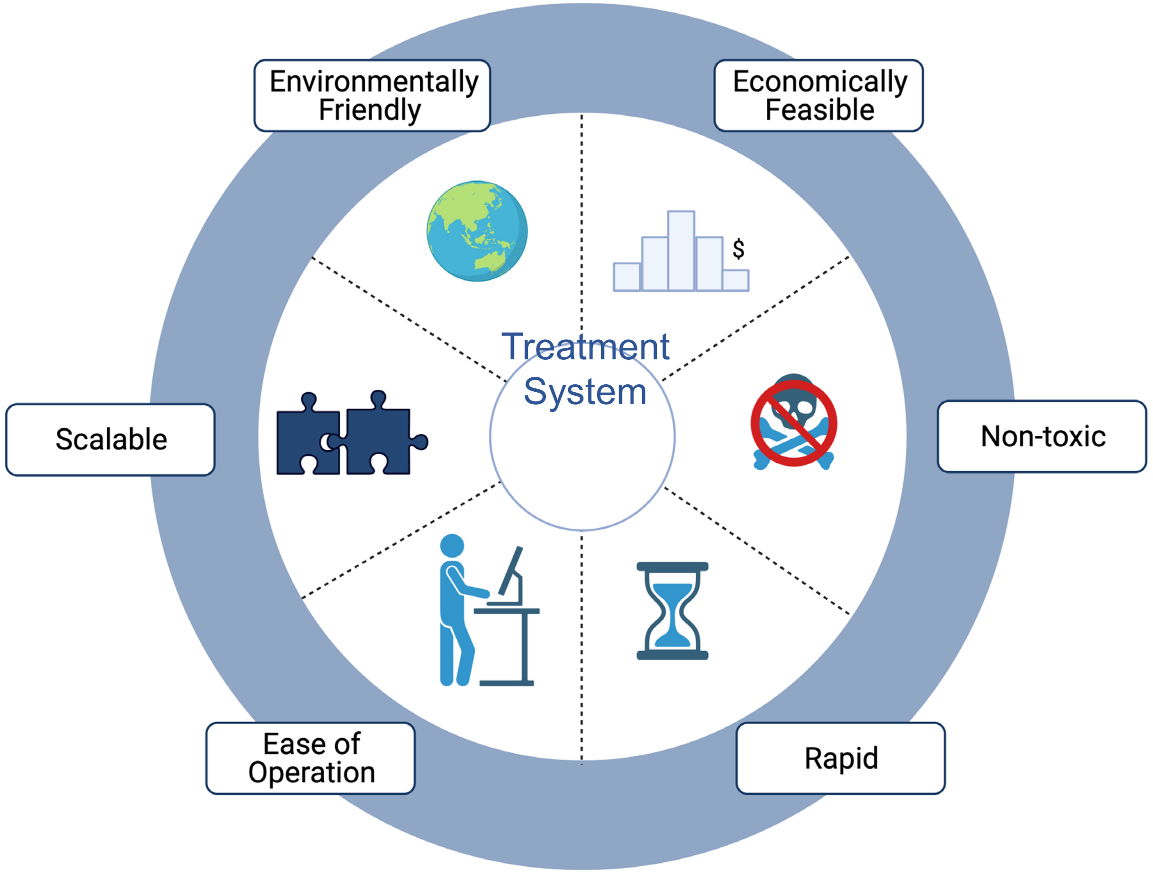
Research Goal

Develop an **energy efficient** treatment system for PFAS-laden AXR regenerati RO retentate waste streams.

- Design a lab-scale MDC system
- Identify optimal operating conditions (i.e., temperature)
- Evaluate the performance of four commercia available MD membranes (i.e., permeate flux rejection measurements)



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Experimental Overview

- **Four commercial MD membranes (Sterlitech):** Polytetrafluoroethylene (PTFE); Polytetrafluoroethylene (PTFE); Polyvinylidene difluoride (PVDF) ; Polyether ether ketone (PEEK)
- **Selected PFAS:** 10 mg/L Perfluoropentanoic Acid (PFPeA)
- **Salt:** 10% (w/v) NaCl
- **Crossflow rate**: 0.75 L/min
- **Operating temperature:** 50, 60 or 70 °C ± 2 °C
- **Active membrane area:** 42 cm^2 or 140 cm^2

Material	Membrane ID	Pore Size (µm)	pH	Water Entry Pressure (psi)
PTFE	Unlaminated PTFE	0.2	no limit	37
	Laminated PTFE	0.1	1-14	60
PVDF	PVDF100	0.1	1-12	43
PEEK	PEEK100	0.1	1-14	29

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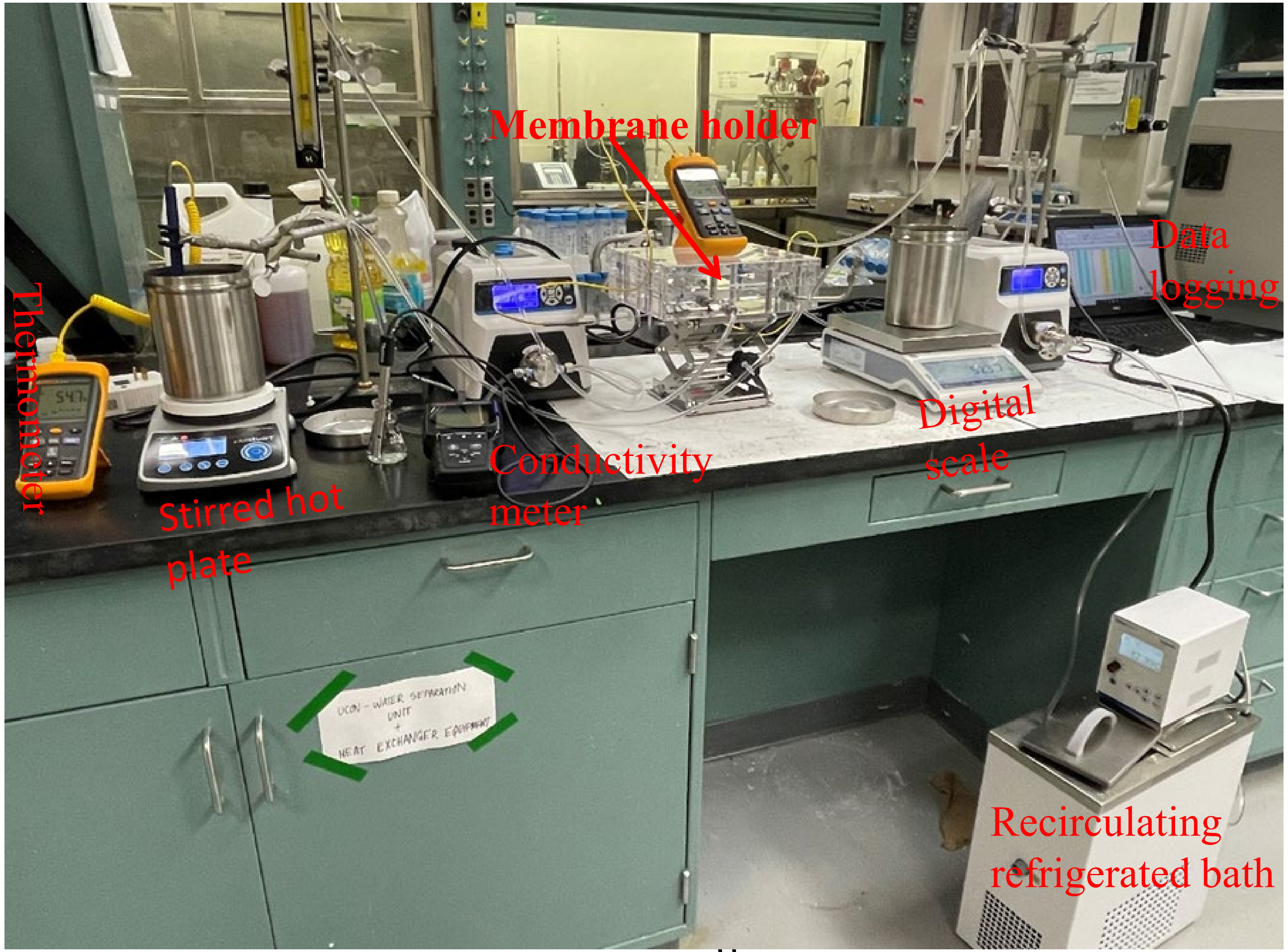
MD Setup



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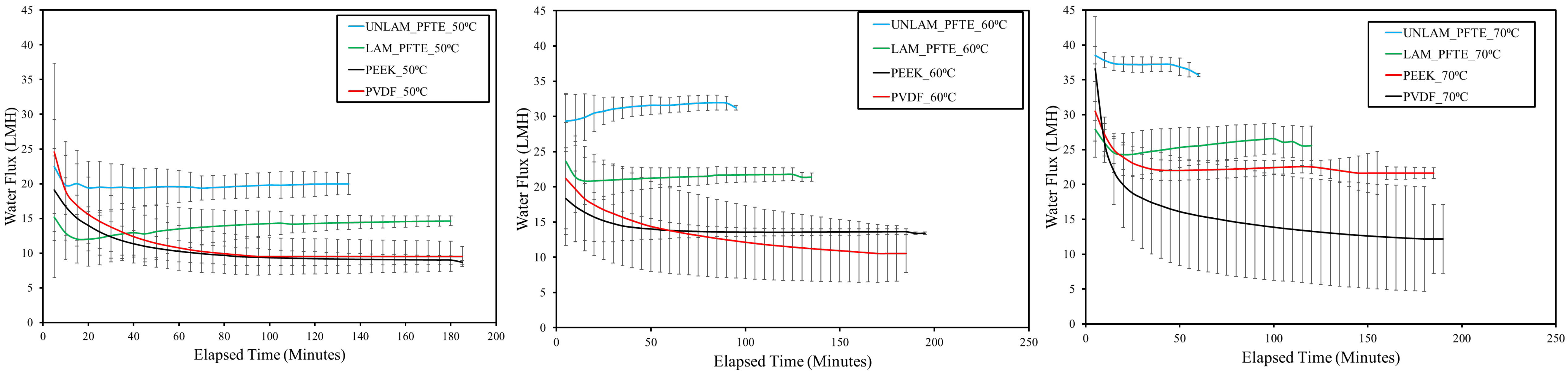
Clean Water Flux

50 °C 60 °C 70 °C



- The higher the feed temperature, the higher the flux of water
- The PFTE membrane showed the highest water flux at all temperatures
- The laminated layer reduced the water flux
- The PVDF membrane has lower water flux, PFAS rejection and mechanic strength

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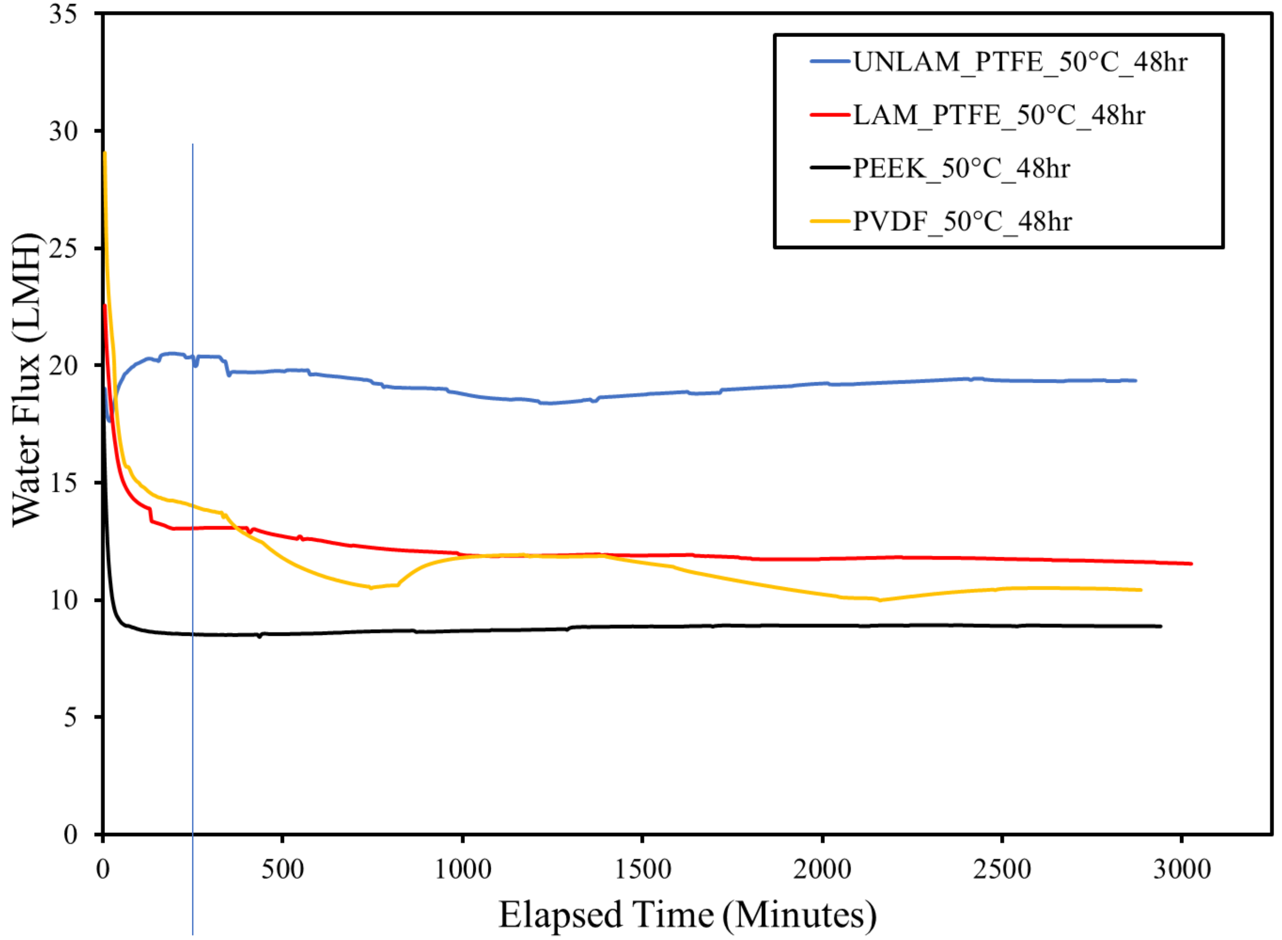
Water flux after 48 hours

- 48-h MD experiments with a feed temperature of 50 °C and a permeate temperature of 20 °C
- The permeate fluxes were very stable during the 48-h run
- The PFPeA rejections were satiable
- Low membranes compaction and fouling during the testing period



- The water flux stabilizes within ~200 min

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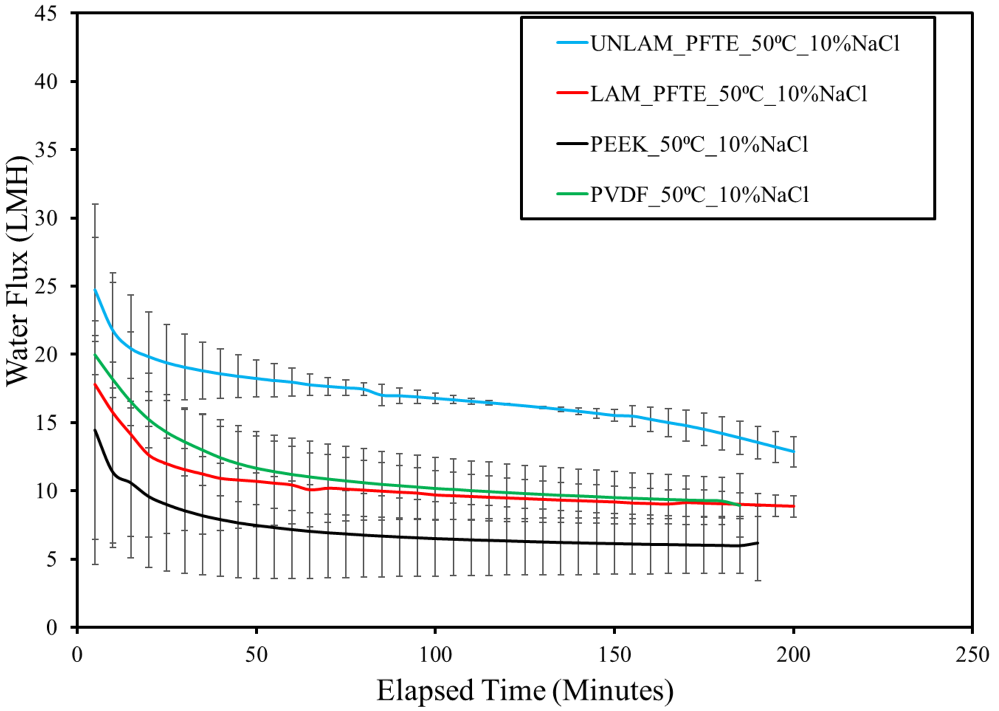
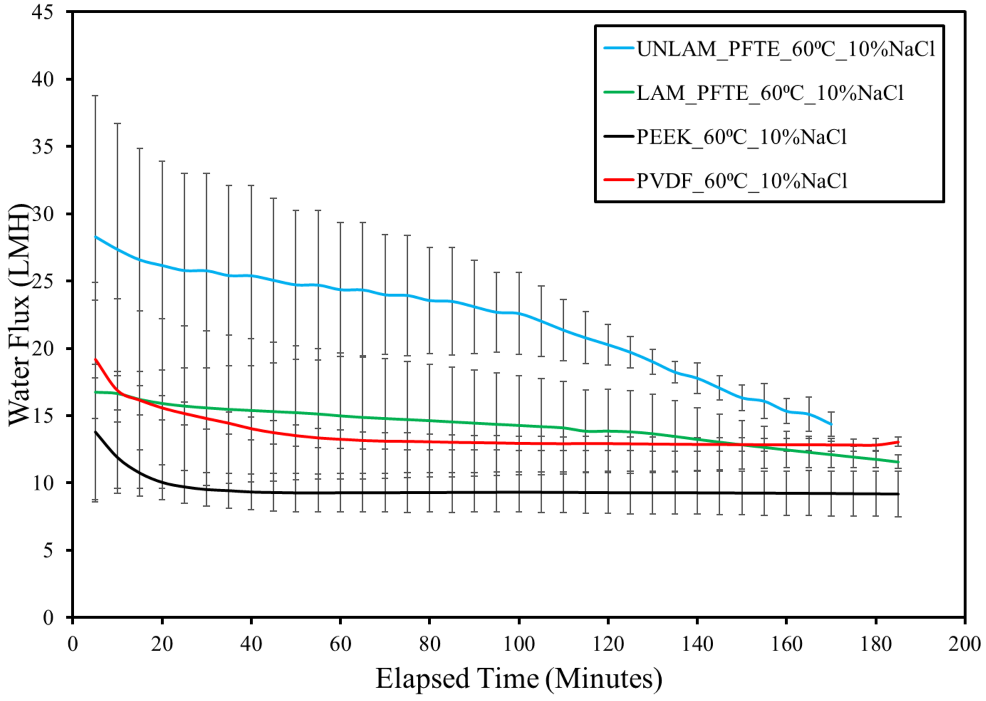
Conditioning with 10% NaCl





- The higher the feed temperature, the higher the flux of water
- The PFTE membrane showed the highest water flux at all temperatures

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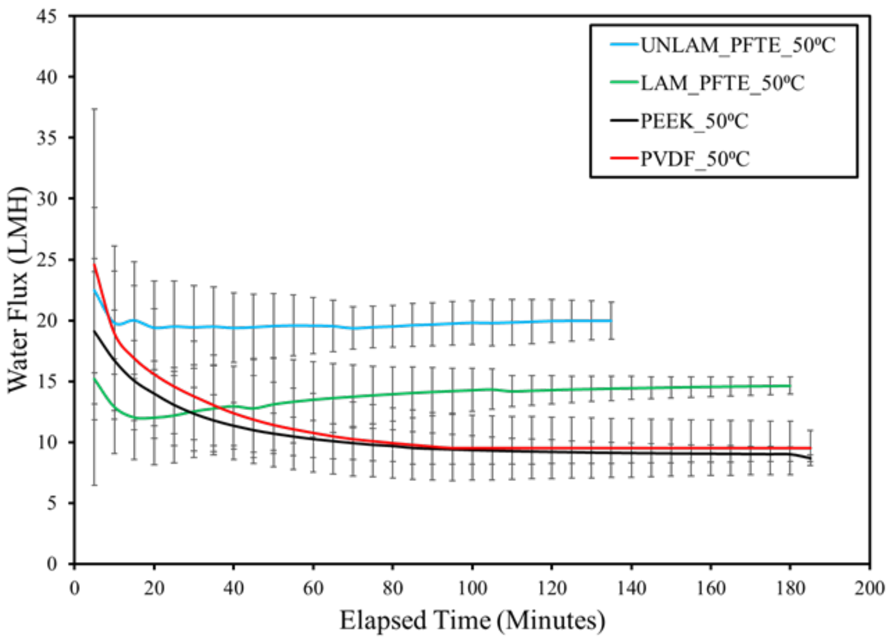
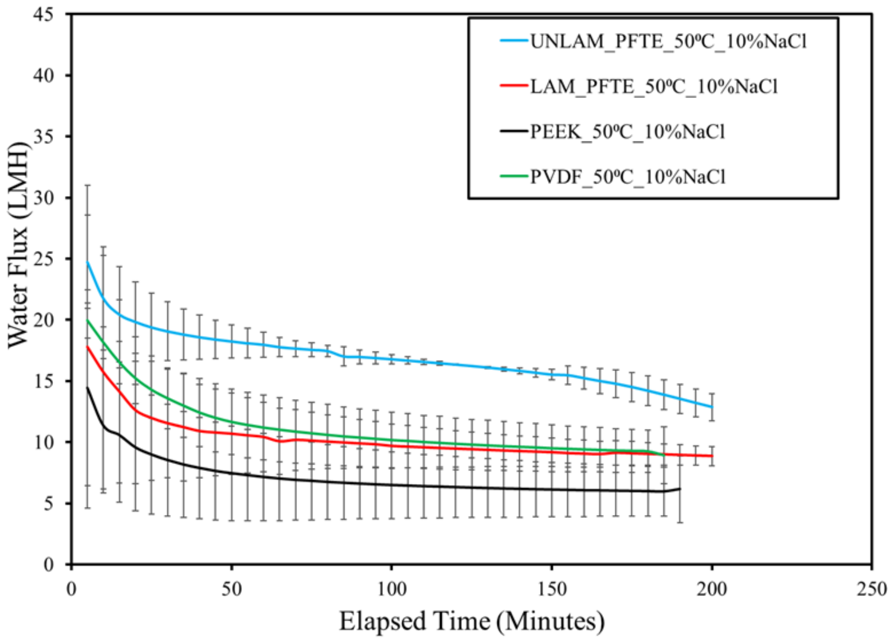
Water Flux in the presence and absence of NaCl

Only DI water



Conditioning with 10% NaCl



- The water flux decreased in the presence of high NaCl concentration
- Attributed to increased boiling point of the feed solution due to the NaCl molecules formed hydrogen bonds with the water molecules
- More kinetic energy is needed to create enough movement to break their hydrogen bonds and convert the water from liquid into vapor

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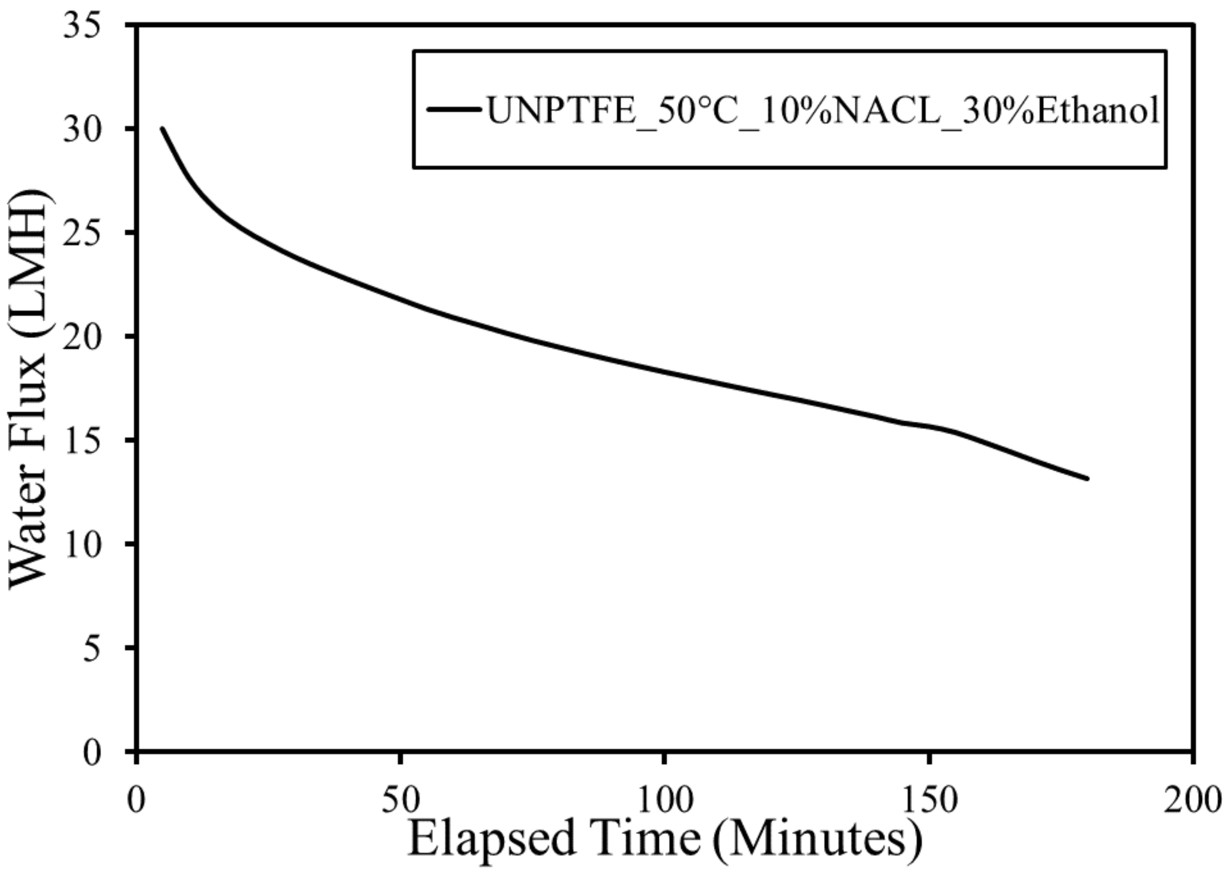
Unlaminated PTFE Membrane Performance

- Brine solutions combined with organic solvent (such as ethanol) may be required to effectively desorb the anionic head and the hydrophobic carbon-fluorine of the PFAS molecule from the resin ion exchange site
- The presence of ethanol has no adverse impact on the PTFE membranes
- Membrane damage observed with the PVDF and PEEK membranes



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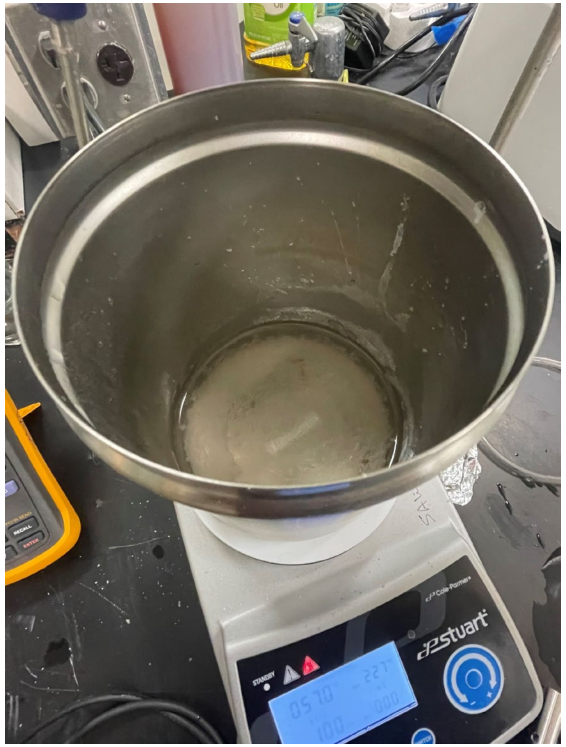
NaCl perception during MD experiments

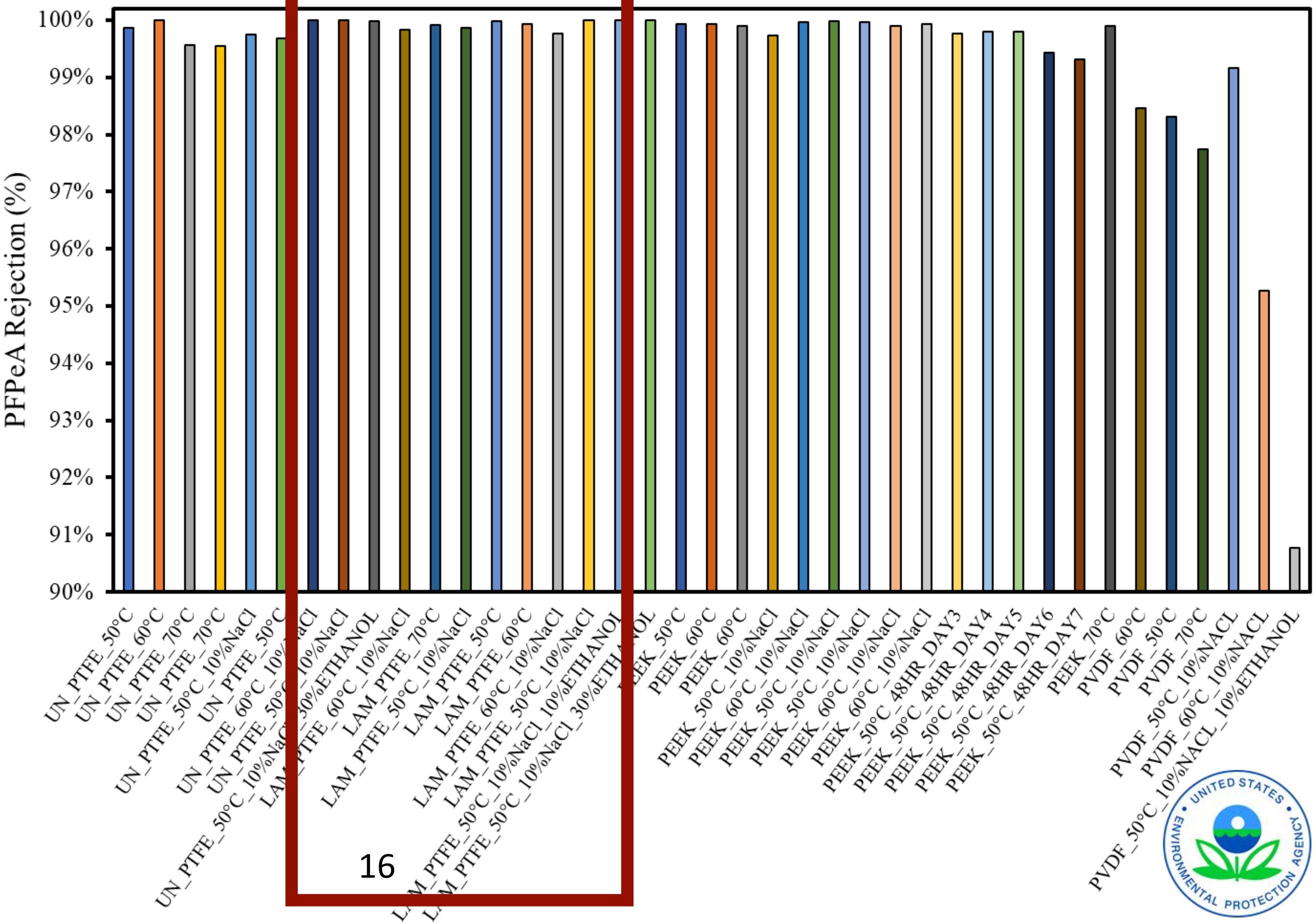
- Successful separation of NaCl by MD

- Large percentage of water was removed from the feed solutions before reaching the NaCl supersaturation and precipitate/crystallize the NaCl



PFPeA Rejection

- The PFPeA rejection was calculated using the actual PFPeA concentration in the feed and permeate solutions, obtained by LC-MS-MS



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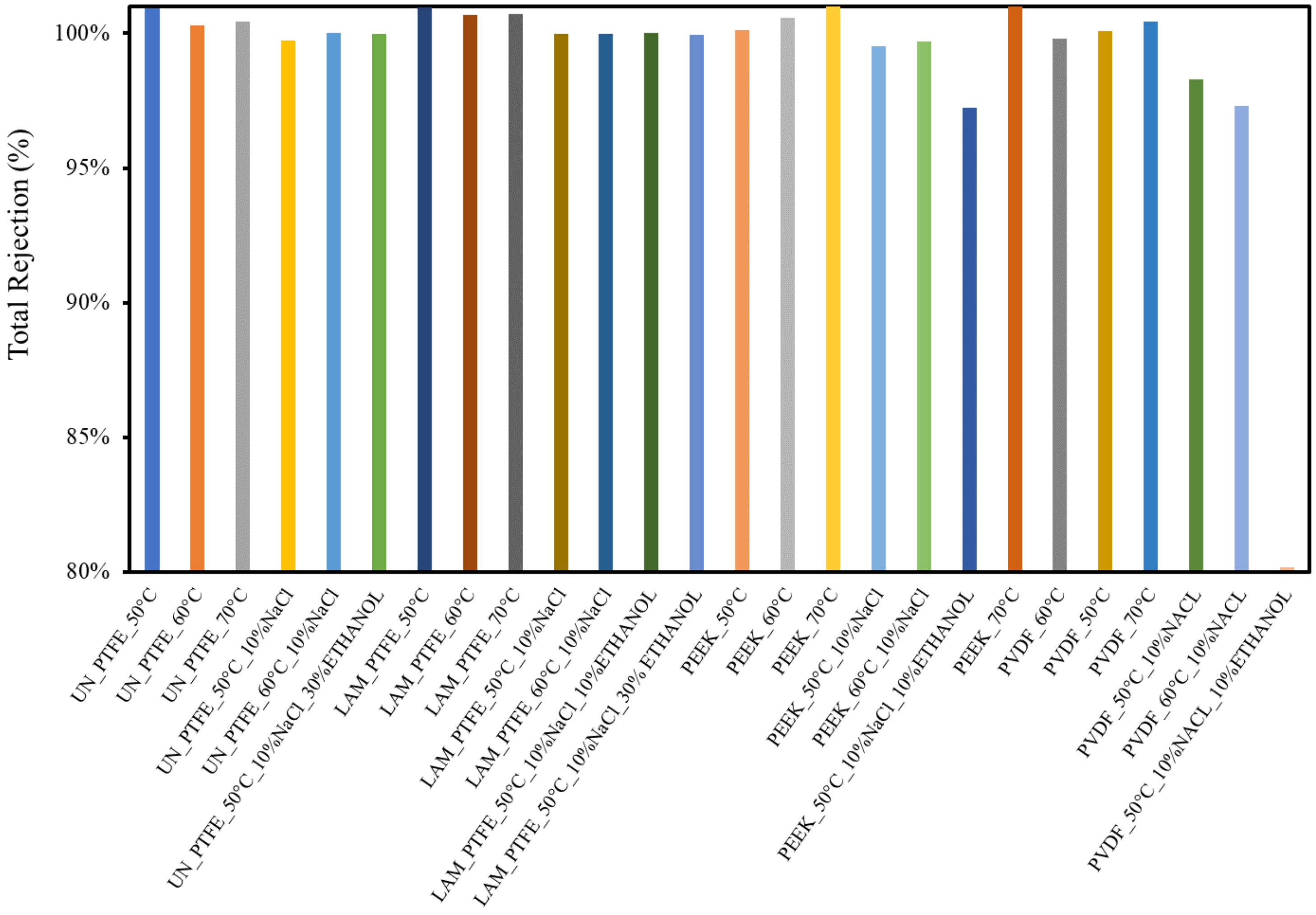
NaCl and PFPeA Rejection

- The total rejection was calculated using the initial and final conductivity of the feed and permeate solutions obtained by conductivity meter



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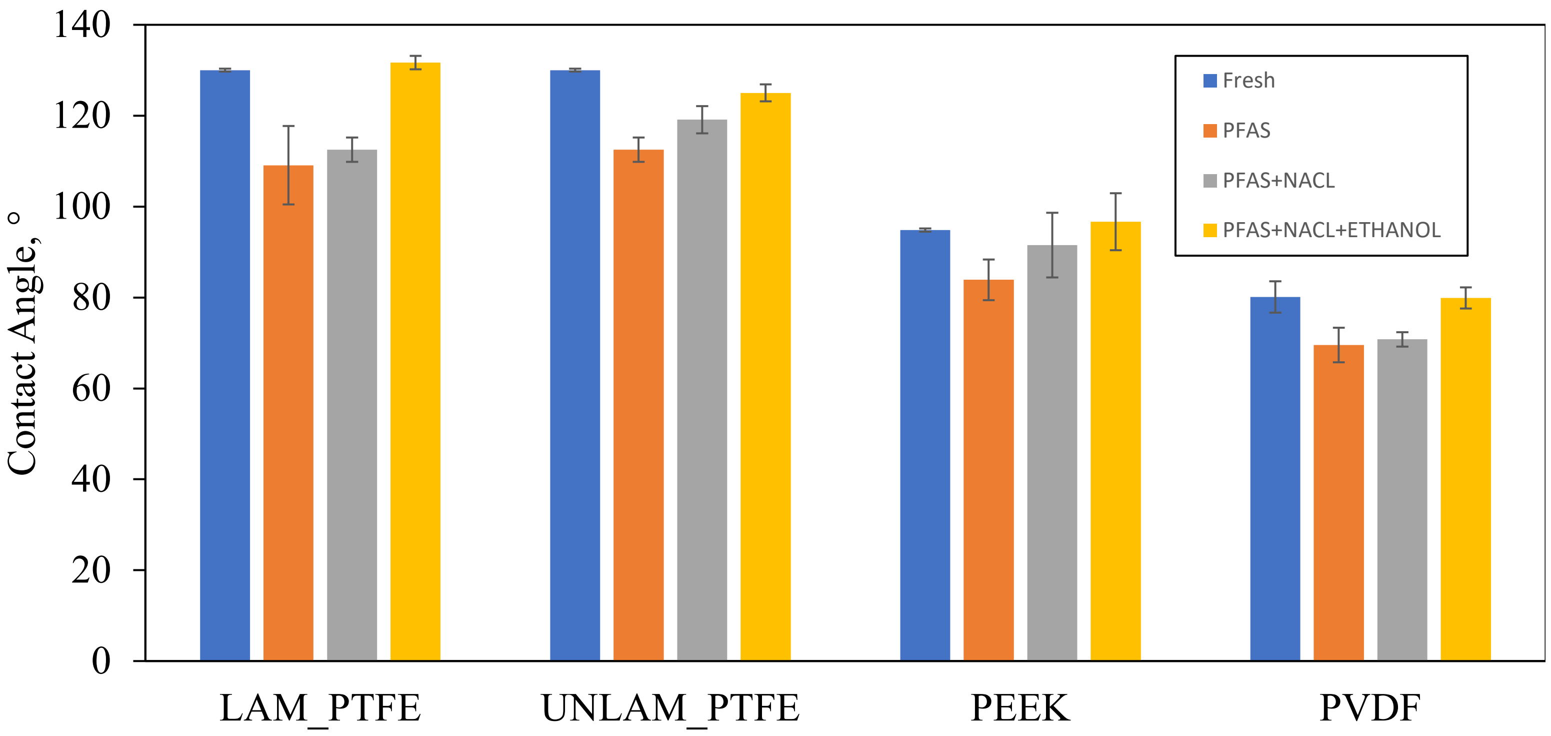
Membrane Wettability by PFPeA

- The presence of the ethanol/NaCl mixture in the feed solution resulted in restoring the membranes hydrophobicity



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Conclusions & Future Work

- Unlaminated PTFE membrane outperformed the other membranes at all tested temperatures.
  - Almost complete PFPeA rejection was achieved (>99.7%).

- In the presence of PFPeA, the membrane became more hydrophilic, but the addition of NaCl and ethanol had an opposing effect.

- Future experiments will evaluate additional PFASs and mixture of salts.

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