PFAS TREATMENT REMOVAL & DEGRADATION RESEARCH & INDUSTRY

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INTRODUCTIONS

- Graduate Researcher in Dr. Spyros Pavlostathis's Lab at **Georgia Institute of Technology**

-- PAA and H_2O_2 Fate in wastewater and effect on wastewater treatment

Publications

- Postdoctoral Researcher in Dr. Mei Sun's Lab (Publications) at **University of North Carolina**

-- PFAS removal and degradation homogeneously and heterogeneously

-- Spent Ion Exchange Resin Regeneration Train

- Environmental Engineer and Researcher at **Atlas**

--Water and Wastewater Treatment

--PFAS Team Member and PFAS Researcher

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Georgia Tech
College of Engineering

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AGENDA

Background	• PFAS OVERVIEW -- PROPERTIES & SPECIES
Treatment Overview	• PFAS REMOVAL AND DEGRADATION PROCESSES
GAC & IX	• PFAS REMOVAL MATERIALS
IX SUSTAINABIILITY	• PFAS-EXHAUSTED ION EXCHANGE RESIN REGENERATION *
RESEARCH & INDUSTRIAL	• **TO BE DISCUSSED – Q&A**

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PFAS BACKGROUND

Per- and polyfluoroalkyl substances (PFAS) refer to a large group of **fluorinated aliphatic** chemicals, with an estimated number of 5000 types existing over the globe (ITRC, 2020; USEPA, 2019).

Properties

- High recalcitrance in natural environments: resistance to water, oil, and heat, so intensive use in industrials, household products and firefighting applications;
- Bioaccumulation and diverse toxicities to animals and health concerns for humans;

Two Major Gorups

- Perfluorocarboxylates (PFCAs, $C_nF_{2n-1}O_2-$) e.g. PFOA
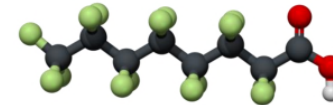
- Perfluorosulfonates (PFSAs, $C_nF_{2n+1}SO_3-$) e.g. PFOS
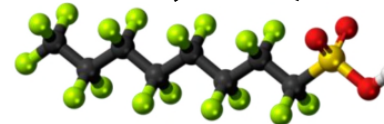
- PFSAs are intrinsically more recalcitrant than PFCAs to degradation because of the SO_3- head group.

TREATMENT OVERVIEW

PFAS Removal

-- From one media to another media

-- From aqueous to solid phase

- Granular activated carbon (GAC)
- Ion exchange (IX)
- Membrane Filtration: Reverse Osmosis (RO) and Nanofiltration

PFAS Degradation

-- Break C-F bond

-- Release inorganic fluoride ion (F-)

- Sono-chemical or Sonolysis
  --by forming active cavity
- Thermal-chemical
  e.g. heat-activated persulfate oxidation
- Photo-chemical
  e.g. UV/Sulfite
- Electro-chemical
  e.g. Ti/SnO$_2$-Sb-Bi anode

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PFAS REMOVAL -- ADSORPTION

Granular Activated Carbon (GAC)
- Low unit media cost.
- Consistent PFAS and co-contaminant adsorption.
- More effective at long-chain PFAS than short-chain PFAS.
- Rapid breakthrough.
- Larger sorbent volume needed.
- **Disposal of spent GAC.**

Ion Exchange (IX)
- Greater effectiveness in removing short-chain PFAS.
- Overall higher PFAS removal capacity than GAC.
- Regeneration capabilities.
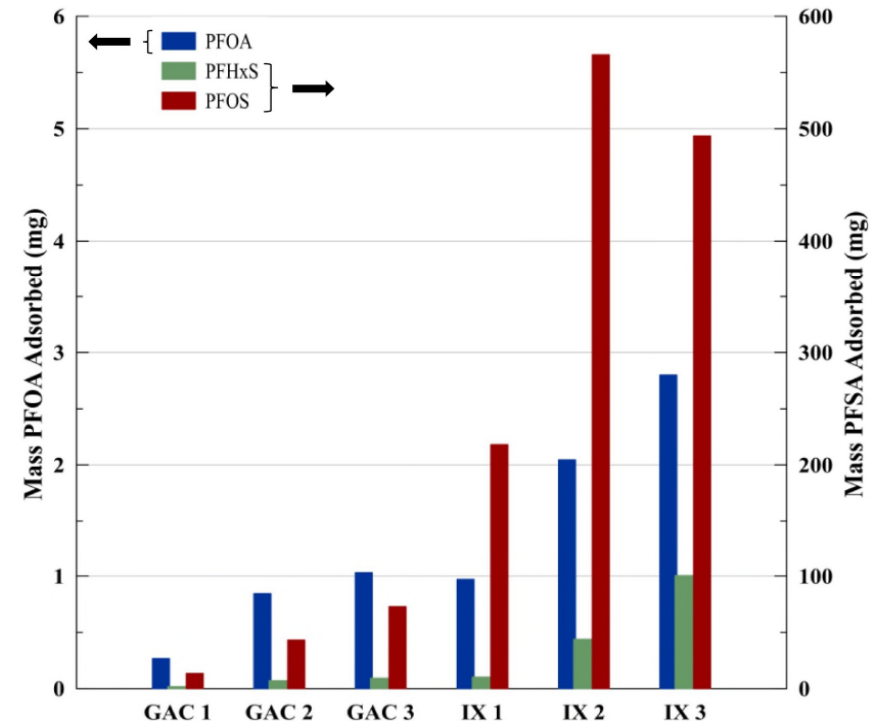- Higher unit cost.
- **Disposal of spent IX resins.**

GAC VS. IX RESIN
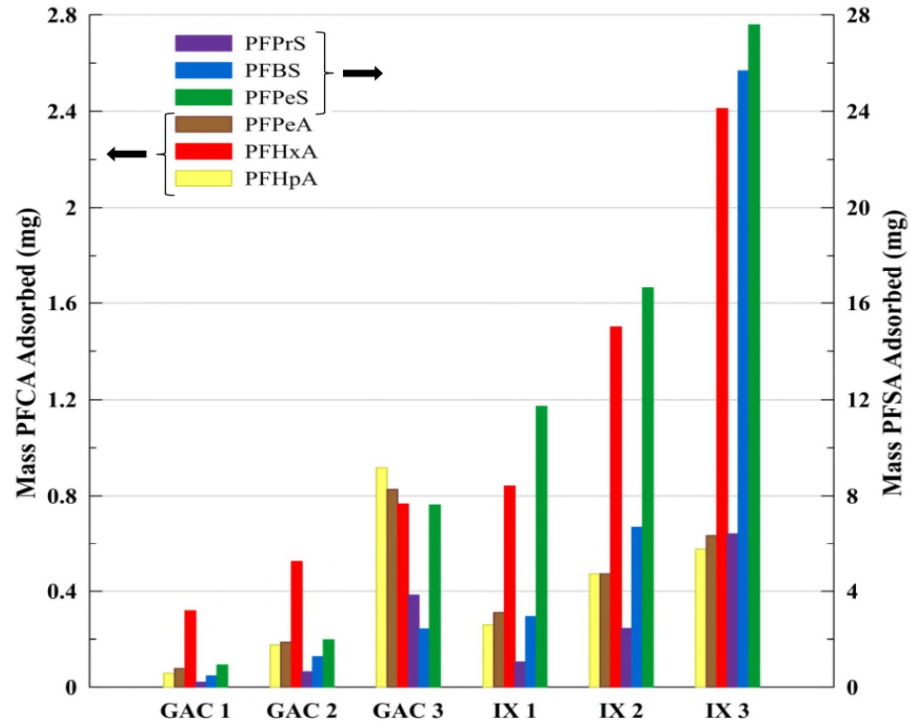
Conner C. Murray, et. al., PFAS treatment with granular activated carbon and ion exchange resin: Comparing chain length, empty bed contact time, and cost. Journal of Water Process Engineering, 44, 2021,102342.
https://doi.org/10.1016/j.jwpe.2021.102342.

PFAS REMOVAL -- TAKEAWAYS

❖**IX outperformed GAC for removal of both short and long chain PFAS.**

GAC: PFAS removal primarily driven by **hydrophobic interactions**

IX Resin: PFAS removal primarily driven by **hydrophobic interactions**

+

electrostatic interactions

Alert !!!

Both has disposal issue and may have regulation on disposal of spent GAC/IX Resin in the future.

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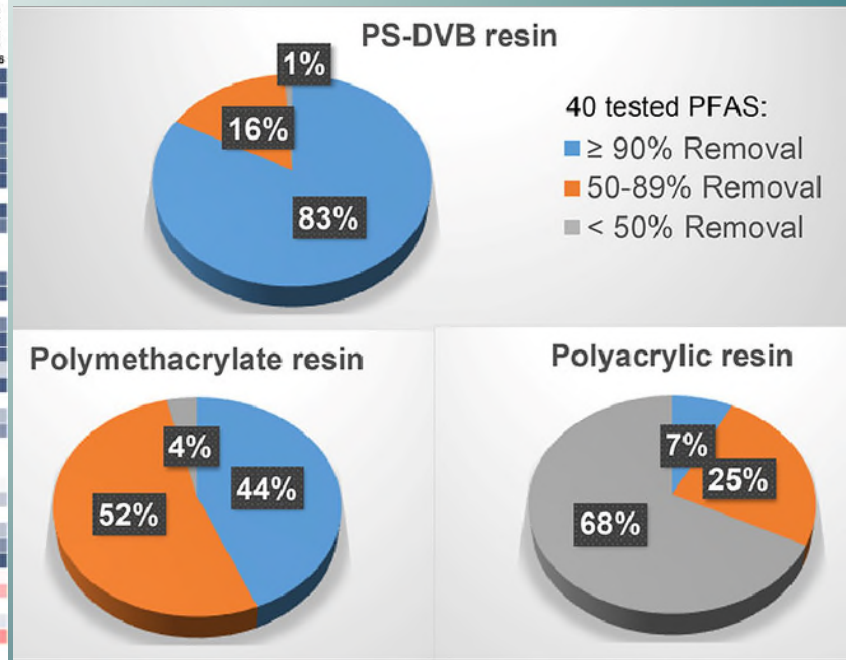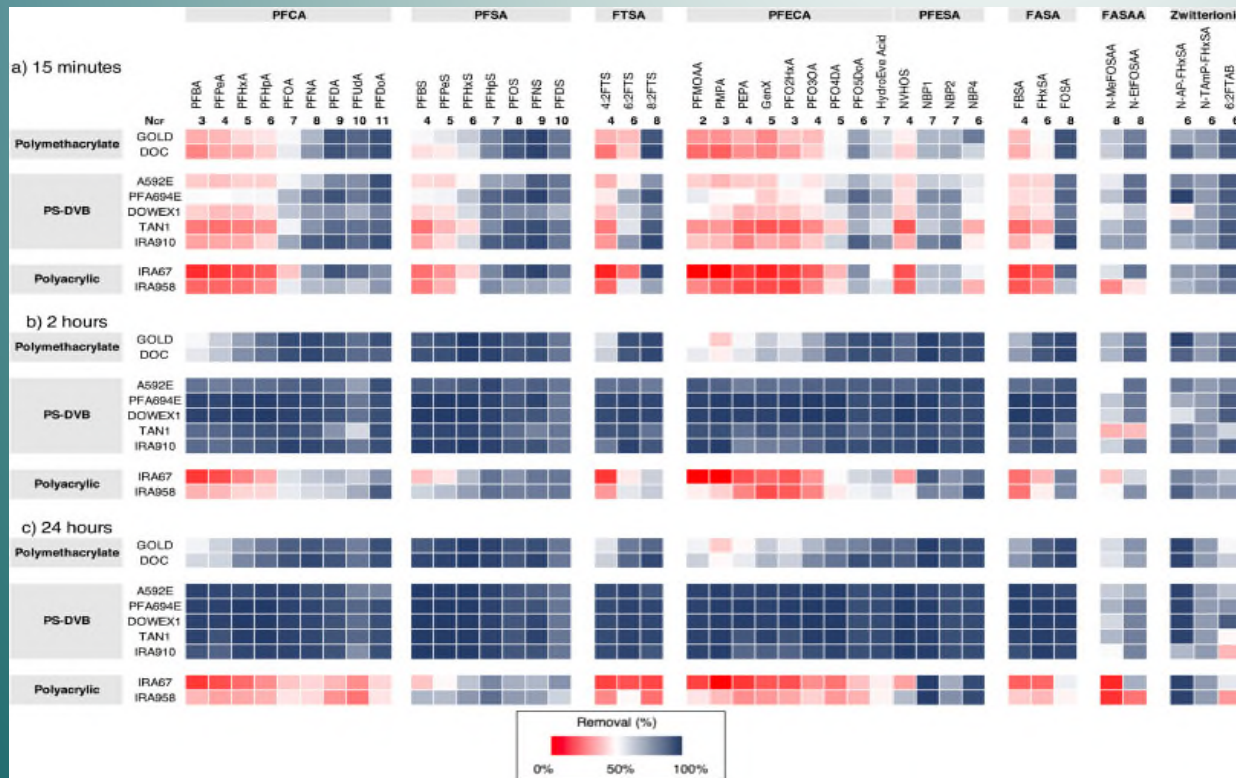
PFAS REMOVAL – IX RESIN MATERIALS

Ion Exchange (IX) Resin Materials

1) Polymethacrylate Resin 2) Polyacrylic Resin 3) Polystyrene-divinylbenzene (PS-DVB) Resin

The removal of 40 PFAS by nine IX resins with 5 mL/L resin dose in 600 ng/L PFAS-spiked groundwater at a) 15 min, b) 2 h, and c) 24 h. The numbers of fluorinated carbon atoms in each PFAS (NCF) are labeled next to each PFAS name.

PFAS-EXHAUSTED IX RESIN REGENERATION

PFOS was selected as the representative in the evaluation of IX resin regeneration

WHY PFOS?

✓ PFOA & PFOS are the two representatives of PFAS

✓ PFSA is more recalcitrant to most of the degradation methods

✓ Method works for degrading PFOS also works for PFOA

✓ In addition, my postdoc advisor found PFOS dominants in one of her resaerches:

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From the journal:
Environmental Science: Processes & Impacts

PFOS dominates PFAS composition in ambient fine particulate matter (PM$_{2.5}$) collected across North Carolina nearly 20 years after the end of its US production†
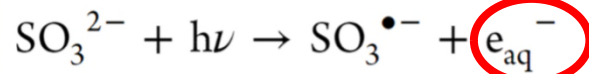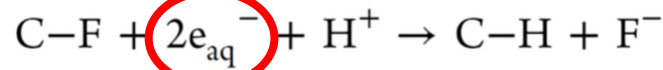
Check for updates

AQUEOUS PFOS DEGRADATION SUMMARY
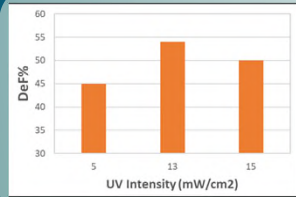
- **Thermal-chemical & Photo-chemical treatments**

Method	Chemical dose (H_2O_2, PAA, persulfate, or sulfite) (mM)	254 nm UV radiation time (hour)	Heat (Water bath)	Degradation
UV/ H_2O_2	5	1	-	None
	10	1	-	None
	50	1	-	None
	5	24	-	None
	10	24	-	None
	50	24	-	None
UV/Heat/ H_2O_2	50	24	45°C 48 hour	None
	50	24	85°C 48 hour	None
UV/PAA	10	24	-	None
	20	24	-	None
Heat/PAA	20	-	85°C 48 hour	None
UV/Heat/PAA	20	24	85°C 48 hour	None
UV/Persulfate	20	24	-	None
UV/Sulfite	20	24	-	**Yes**

$$C-F + 2e_{aq}^- + H^+ \rightarrow C-H + F^-$$

$$SO_3^{2-} + h\nu \rightarrow SO_3^{\bullet-} + e_{aq}^-$$

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AQUEOUS PFOS DEGRADATION BY UV/S

UV intensity (mW/cm^2)	Defluorination efficiency (%)
5	45
13	54
15	50

- **UV Intensity**

- **Sulfite dosage**

Condition	Defluorination efficiency (%)
With stirring	29
Without stirring	56
With stirring, all gaps sealed	52

- **Mixing**

- **Light Path Length**

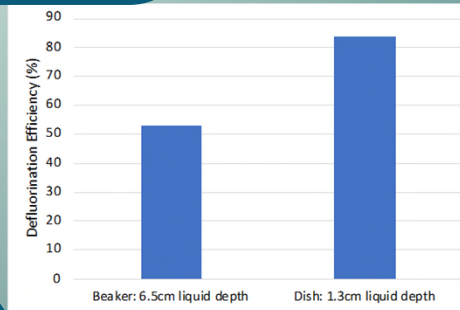- **Following Persulfate Treatment**

Optimal Settings:
12.5 ppm PFOS
In 50mL Glass Dish w/ Depth 1.3 cm
pH 9.5 (NaHCO3 +NaOH)
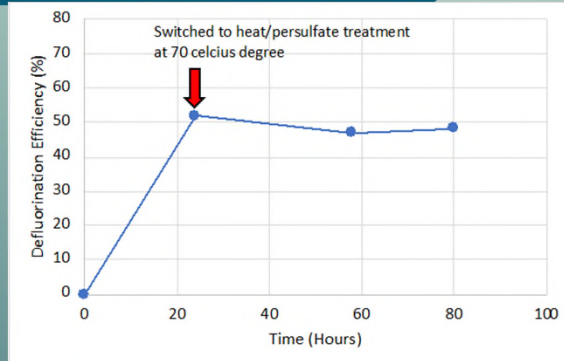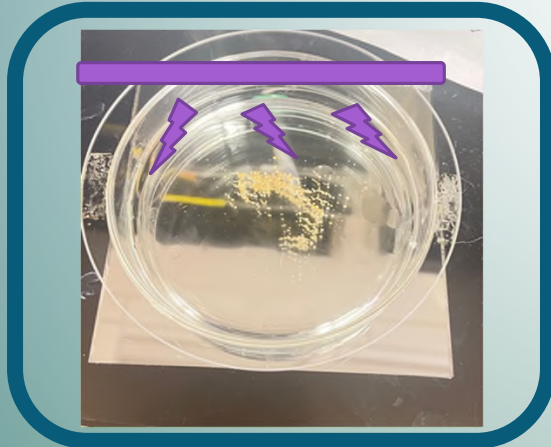UV: 15 mW/cm^2 (4x10^{-5} Einstein/L-s)
Sulfite: 20mM

HETEROGENEOUS PFOS DEGRADATION ON IX RESINS (3 PS-DVB RESINS)

❖ **UV Bar Light**

❖**UV-LED Lens**
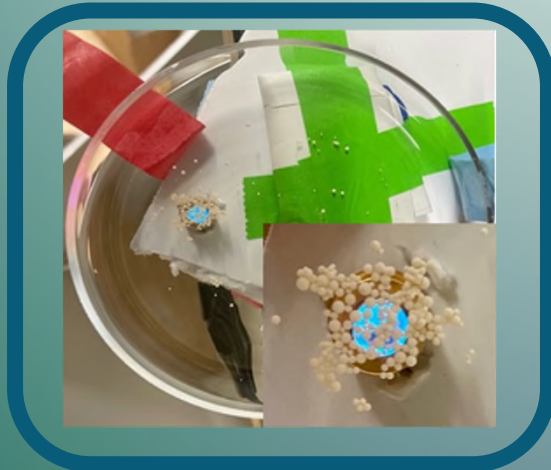
Resin	Defluorination efficiency (%)
DuPont IRA910	9.0
Purolite PFA694E	20.2
Purolite A592E	4.5
Purolite A592E with a reflection mirror	9.0

❖ PFA694E demonstrated the maximum PFOS defluorination efficiency among the three tested resins, possible because of its smallest particle size among the three resins and thus the largest surface area accepting UV radiation

❖ Very poor defluorination was observed

PFOS EXTRACTION FROM EXHAUSTED RESINS
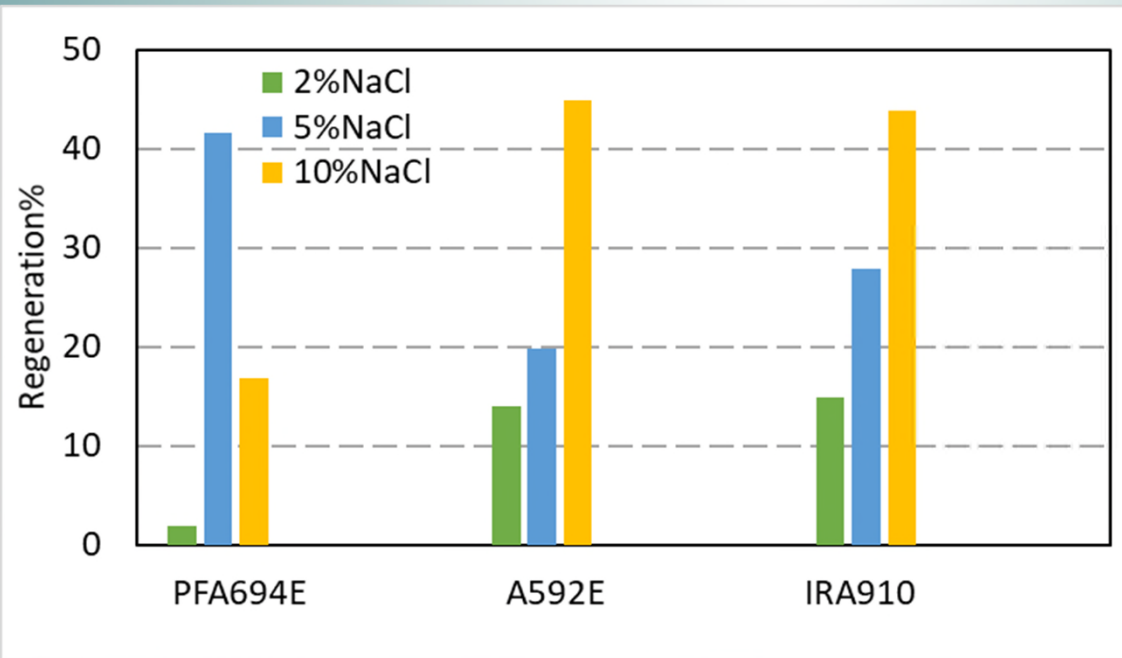
PFOS extraction by 50% methanol solution with 2, 5, or 10% NaCl from three resins (PFA694E, A592E, and IRA910).

- ➤ **DuPont IRA910 showed the best regeneration.**
- ➤ **Further increasing the methanol content to 60% greatly improved PFOS extraction from the resin, to approx. 90%.**

	50% methanol	60% methanol
5% NaCl	27.9	89.4
10% NaCl	43.9	85.4

UV/S TREATMENT OF REGENERANT
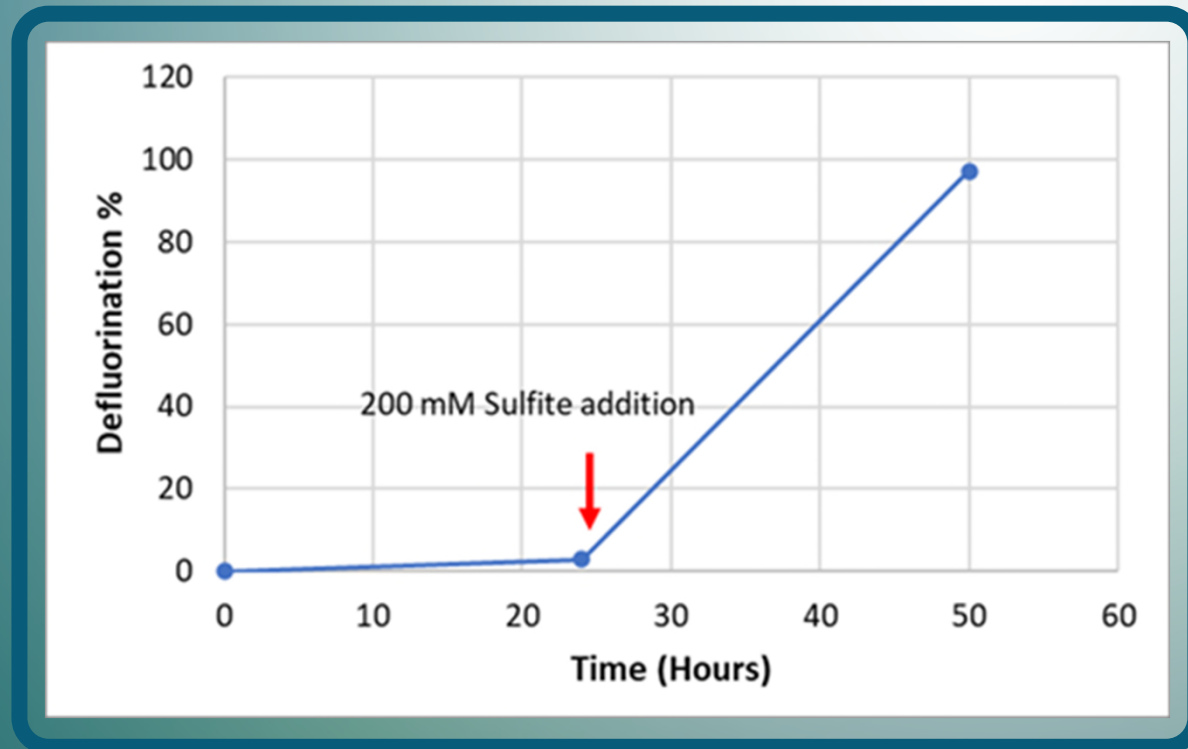
- **12.5 mg/L PFOS, 5% NaCl, and 70% methanol. UV intensity = 15 mW/cm2, initial sodium sulfite dose = 20 mM, sodium sulfite re-spike after 24 hours = 200 mM. TOO MUCH SULFITE DEMAND!!**

- **Thus, methanol% has to be reduced before UV/S treatment**

DISTILLATION OF WASTE REGENERANT
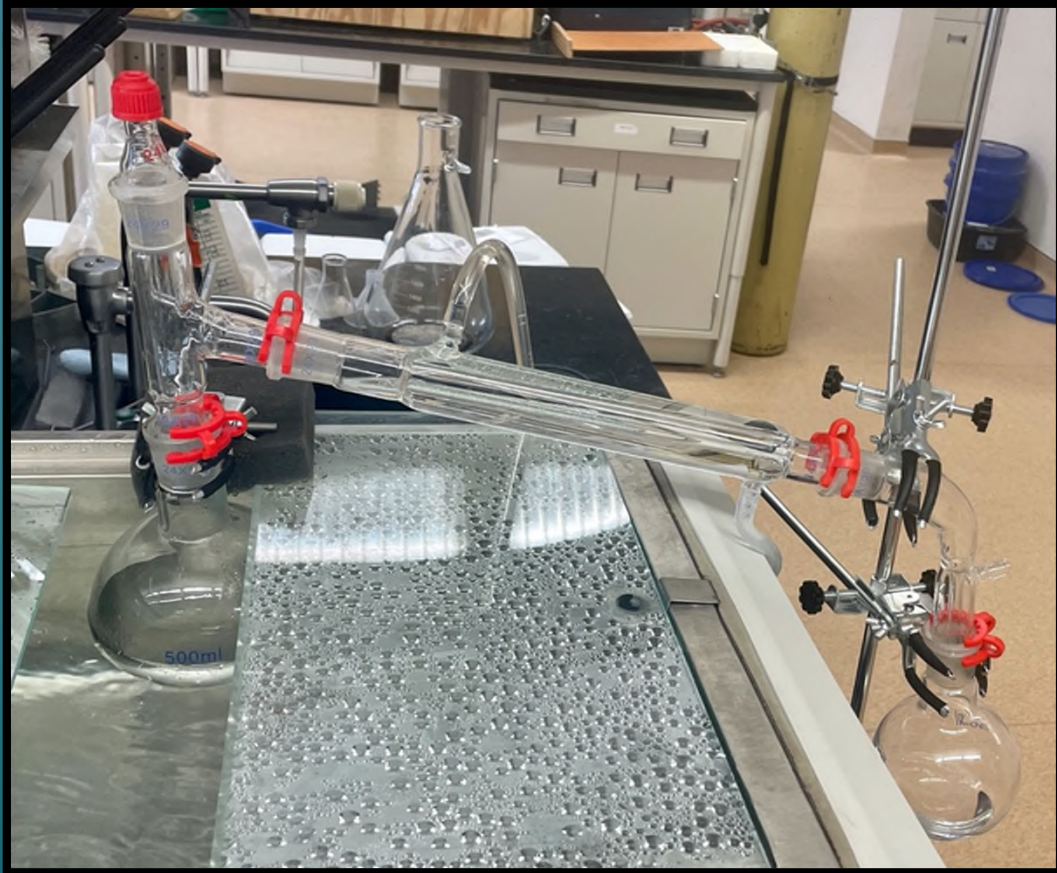
Regenerant composition	Distialltion Tempurature (ºC)	Distillation Time (hour)	Remaining methanol after distillation
60% Methanol	85	2	29.6%
60% Methanol	85	5	27.5%
60% Methanol +5% NaCl	85	5	31.4%
60% Methanol +5% NaCl	80	5	50.0%
60% Methanol +5% NaCl	75	5	59.3%

- 100 mL methanol was completely evaporated after 55 minutes of distillation at 85oC.
- Water was not distilled at all after 5 hours of distillation at 85oC.
- Due to the strong hydrogen bonding between methanol and water molecules, distillation was much more challenging in the methanol/water mixture than in pure methanol.
- And the presence of NaCl further reduced the amount of methanol that can be separated via distillation.

DISTILLATION OF WASTE REGENERANT

❖ **Simulated waste regenerant (60% methanol +5% NaCl) was spiked with a PFAS mixture and distilled at 85oC for 4 hours.**

PFAS name	Abbreviation	Concentration in remaining regenerant (µg/L)	Concentration in recovered methanol (ng/L)	Retention in remaining regenerant	Loss to recovered methanol
Perfluorobutanesulfonic acid	PFBS	44 ± 1	23 ± 14	95 ± 2 %	0.0 ± 0.0 %
4:2 Fluorotelomer sulfonic acid	4:2FTS	49 ± 1	9 ± 2	107 ± 2 %	0.0 ± 0.0 %
Perfluorohexanoic acid	PFHxA	45 ± 1	14 ± 7	97 ± 3 %	0.0 ± 0.0 %
Perfluoropentanesulfonic acid	PFPeS	43 ± 2	9 ± 5	93 ± 5 %	0.0 ± 0.0 %
Perfluoroheptanoic acid	PFHpA	45 ± 3	20 ± 26	97 ± 7 %	0.0 ± 0.1 %
Perfluorohexanesulfonic acid	PFHxS	50 ±	27 ± 14	108 ± 13 %	0.1 ± 0.0 %
6:2 Fluorotelomer sulfonic acid	6:2FTS	38 ± 6	9 ± 10	83 ± 13 %	0.0 ± 0.0 %
Perfluorooctanoic acid	PFOA	47 ± 5	21 ± 15	103 ± 12 %	0.0 ± 0.0 %
Perfluoroheptanesulfonic acid	PFHpS	44 ± 7	37 ± 34	95 ± 15 %	0.1 ± 0.1 %
Perfluorooctanesulfonic acid	PFOS	31 ± 6	51 ± 24	66 ± 12 %	0.1 ± 0.1 %
Perfluorononanoic acid	PFNA	49 ± 11	13 ± 16	106 ± 24 %	0.0 ± 0.0 %
Perfluorononanesulfonic acid	PFNS	23 ± 1	16 ± 9	49 ± 2 %	0.0 ± 0.0 %
Perfluorodecanoic acid	PFDA	44 ± 5	27 ± 23	96 ± 10 %	0.1 ± 0.1 %
8:2 Fluorotelomer sulfonic acid	8:2FTS	41 ± 4	6 ± 3	90 ± 9 %	0.0 ± 0.0 %
2-(N-Methylperfluorooctanesulfonamido)acetic acid	N-MeFOSAA	49 ± 5	1674 ± 146	106 ± 11 %	3.6 ± 0.3 %
Perfluorodecanesulfonic acid	PFDS	11 ± 0	24 ± 27	23 ± 1 %	0.1 ± 0.1 %
Perfluoroundecanoic acid	PFUdA	44 ± 3	19 ± 14	95 ± 8 %	0.0 ± 0.0 %
2-(N-Ethylperfluorooctanesulfonamido)acetic acid	N-EtFOSAA	58 ± 8	43 ± 27	126 ± 18 %	0.1 ± 0.1 %
Perfluorooctanesulfonamide	FOSA	56 ± 2	67 ± 29	122 ± 4 %	0.1 ± 0.1 %
Perfluorododecanoic acid	PFDoA	47 ± 0	119 ± 27	101 ± 1 %	0.3 ± 0.1 %

- Most of PFASs remained in the remaining regenerant.
- PFAS concentrations in the recovered methanol after distillation were minimal. Except for a few exceptions of long-chain sulfonates (PFOS, PFNS, and PFDS) known to sorb strongly to solid phases.
- 17 PFASs compounds exhibited >80% retention in the distilled regenerant, and concentrations of all PFAS evaporated to the recovered methanol phase were very low.

➢ Hence, it would be possible to reuse the recovered methanol in the next cycle of resin regeneration, while treating concentrated PFAS in the distilled regenerant in the homogeneous UV/sulfite system.

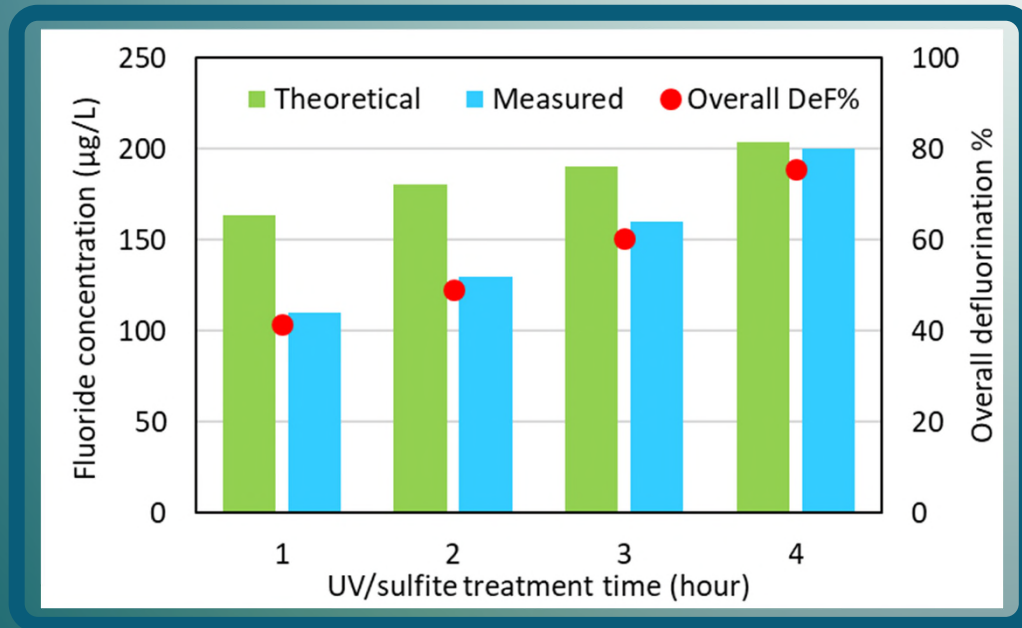# PFAS DEGRADATION AND DEFLUORINATION IN DISTILLED REGENERANT

❖ **The distilled regenerant containing 24 PFASs compounds at ~45 μg/L each was diluted by an equal volume of water and treated with UV/sulfite**
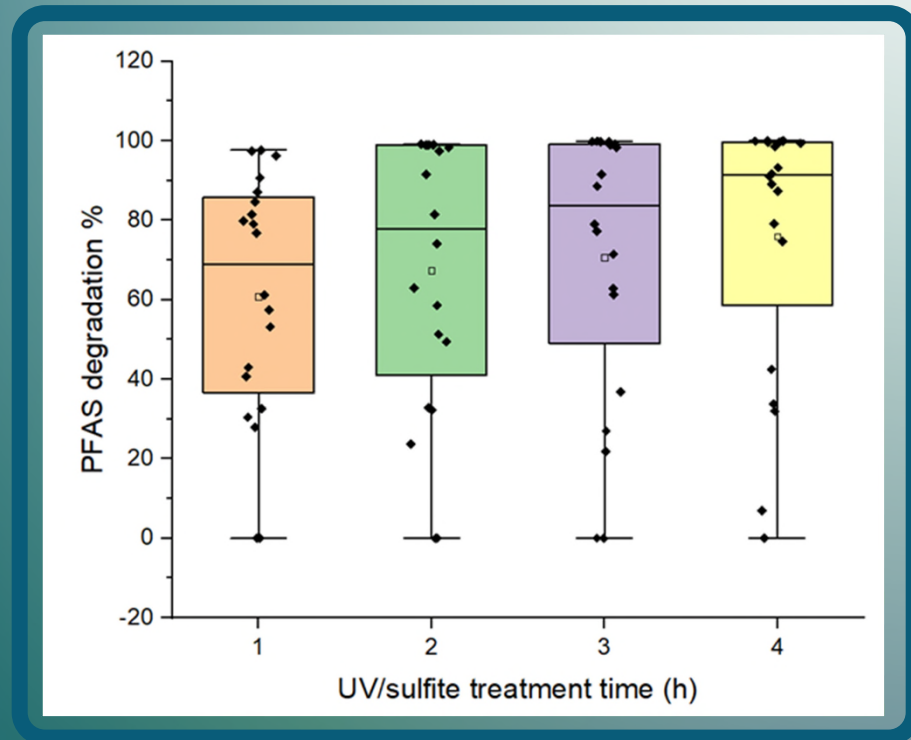
- Degradation percentage differed among PFAS compounds, most compounds were removed as the reaction time increased.
- The median degradation percentage after 1, 2, 3, and 4 hours are 69%, 78%, 84%, and 91%, respectively.
- After 4 hours, 11 PFAS achieved >90% degradation, and all compounds achieved >75% degradation except sulfonates with ≤6 perfluorinated carbons in the molecules (i.e., PFBS, PFPeS, PFHxS, 4:2 FTS, and 6:2 FTS).

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PFAS DEGRADATION AND DEFLUORINATION IN DISTILLED REGENERANT

❖ **The distilled regenerant containing 24 PFASs compounds at ~45 µg/L each was diluted by an equal volume of water and treated with UV/sulfite**

- Measured fluoride concentration closely matched the theoretical level after 4 hours of treatment, suggesting that most observed PFAS degradation went through complete mineralization.

- After 4 hours of treatment, the defluorination percentage was 76%, with the part not defluorinated mostly contributed by the short-chain sulfonates.

- Defluorination of short-chain sulfonates was demonstrated more challenging than other PFAS structures.

RESEARCH WORK CONCLUSIONS

- Peracetic acid, hydrogen peroxide, and persulfate in combination with UV and/or heat are not capable of defluorinating PFOS.
- Significant PFOS degradation (up to 98%) and defluorination (up to 84%) can be achieved by the UV/sulfite treatment in the aqueous phase.
- UV intensity, sulfite dosage, light path, and mixing conditions can affect the UV/sulfite treatment performance.
- Very limited PFOS defluorination was achieved on resins, due to limited contact between the sulfite radicals and hydrated electrons and the PFOS molecules sequestered by the resin surface.
- The IX resin loaded with PFAS can be regnerated by NaCl/methanol regenerant, and the distilled regenerant can be further treated by UV/sulfite for defluorination. Methanol separated from distillation can be reused.
- Effective PFAS recovery (>80%) from the test resin achieved for most PFASs tested by a 70% methanol/5% NaCl regenerant; high PFAS degradation (>75%) and overall defluorination (76%) were achieved in the distilled regenerant.
- The future research plan for this project includes optimizing the UV/sulfite treatment of the distilled regenerant with a focus on short-chain sulfonates and other PFAS structures yet to be tested (e.g., GenX), demonstrating PFAS removal through the whole treatment train, assessing the performance of regenerated resins, and evaluating matric effects on the treatment train.

RESEARCH & INDUSTRIAL

Industrial

- Sustainable efficient PFAS removal
- Lower cost
- Full scale data

Research

- Better material for higher removal efficiency
- Regeneration of PFAS remover for sustainability