# **REMTEC** EMERGING CONTAMINANTS SUMMIT OCTOBER 3-5, 2023

# Synergistic Defluorination and Mineralization of

# Perfluoroalkyl Substances (PFAS)

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# **BRIEF INTRODUCTION TO PFAS**

- Used as refrigerants and flame retardants
- In materials such as fabrics and food packaging
- Dominant agent for fighting fires at airports and military installations (AFFF)
- Widespread and persistent water contaminants ("forever compounds")

PFOA and PFOS are major components of AFFF



# WHY IS AFFF SO USEFUL IN FIGHTING FIRES?





- 1. AFFF rapidly spreads across the surface of the fire and "suffocates" the combustion.
- 2. It does not itself combust; it is inert to reaction.

# Properties of PFAS compounds

The C-F bond is the strongest in organic chemistry. Polar and short bond.

<b>Bond dissociation energy</b>			
Bond	kcal/mol		
C-F	105.4		
C-H	98.8		
C-0	84.0		
C-C	83.1		



Table 1	Electronegativities	F is ver of selected elem	y electronegat ents on the Paul	t <b>ive.</b> ing scale <sup>5</sup>
H (2.1)				
Li 1.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8				Br 2.8
Cs 0.7				I 2.5

# We would love to biodegrade PFAS, but it is difficult because.....

The C-F bond is so strong Perfluorination prevents enzyme access to target sites

So, let's "knock off" some F substituents by taking advantage of the the strong

# **Reductive defluorination!**





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# THE SYNERGISTIC PLATFORM

Stage 1:
H<sub>2</sub>-induced defluorination catalyzed by precious-metal nanoparticles, e.g.,

$$C_7F_{15}COOH + H_2^{\longrightarrow} C_7H_nF_{15-n}COOH + nF^{-} (1 \le n \le 15)$$

■ Stage 2: O<sub>2</sub>-induced mineralization mediated by microorganisms, e.g.,

$$C_7 H_n F_{15-n} COOH + O_2^{>} 8CO_2 + (15-n)F^- (1 \le n \le 15)$$



# THE SYNERGISTIC PLATFORM

Defluorination and mineralization of PFAS





# We also have extensive results for PFOS, and they are similar to the results for PFOA.

Less-extensive results are likewise similar for GenX, PFBS, PFNA, and PFHXS.







# Reductive Defluorination in the H<sub>2</sub>-based MCfR





# In situ Synthesis and Deposition of Pd<sup>0</sup> on gas-transfer membranes



# Catalytic defluorination in the $H_2$ -MCfR (1)

### **Pd<sup>0</sup>** is capable of catalyzing reductive defluorination of PFOA



# Catalytic defluorination in the $H_2$ -MCfR (2)

C8H2F14O2 **Products of Pd-catalyzed defluorination:** partially to totally defluorinated OAs C8H16O2  $C_8F_{15}O_2^- + 2H_{ads}^* \rightarrow C_8HF_{14}O_2^- + F^- + H^+$  $C_8F_{15}O_2^- + 4H_{ads}^* \rightarrow C_8H_2F_{13}O_2^- + 2F^- + 2H^+$ C8H8F8O2  $C_8F_{15}O_2^- + 12H_{ads}^* \rightarrow C_8H_6F_9O_2^- + 6F^- + 6H^+$  $C_8F_{15}O_2^- + 14H_{ads}^* \rightarrow C_8H_7F_8O_2^- + 7F^- + 7H^+$ C8H7F9O2  $C_8F_{15}O_2^- + 30H_{ads}^* \rightarrow C_8H_{15}O_2^- + 15F^- + 15H$ C8H3F13O2

HPLC-QTOF-N

# Catalytic defluorination in the $H_2$ -MCfR (3)

Mechanisms – Adsorption and Hydrodefluorination

![](_page_13_Figure_2.jpeg)

# Catalytic defluorination in the $H_2$ -MCfR (4)

# 70-day continuous tests

- >99% PFOA removal within one day
- Effluent PFOA 20±16  $\mu$ g/L (less than 1/3<sup>rd</sup> the EPA health-advisory level)

![](_page_14_Figure_4.jpeg)

# Catalytic defluorination in the $H_2$ -MCfR (5)

# A potential pitfall of

# monometallic catalysts:

• Slower defluorination at

increasing pH over 4

Minimal defluorination for neutral

![](_page_15_Figure_6.jpeg)

![](_page_15_Figure_7.jpeg)

# Catalytic defluorination in the H<sub>2</sub>-MCfR (6)

Density Function Theory (DFT) tells us why the large pH effect. At higher pH, the PFOA anion outcompetes H for chemisorption. Low-pH physisorption allows adsorption of reactive H.

![](_page_16_Figure_2.jpeg)

# Catalytic defluorination in the H<sub>2</sub>-MCfR (7)

# **Pd-based Bimetallic catalysts:**

• Type, coating method, and mass

ratio affect defluorination efficiency

• Promising catalysts so far:

Pd/Rh (5:0.5 mol/mol decor)

Pd/lr (2.5:2.5 mol/mol mixed)

![](_page_17_Figure_7.jpeg)

![](_page_18_Picture_0.jpeg)

# Oxidative Defluorination and Mineralization in the O<sub>2</sub>-based MBfR

![](_page_18_Picture_2.jpeg)

![](_page_18_Picture_3.jpeg)

# Microbial degradation in the O<sub>2</sub>-MBfR (1) Continuous operation:

• OA-oxidizing biofilm was able to oxidatively defluorinate mono-fluoro-OA

![](_page_19_Figure_2.jpeg)

# Microbial degradation in the $O_2$ -MBfR (2)

# **Continuous operation:**

• OA-oxidizing biofilm was able to oxidatively defluorinate 2H-PFOA

![](_page_20_Figure_3.jpeg)

# Microbial degradation in the O<sub>2</sub>-MBfR (3)

Genus-level community structure of the biofilm through the stages

Cupriavidus (7%~49%), Mesorhizobium (1%~9%), Dokdonella (1%~8%), Pseudomonas (2%~10%) and "others" (33%~57%) were dominant genera in the biofilm community.

Strains in the genus *Dokdonella* are known to biodegrade the 6:2 fluorotelomer alcohol (6:2 FTOH), a partially fluorinated 8C alcohol. Pseudomonas are famous for metabolic diversity.

![](_page_21_Figure_4.jpeg)

# Microbial degradation in the O<sub>2</sub>-MBfR (4)

The heat map of relative abundances of genes related with  $\beta$ -oxidation shows that four had relatively higher abundances (CPM > 100, red coloration) than other genes, particularly in later stages.

КО	Gene	Function	1-1	1-2	1-4	2-2	2-5	2-6
K00232	ACOXI	acyl-CoA oxidase	28.0	2.4	18.2	4.8	14.1	20.7
K00249	ACADM	acyl-CoA dehydrogenase	487.4	684.0	417.6	880.3	310.8	283.3
K00255	ACADL	ong-chain-acyl-CoA dehydrogenase	22.0	20.4	10.5	12.2	26.3	22.8
K06445	fadE	acyl-CoA dehydrogenase	97.9	98.4	115.2	95.7	90.9	133.2
K09479	ACADVL	very long chain acyl-CoA dehydrogenase	0.0	9.7	0.0	4.1	7.1	5.3
K01692	paaF	enoyl-CoA hydratase	311.9	419.9	249.4	575.3	175.8	169.7
K07511	ECHS1	enoyl-CoA hydratase	109.6	75.7	70.5	86.8	67.6	76.8
K13767	fadB	enoyl-CoA hydratase	0.0	0.0	0.0	0.0	4.6	0.0
K00022	HADH	3-hydroxyacyl-CoA dehydrogenase	3.1	0.0	10.4	0.0	0.0	0.0
K07516	fadN	3-hydroxyacyl-CoA dehydrogenase	155.2	254.4	194.9	275.9	129.7	167.3
K01825	fadB	3-hydroxyacyl-CoA dehydrogenase	11.2	9.9	9.6	13.2	7.5	6.5
K01782	fadJ	3-hydroxyacyl-CoA dehydrogenase	85.7	84.2	110.3	27.2	105.3	108.2
K07514	EHHADH	enoyl-CoA hydratase	8.2	0.0	0.0	0.0	5.1	5.7
K07515	HADHA	enoyl-CoA hydratase	0.0	0.0	3.2	0.0	0.0	0.0
K10527	MFP2	enoyl-CoA hydratase	0.0	0.0	0.0	0.0	3.7	0.0
K00632	fadA	acetyl-CoA acyltransferase	432.5	623.8	351.3	562.0	340.1	357.9
K07508	ACAA2	acetyl-CoA acyltransferase 2	1.4	0.0	0.0	9.1	3.6	0.0
K07509	HADHB	acetyl-CoA acyltransferase	11.1	0.0	5.6	5.7	7.2	3.6
K07513	ACAA1	acetyl-CoA acyltransferase 1	69.4	36.3	34.9	40.7	38.3	51.5
τ	Jnit: Counts p	er million (CPM); Color gradent:	0	50	100	200	400	900

# Microbial degradation in the $O_2$ -MBfR (5)

# Batch studies show $\beta$ -oxidation products:

• Partially fluorinated OAs were defluorinated via beta oxidation (shown):

![](_page_23_Figure_3.jpeg)

![](_page_23_Figure_4.jpeg)

![](_page_24_Figure_0.jpeg)

# The Synergistic Platform (2)

- 1. PFOA removal in the MCfR, but not in the MBfR as expected
- 2. Defluorination in the MCfR and MBfR roughly equal degrees!
- Gradual deactivation of the Pd<sup>0</sup> catalysts – due to the high PFOA input concentration (>400 ppb)
- 4. Reactivation with base treatment (gray bars).
- Lower influent PFOA concentration (83 ppb) extended the activity -- what we always see.

![](_page_25_Figure_6.jpeg)

![](_page_26_Picture_0.jpeg)

- 1. In-situ formation of robust Pd<sup>0</sup>-based catalytic films on gas-transfer membranes is simple.
- 2. Ours is first report of Pd<sup>0</sup>-catalyzed hydrodefluorination of PFOA (and PFOS and others).
- Using bi-metallic catalysts extends the pH range of Pd<sup>0</sup> catalysts.
   Pd/Rh is especially promising.
- 4. The  $H_2$ -based MCfR was able to continuously remove PFOA (and PFOS and others) below the advisory level of 70 ppt.
- The O<sub>2</sub>-based MBfR was able to defluorinate the partially defluorinated reduction products from the MCfR and mineralize fully defluorinated products.

# Acknowledgements

- Funding: SERDP (DoD), Xylem, NEWT ERC (NSF)
- Essential ASU researchers for this work: Drs. Chen Zhou, Min Long, Yihao Luo, and Jie Cheng
- Collaborators at Rice University: Dr. Mike Wong, Dr. Thomas Senftle, Dr. Welman Elias, Juan Donosa, Kimberly Heck

![](_page_27_Picture_4.jpeg)

![](_page_27_Picture_5.jpeg)

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# Perfluoroalkyl Substances (PFAS)

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![](_page_28_Picture_7.jpeg)

# Developing PFAS Source Remediation Priorities Using Predictive Groundwater Modeling

Jonathan Johnson PhD Jinjun Wang PhD PE Scott Tucker

![](_page_29_Picture_2.jpeg)

![](_page_29_Picture_3.jpeg)

# Challenge to Modeling PFAS

Modeling PFAS movement in groundwater is problematic

- Large population of PFAS compounds
- Transport properties unique to each PFAS
- Transformation from one PFAS to a different PFAS
- Lack of well constrained literature values for these transport properties such as distribution coefficients

![](_page_30_Picture_6.jpeg)

![](_page_30_Picture_7.jpeg)

# Our Endpoint

- Calibrated site-specific distribution coefficients (K<sub>d</sub>)
   PFOS, PFOA, PFNA, PFUnA, PFTrDA
- Calibrated groundwater source concentrations
- Prioritized source remediation locations among many separate source areas
- Prioritized by magnitude of impact at the Treatment Plant

![](_page_31_Picture_5.jpeg)

![](_page_31_Picture_6.jpeg)

#### **Groundwater Monitoring**

- >100 Monitoring wells
  - All 4 hydrogeologic units
  - Distributed throughout the site
- > 10 Years of water level data
- 2 Extraction wells
  - Onsite treatment plant constructed for VOCs

### Surface Water Monitoring

- Flow
- Elevation

### History of AFFF Use

- Required Insurance testing dates
- Leaking stormwater infrastructure

### PFAS Data

- Three rounds of groundwater sampling data
- Two years of treatment plant influent and data at each extraction well

Site Map

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• Soil sampling events

### Multiple AFFF Source Areas

- Each with different mixture of PFAS in soil and groundwater
- Creating a commingled plume

### Model Construction

![](_page_33_Figure_1.jpeg)

## **Flow Model Calibration**

#### **Calibration Parameters**

- Hydraulic conductivity
- River boundary
- GHB boundary

#### **Calibration Targets**

- Water level
- Streamflow

#### **Calibration Method**

- Manual
- Automated

#### Validation

- Transient data 11 years
- Water level
- Groundwater extraction

![](_page_34_Figure_15.jpeg)

![](_page_34_Picture_16.jpeg)

# **Transport Model Construction**

# Distribution Coefficient K<sub>d</sub>

• PFOS, PFOA, PFNA, PFUnA, PFTrDA

# Source Zone Identification

- Comingled plumes many sources
- Groundwater samples
- Soil samples
- Spatial distribution of plumes

# PFAS Compounds

• Mix varied with source area

# Source Strength

Varied with source area

![](_page_35_Figure_12.jpeg)

### **Transport Model Calibration**

- K<sub>d</sub> for each PFAS compound
- Source concentration for each PFAS compound at each source zone

![](_page_36_Figure_3.jpeg)

DEAS Compound	K <sub>d</sub> (L/kg)		
PFAS Compound	Calibrated Value	Literature Value*	
PFNA	0.43	0.23 – 7.94	
PFOA	0.12	0.05 – 0.79	
PFOS	0.60	0.37 – 200	
PFUnA	1.98	3.63 – 630	
PFTrDA	16.25	5.13 – only value	
*: K <sub>d</sub> values calculated based on ITRC Log(K <sub>oc</sub> ) values for PFAS mixture in solution in soil assuming f <sub>oc</sub> of 0.001			

![](_page_36_Picture_5.jpeg)

### Predictive Simulation Baseline Condition

#### Predict influent concentration

- Individual wells
- Combined influent

Each PFAS compound

Predict to 30 years into future

![](_page_37_Figure_6.jpeg)

# Effect of Potential Remediation

Reduce one source's mass by 50%

- Each PFAS compound
- Magnitude of change
  - Monitoring wells
  - Extraction wells

Predict extraction well impact over 30 years

- Change in concentration over time
- Change in mass loading over time
- Change in PFAS mix over time

#### Source remediation priorities

- Which source
- Maximize effect at the treatment plant for least cost

![](_page_38_Figure_13.jpeg)

### Effect of Potential Remedial Effort

![](_page_39_Figure_1.jpeg)

#### Simulated PFUnA Concentration Reduction In Extraction Wells

![](_page_39_Picture_3.jpeg)

### Simulated PFNA and PFUNA Mass Flux Into Treatment Plant

![](_page_40_Figure_1.jpeg)

#### **Simulated PFNA Mass Flux at Treatment Plant**

#### Simulated PFUnA Mass Flux at Treatment Plant

# Source Remediation Prioritization

Source	Ranking					
Zone	PFNA	PFOA	PFOS	PFUnA	Sum	Overall
SZ-D	2	1	2	1	6	1
SZ-C	3	3	1	2	9	2
SZ-A	1	2	4	4	11	3
SZ-B	4	4	3	3	14	4
SZ-F	5	5	6	7	23	5
SZ-E	6	7	5	5	23	5
SZ-G	7	6	7	6	26	7
SZ-H	8	8	8	8	32	8

Impact on cost of remediation at the treatment plant

At Source Zone D remedial action would have the largest impact on total PFAS influent concentration at the treatment plant At Source Zone H remedial action would have the least impact on total PFAS influent concentrations at the treatment plant

![](_page_41_Picture_4.jpeg)

![](_page_42_Figure_0.jpeg)

DEAS	Calibrated Value (L/kg)			
Compound	K <sub>d</sub>	log K <sub>d</sub>		
PFNA	0.43	-0.37		
PFOA	0.12	-0.92		
PFOS	0.60	-0.22		
PFUnA	1.98	0.30		
PFTrDA	16.25	1.21		

- Adsorption vs. Desorption
- Long-term field scale vs. Short-term lab scale
- Low concentration vs. High concentration

![](_page_42_Picture_5.jpeg)

![](_page_42_Figure_6.jpeg)

From: Rovero et. al., Ground Water Monit Remediat. 2021 September 30; 41(4): 62-75. Figure 1.

Bright ideas. Sustainable change.

![](_page_43_Picture_1.jpeg)

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# Abstract

Developing PFAS Source Remediation Priorities using Predictive Groundwater Modeling

Jonathan Johnson; Jinjun Wang; and Scott Tucker

Ramboll

Abstract

Adequately modeling PFAS movement in groundwater is problematic because of the large population of PFAS compounds, the transport properties unique to each PFAS, and the lack of well constrained literature values for these transport properties such as distribution coefficients. However, Ramboll calibrated site-specific distribution coefficients and groundwater source concentrations for PFOA, PFOS, PFNA, and longer chain PFAS compounds by fitting the model to several rounds of site groundwater monitoring data and data from the influent to an on-site treatment system. The calibrated site-specific distribution coefficients were found to be at the low end or below the range of literature values reviewed. This modeling approach was used to successfully prioritize source remediation at an AFFF site.

Site features included a fire-fighting training area and leaking stormwater infrastructure which resulted in multiple locations of soil and/or groundwater impacts, and relatively minor PFAS impacts at other locations at the site. Source areas were identified based on history of AFFF use and contaminant distribution. Each source modeled included a different combination of PFAS compounds based on the groundwater monitoring data. The on-site treatment system was previously constructed to address other COCs present at the site and consists of two primary extraction wells with combined discharge to a treatment plant.

Predictive contaminant transport simulations were run to simulate PFAS transport from the beginning of AFFF use to 30 years into the future as a baseline. Subsequently, each source area was assigned a 50% reduction of mass flux in the model to quantify the impact of remedial actions at individual source areas as measured by the changes observed in the influent of the treatment system.

Along the stormwater infrastructure, shorter chain PFAS sources closer to the extraction wells had the largest and earliest impact on concentration reduction at the treatment plant, however the treatment plant would not experience a measurable reduction in concentrations until a few years later. Magnitude of the impact at the treatment plant was primarily related the amount of mass reduction at the source, but the timing of the impact at the treatment plant was related to distance from the extraction well and the site-specific distribution coefficient for the PFAS compound. Sources further from the extraction wells would not result in measurable impacts at the treatment plant until several years to a decade after the remedial action.

Based on these PFAS modeling results Ramboll was able to recommend potential future remedial actions that would be expected to have the greatest material impact on operating costs and timeframes of the treatment system.

![](_page_44_Picture_10.jpeg)

![](_page_45_Picture_0.jpeg)

![](_page_45_Picture_1.jpeg)

![](_page_46_Picture_0.jpeg)

## A Circular PFAS Treatment System Capable of Sorption of Short and Long Chain PFASs and Aqueous Desorption, Yielding a Concentrate for Destruction

Seetha Coleman-Kammula, PhD

Center for PFAS Solutions

Wilmington Delaware (<u>www.pfasolutions.org</u>)

![](_page_46_Picture_5.jpeg)

![](_page_47_Picture_0.jpeg)

### **Center for PFAS Solutions**

#### **Governance**:

• Independent non-for-profit 501(C)(3) organization, started in 2020 with a grant from the Longwood Foundation in Delaware.

#### **Team and Core Competencies:**

- Seetha Coleman-Kammula, PhD: Polymers and Materials
- Charles Powley, PhD: PFAS Analytical Methods and Chromatography
- Stephen Lyke PhD: Chemical Engineer, Modeling
- Brian Coleman, PhD: Organic Chemist, NMR, Quality, Accreditations
- Jessica Anton, MSc: Environmental Sciences, PFAS Analysis
- Xiaohuan Qin, MSc; in Chemistry, PFAS Analysis ,Ionomer Synthesis
- Dunping Cao, PhD: PFAS Analysis, Non-targeted methods

#### **Equipment and Capabilities:**

Agilent LC-MS/MS mass spectromètre Model G6495C plus Agilent HPLC Model 1290

Agilent Technologies Gas Chromatography-Mass Spectrometer (GC-MSD) [Agilent Technologies 6890-GC 5973N-MSD]

Two PromoChrom Automated SPE

Accredited by NELAP, Certified by NJ, and DE

![](_page_47_Picture_17.jpeg)

![](_page_48_Picture_0.jpeg)

### Activities, Partners and Funders

<b>PFAS Analytical Services</b> Methods 537.1, 533	Delaware Public Drinking Water Suppliers
<b>R&amp;D on Prevalence of PFAS</b> Method 1633 TOP Assay	PFAS on farms treated with biosolids. 3-year study, 25 Pennsylvania farms, partner with Stroud Water Research Center; funded by USDA
	PFAS in wastewater; partner with Delaware Rural Water Association; funded by the US EPA
Water Treatment Solutions	PFAS treatment studies for 5 public water systems; funded by Delaware Department of Public Health
	Ionomer development; partner with University of Delaware; funded by SERDP

![](_page_48_Picture_3.jpeg)

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![](_page_49_Picture_0.jpeg)

### Why Yet Another PFAS Sorbent?

### Because we believe there is room for sorbents with lower energy and chemical inputs and lower green house gas and hazardous waste outputs from Cradle to Cradle

Maintain the highest value of all resources used from cradle to cradle as long as possible - a definition of Circular Economy

![](_page_49_Picture_4.jpeg)

![](_page_49_Picture_5.jpeg)

![](_page_50_Figure_0.jpeg)

![](_page_51_Picture_0.jpeg)

# Ionomers as PFAS Sorbents Have Not Been Investigated

#### What are Ionomers?

- <u>Ionomers</u> are polymers containing both electrically neutral and ionized groups.
- <u>Polymers</u> are macromolecules composed of a large number of repeating units called <u>monomers</u>.
- Depending on the type of monomers, there are different types of Ionomers
- Our Ionomers are solid water insoluble cationic polymers containing amines and cationic ammonium sites.

![](_page_51_Picture_7.jpeg)

![](_page_52_Picture_0.jpeg)

### **Todays Presentation**

- Chemistry and Structure of our Ionomer in this study called HG-1
- SERDP Limited Scope Proposal
- Relative rates and sorption capacities of HG-1, GAC and Ion Exchange resin in deionized water with:
  - PFBA, PFBS, PFOA and PFOS individually and
  - Mix of all 4 PFAS at high and low (environmentally relevant) concentrations.
- Sorption of PFAS from well water contaminated with AFFF by HG-1
- Desorption and concentration using an all-aqueous formulation
  - Desorption data
  - Concentration factor
- Destruction of PFAS in the desorbed solution using Hydrothermal Alkaline Treatment

![](_page_52_Picture_12.jpeg)

![](_page_53_Figure_0.jpeg)

- Made in a single step from two commercially available chemicals (monomers)
- 2. Tunable for short and long chain PFAS by varying the length of the two monomers from C5 to C12.
- 3. Potential for high sorption capacity -the entire polymer mass has amine sites distributed along and within the polymer- no resin core
- 4. Potential to influence

**desorption** by varying amount of weak base and strong base (quaternary amine) sites.

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![](_page_54_Picture_0.jpeg)

#### Proof of Concept Data Used for SERDP Limited Scope Proposal

![](_page_54_Figure_2.jpeg)

- C<sub>4</sub>-C<sub>12</sub> PFAS (0.1 mg/L) were all removed from water by 10 mg of HG-1, compared to Filtrasorb® 400, and CalRes 2304 (10 mg each) in 1 hour
- Long-chain (>C<sub>9</sub>) PFAS sorbed to inner walls of polypropylene vials ( known as bottle effect)
- IX and GAC removed 40–80% of PFAS from water relative to blank, with GAC slightly outperforming IX for most PFAS
- Ionomer (HG-1) removed all PFAS completely except 2 C<sub>4</sub>, 1 C<sub>10</sub> and 1 C<sub>12</sub> (all *ca*. 90%)

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![](_page_55_Picture_0.jpeg)

### SERDP Limited Scope, One year Project, Goals etc.,

#### Goal: Démonstrate that Cross-linked polymeric Ionomers:

- 1. Sorb short and long chain PFAS faster than GAC and IX
- 2. PFAS can be desorbed by raising pH, without using organic solvent
- 3. On-site destruction of PFAS and regeneration of ionomers for reuse

# Tasks: Using mix of PFBA, PFBS, PFOA, PFOS on GAC, IX and Ionomer, using batch scale tests

- Measure relative rates of sorption
- Measure relative sorption capacity
- Find aqueous desorption reagents
- Conduct Hydrothermal destruction

#### Hypothesis

- PFAS "heads" interact with amine sites via ionic (ion-exchange and in-pair) forces and the tails via Van der Waals forces.
- They swell and shrink in response to change in pH sorb and desorb to release PFAS with change in pH

![](_page_55_Figure_14.jpeg)

![](_page_56_Picture_0.jpeg)

### Kinetics of PFOA sorption by Ionomer HG-1, Vs GAC, IX

![](_page_56_Figure_2.jpeg)

HG-1 kinetics orders of magnitude faster than GAC Filtrasorb 400 and IX (CalRes 2304).

We used 10x more dosing of GAC and IX to obtain more comparable rates.

Below are pseudo-2<sup>nd</sup> order rate constants fitting our data compared with published values .

Material	k <sub>obs</sub> ,
	g/mg/hr
HG-1	1700
CCAC (Xiao, et al., 2017)	60
PEI-f-CMC (Ateia, et al., 2018)	12.8
DFB-CDP (Xiao, et al., 2017)	2.9

Testing conducted in 1 µg/L PFOA at 10 mg/L except PEI-f-CMC was tested at 20 mg/L.

![](_page_56_Picture_8.jpeg)

![](_page_57_Picture_0.jpeg)

Kinetics HG-1 vs GAC at environmentally relevant concentrations 10 ppb each of PFBA, PFBS, PFOA and PFOS

![](_page_57_Figure_2.jpeg)

HG-1 sorbs all 4 PFAS at a faster rate than GAC in mixture of 4 PFAS at environmentally relevant concentrations

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![](_page_58_Picture_0.jpeg)

### Kinetics of sorption HG-1 at high concentrations of Mix of 4 PFAS

![](_page_58_Figure_2.jpeg)

Kinetics of mix of 4 PFAS. at 10ppb by HG-1, GAC and IX. Relative rate constants First order L/g/hr

![](_page_58_Figure_4.jpeg)

![](_page_58_Picture_5.jpeg)

![](_page_59_Picture_0.jpeg)

#### PFOA Sorption Capacity of HG-1, GAC, IX and others

HG-1 capacity for PFOA exceeds that of GAC and IX resins.

HG-1 can sorb up to 10% its mass (100 mg/g) of PFOA, a capacity that is significantly greater than the comparison sorbents

![](_page_59_Figure_4.jpeg)

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![](_page_60_Picture_0.jpeg)

HG-1 Isotherms in Mixture of PFBA, PFBS, PFOA, PFOS

![](_page_60_Figure_2.jpeg)

Sorption capacity of HG-1 in mg/g (measured at 1ppb) is higher than GAC for all four PFAS and higher than IX for PFOA and PFOS

	GAC	IX	
	<b>F400</b>	<b>CR2304</b>	HG-1
PFBA	0.26	2.59	0.43
PFBS	0.60	>10	5.10
PFOA	0.35	0.17	1.42
PFOS	0.23	0.02	0.47
4 PFAS	1.44	>13	7.42

![](_page_60_Picture_5.jpeg)

![](_page_61_Picture_0.jpeg)

### Well water contaminated with AFFF tested with HG-1 Total PFAS 2733 ppt

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SUM

![](_page_61_Figure_2.jpeg)

![](_page_61_Picture_3.jpeg)

![](_page_62_Picture_0.jpeg)

### Desorption by an Aqueous Formulation Using Batch Tests

	Total % PFAS desorbed	
	based on PFAS Sorbed	Time
τν π	23.2	lhr
	59.6	22hr
IX B	30.3	lhr
	58.5	22hr
IX C	13.9	lhr
	42.4	22hr
HG-1	92.2	lhr
	90.7	22hr

![](_page_62_Picture_3.jpeg)

![](_page_62_Picture_4.jpeg)

![](_page_63_Picture_0.jpeg)

Batch Desorption Data Indicate 1000x Concentration is Possible

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![](_page_63_Figure_2.jpeg)

Desorption data is for one sorbent loading only.

we don't yet have data at sufficiently different sorbent loadings. But we anticipate isotherms in the desorption solution with slopes close to 1, like the adsorption isotherms.

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![](_page_64_Picture_0.jpeg)

#### Destruction by Hydrothermal Alkaline Treatment of Desorbed PFAS in the Aqueous Formulation

Studied by Dr. Pei Chiu at University of Delaware

 $R^2 = 0.9698$ 

**OCTOBER 3-5, 2023** 

![](_page_64_Figure_3.jpeg)

![](_page_65_Picture_0.jpeg)

### **Conclusions-Observations**

- Ionomer labelled HG-1 sorbed mix of PFBA, PFBA, PFOA and PFOS, faster than GAC (Filtrasorb 400) and IX resin (CalRes 2304)
- Sorption capacity of HG-1 for PFOA exceeds that of other sorbents tested
- Sorption capacity of HG-1 (measured at 1ppb) is higher than GAC for all four PFAS and higher than IX for the longer chain PFAS
- Preliminary data shows an all-aqueous formulation for desorption and concentration is feasible and can be improved
- Demonstrated defluorination of PFAS in the de-sorbed liquid formulation= the additive does not interfere with destruction

![](_page_65_Picture_7.jpeg)