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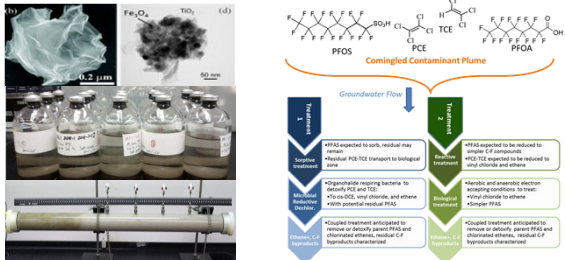
Objectives

Develop *in situ* remediation approaches to treat groundwater plumes containing mixtures of PFAS and chlorinated ethenes, and to understand potential synergies associated with combined remedies:

Specific Objectives:

- Develop and evaluate highly sorptive and reactive materials capable of sequestering and/or degrading PFAS and chlorinated ethenes.
- Develop biological systems to treat chlorinated ethenes and PFAS reaction byproducts following sorptive and reactive treatments.
- Evaluate the performance of the combined physicochemical and biological systems implemented as reactive barrier walls and downhole recirculating wells.

Technical Approach



Schedule

Overall Project Plan	2018	2019	2020	2021
Task 1: Develop and Evaluate Reactive Materials for PFAS Treatment				
A. Develop Sorptive Materials	X	X	X	X
B. Develop Reactive Materials	X	X	X	X
Task 2: Develop Treatment Systems for Chlorinated Solvents and PFAS				
A. Characterization of Reaction Products	X	X	X	X
B. Impacts on Organohalide Respiration	X	X	X	X
C. Coupled Biological Treatment Systems	X	X	X	X
Task 3: Evaluation of Coupled Physicochemical and Biological Treatment Systems				
A. Sorptive and Reactive Column Tests	X	X	X	X
B. Coupled Biological Column Tests	X	X	X	X
C. Treatment Train Testing	X	X	X	X
Task 4: Research Translation and Project Reporting				
A. Quarterly Progress and Interim Reports	X	X	X	X
B. Translational Outreach Activities	X	X	X	X

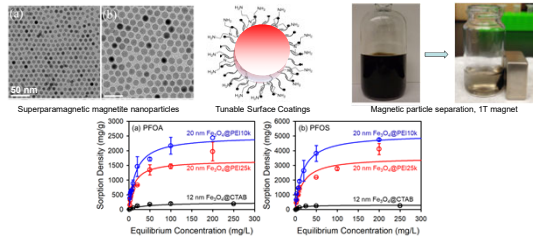
★ **GO/NO-GO Decisions:** ¹ able/unable to development highly sorptive materials (12/31/19) ² able/unable to develop reactive materials (7/31/20)

Results to Date

Task 1: Reactive Materials for PFAS Treatment

Subtask 1A: Development of Highly Sorptive Materials

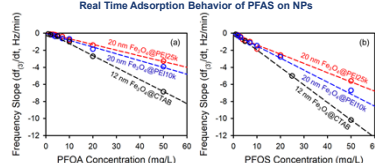
- High surface area with favorable surface chemistries – tailored functionality for targeted PFAS binding
- Base-type functionality + hydrophobic functionality - Polyethylenimine (PEI) polymers (varied MW)



• PEI coated iron oxide (12 nm) NPs showed significant sorption capacities for PFOA (left) and PFOS (right) as measured by QCM-D. PEI10k=10,000 MW PEI polymer; PEI 25k =25,000 MW polymer; CTAB = Cetyltrimethylammonium Bromide.

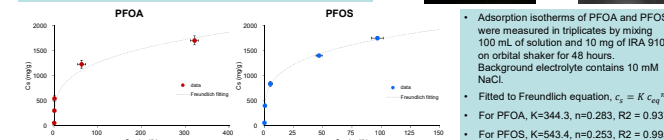
Subtask 1A: Development of Highly Sorptive Materials (continued)

• The rate of adsorption for PFOA (left) and PFOS (right) on PEI coated NPs was relatively lower than that of CTAB coated NPs. We hypothesize that this is a function of PEI polymer (with higher MW) configuration on the NP surface



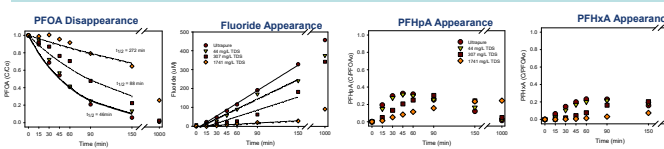
Subtask 1A: Development of Highly Sorptive Materials (Ion Exchange Resin)

- Although our prior work demonstrated that stabilized powdered activated carbon (S-PAC) dramatically enhances PFOA and PFOS sequestration in 40-50 mesh Ottawa sand, the sorption capacity was much lower for shorter-chain length PFAS (e.g., perfluorobutane sulfonate (PFBS)).
- To address this issue, we evaluated several ion exchange resins (IXR). Amberlite IRA 910 was selected due to its outstanding sorption capacity.
- A stable suspension of ion exchange resin (S-IXR) for IRA 910 was developed with a nonionic surfactant Pluronic® F-127.



Subtask 1B: Development of Highly Reactive Materials

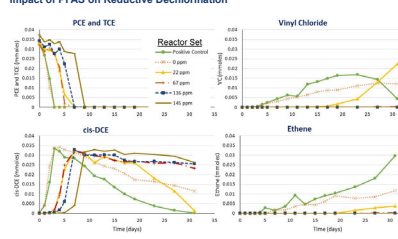
- Heat-activated persulfate (85°C) degradation of PFOA was monitored with positive control, F-mass balance, and daughter product formation.
- Impact of total dissolved solids (TDS) on rates of PFOA degradation by persulfate oxidation was studied by comparing with *unbuffered* solutions.
- PFOA degradation rate was unchanged at 44 mg/L (1.1 mM IS) TDS, reduced at 307 (9.8 mM IS) and 1,741 mg/L (43.4 mM IS) TDS (HCO₃⁻, CaCl₂, NaCl, MgSO₄, KCl).
- Rates of PFHpA and PFHxA formation and disappearance were unchanged in solutions containing 44 mg/L TDS, but were reduced in solutions containing 307 and 1,741 mg/L TDS.



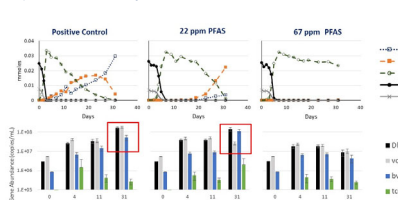
Task 2: Develop Treatment Systems for Chlorinated Solvents and PFAS

Subtask 2B: Assess Impacts of PFAS on Organohalide Respiration

Impact of PFAS on Reductive Dechlorination



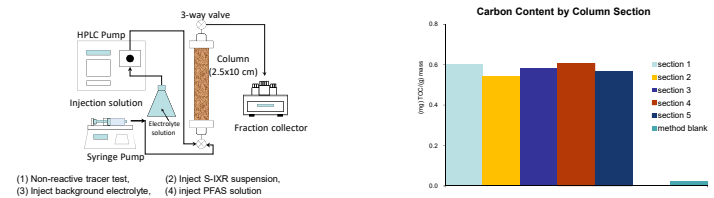
Impact of PFAS on Activity and Growth of Dhc



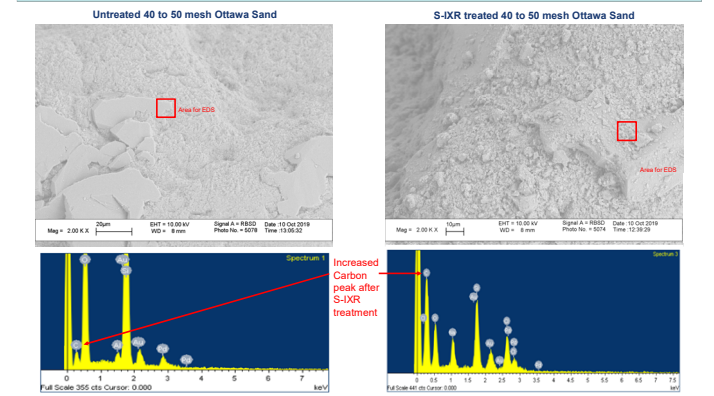
- 22 mg/L PFAS did not inhibit total *Dhc* growth, but shifted population from cells harboring the *bvcA* gene (*cis*-DCE to ethene) to cells harboring the *bvcA* gene (*DCE isomere* to ethene)
- 67 mg/L PFAS reduced total *Dhc* 16S rRNA and reductive dehalogenase (RdhA) gene abundance by greater than 1 order-of-magnitude
- Total *Dhc* abundance increased one order of magnitude less in reactors with 67 mg/L or greater PFAS compared with reactors with 0 or 22 mg/L PFAS
- *bvcA*-harboring cells were preferred in reactors with 22 mg/L PFAS

Task 3: Evaluation of Coupled Treatment Systems

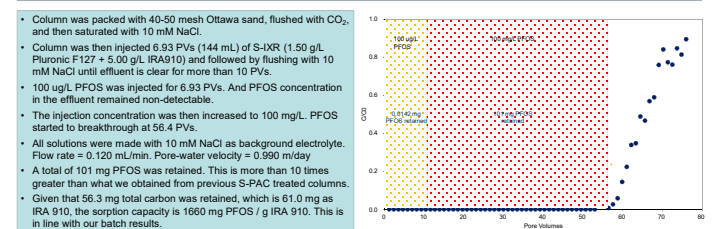
Subtask 3A: Sorptive and Reactive Column Tests



- (1) Non-reactive tracer test.
 - (2) Inject S-IXR suspension.
 - (3) Inject background electrolyte.
 - (4) Inject PFAS solution
- Column was packed with 40-50 mesh Ottawa sand, flushed with CO₂, and then saturated with 10 mM NaCl.
 - Column was then injected 6.93 PVs (144 mL) of S-IXR (1.5 g/L Pluronic F127 + 5 g/L IRAB10) and followed by flushing with 10 mM NaCl until effluent is clear for more than 10 PVs.
 - Packed sand was dissected into 5 segments of roughly 19.0 g of each and dried in oven for 6h at 80 °C.
 - Triplicates of each section were analyzed by TOC-SM. 56.3 mg as TC was retained. And distribution of carbon content within the column was even.



- Sand from S-IXR treated column was compared with untreated 40 to 50 mesh Ottawa Sand under imaging of a Zeiss LEO 1530 VP Scanning Electron Microscope (SEM) coupled with an Oxford Instrument 7426 Energy Dispersive Spectrometer (EDS) system.
- Surface of S-IXR treated sand was covered with clusters of particles while surface of untreated sand was smooth and clean.
- The peak height of carbon of treated sand greatly surpassed the peak height of carbon of untreated sand. And the elemental constituent of carbon was 32.7% by weight and 54.9% by atom, compared to the value of 5.59% by weight and 10.1% by atom of untreated sand.



- Column was packed with 40-50 mesh Ottawa sand, flushed with CO₂, and then saturated with 10 mM NaCl.
- Column was then injected 6.93 PVs (144 mL) of S-IXR (1.50 g/L Pluronic F127 + 5.00 g/L IRAB10) and followed by flushing with 10 mM NaCl until effluent is clear for more than 10 PVs.
- 100 µg/L PFOS was injected for 6.93 PVs. And PFOS concentration in the effluent remained non-detectable.
- The injection concentration was then increased to 100 mg/L. PFOS started to breakthrough at 56.4 PVs.
- All solutions were made with 10 mM NaCl as background electrolyte. Flow rate = 0.120 mL/min. Post-water velocity = 0.390 m/day
- A total of 101 mg PFOS was retained. This is more than 10 times greater than what we obtained from previous S-PAC treated columns.
- Given that 56.3 mg total carbon was retained, which is 61.0 mg as IRA 910, the sorption capacity is 1660 mg PFOS / g IRA 910. This is in line with our batch results.

Lessons Learned

- Synthesized nanomaterials with net positive PEI coatings exhibit large adsorption capacities for PFOA and PFOS, while showed relatively lower adsorption rate compared to CTAB coated nanoparticles.
- Ion exchange resin Amberlite IRA 910 was selected as an upgrade over PAC due to stronger adsorption capacity for PFAS, as well as its stability in suspension.
- Heat-activated persulfate effectively degraded PFOA (*t*_{1/2} = 45 min) and formed reaction byproducts (PFHpA, PFHxA); increasing ionic strength reduced PFOA degradation above 10 mM
- PFAS mixtures inhibited organohalide respiration and reductive dechlorination; not all PFAS have an equal impact, effects are *Dhc* strain specific
- Injection of S-IXR in 40-50 mesh Ottawa sand column resulted in PFOS sequestration with greater sorption capacity compared to previous S-PAC treated columns, which was also consistent with batch results.

Acknowledgements:

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