TETRA TECH

Determination of Fluorine Mass Balance During Sonolytic Treatment of Per and Polyfluorinated Alkyl Substances

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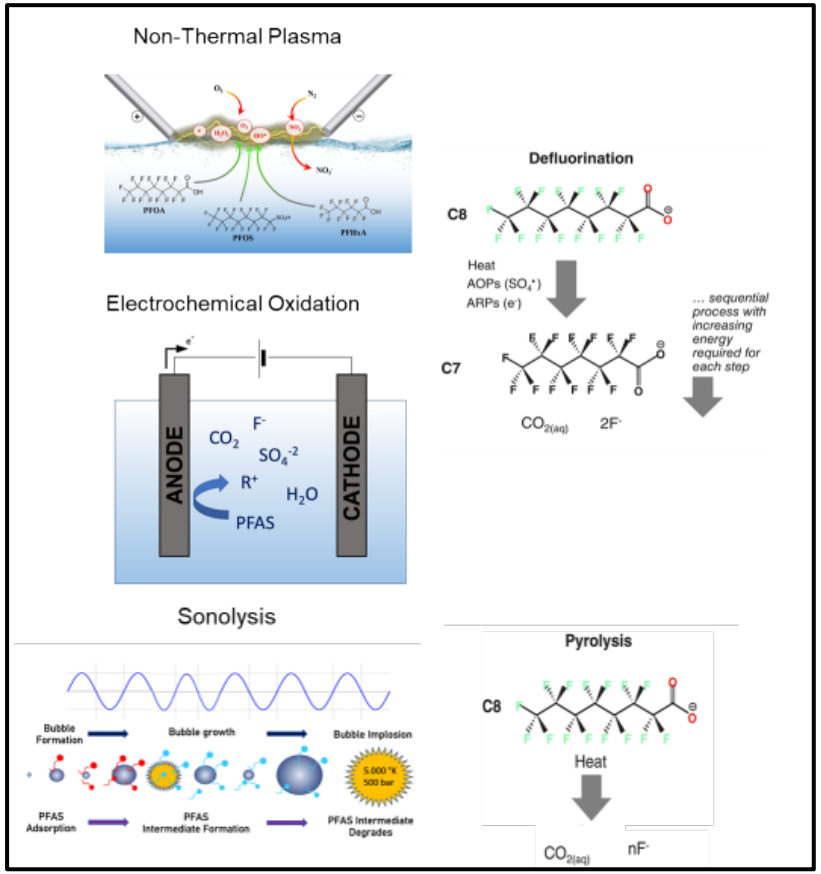
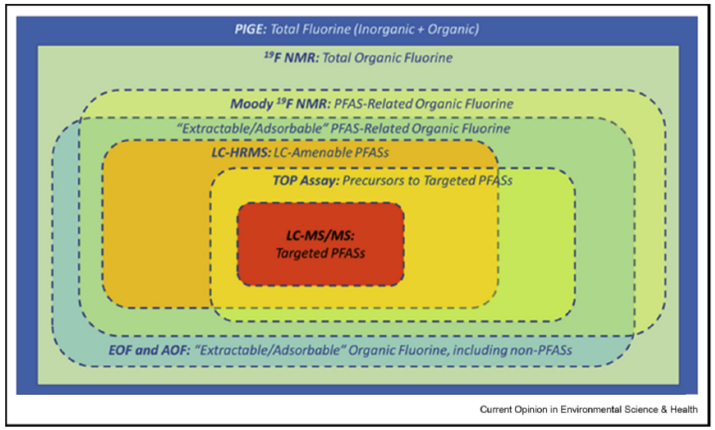
Problem Statement and Significane

- PFAS are difficult to break down - **“Forever Chemicals”**
  - Only Filtration Technologies used
- Destructive technologies mineralize PFAS into benign products through two mechanisms
  - Sequential Defluorination
  - Pyrolytic Destruction



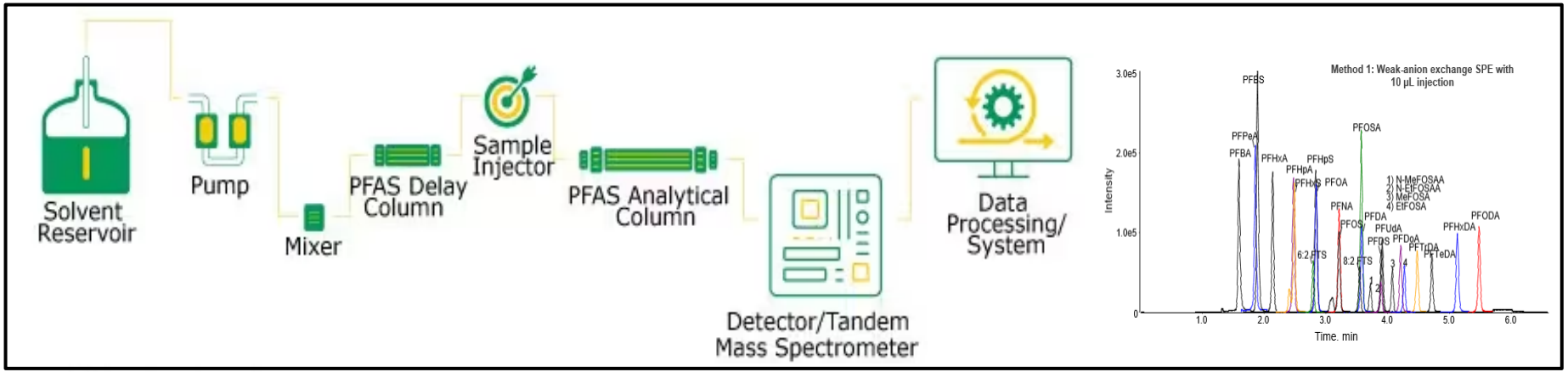
Fluorine Mass-Balance: Goal

- The overall objective of this project is to perform a *mass balance for fluorine using three independent analytical techniques:*
  - ***Targeted PFAS Analysis****: Triple quadrupole* liquid chromatography mass spectrometer *(LC-MS),*
  - ***Total Organic PFAS****:* ^{19}F -nuclear magnetic resonance (^{19}F *-NMR) and*
  - ***End-Product Formation****: Fluoride-* ion selective electrode (F-*ISE)*



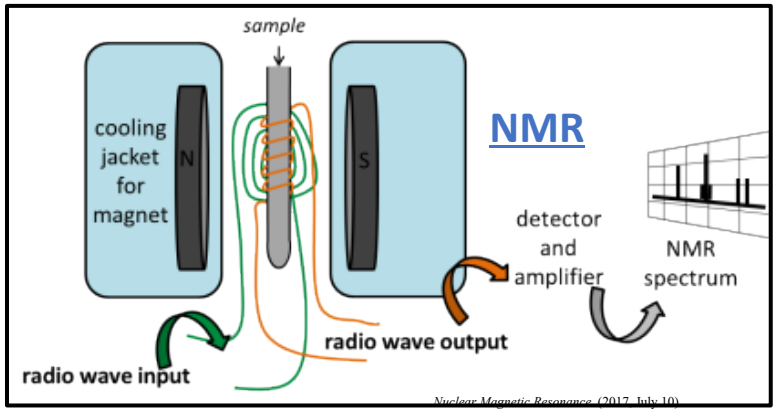
Targeted PFAS Analysis: LC-MS-QQQ

- PFAS are a **family** of 5000 plus chemicals
  - ➢ All contain fluorine
- LC-MS/MS is a very versatile, robust, and sensitive methodology use to determine 25 PFAS by EPA Method 533.

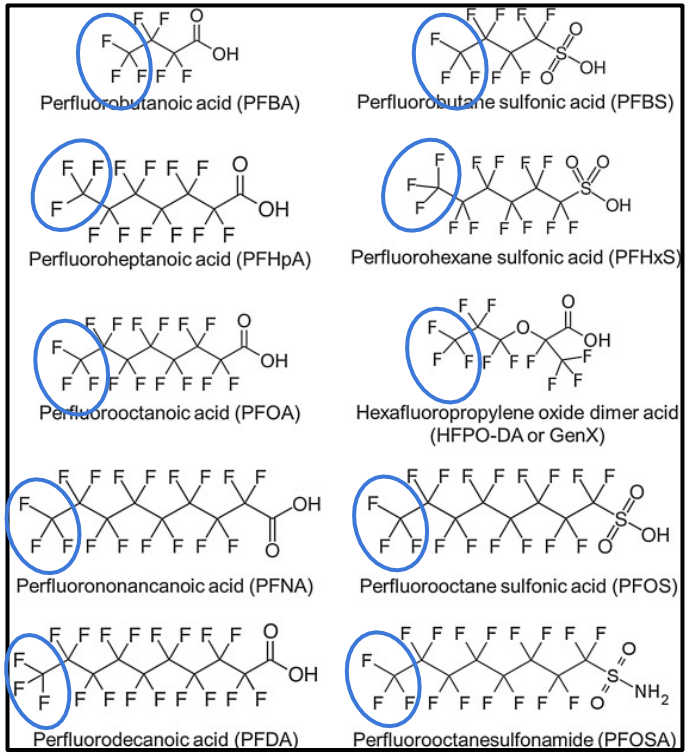


Total Organic PFAS: ^{19}F

- PFAS share terminal CF3 which produces the same NMR response

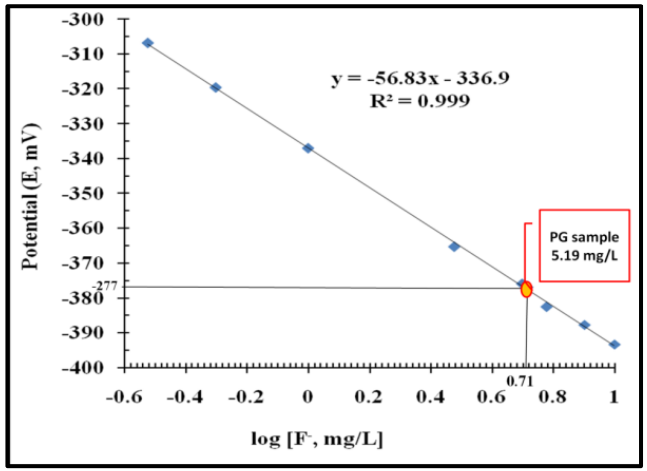


Nuclear Magnetic Resonance. (2017, July 10). https://chembam.com/techniques/nmr/



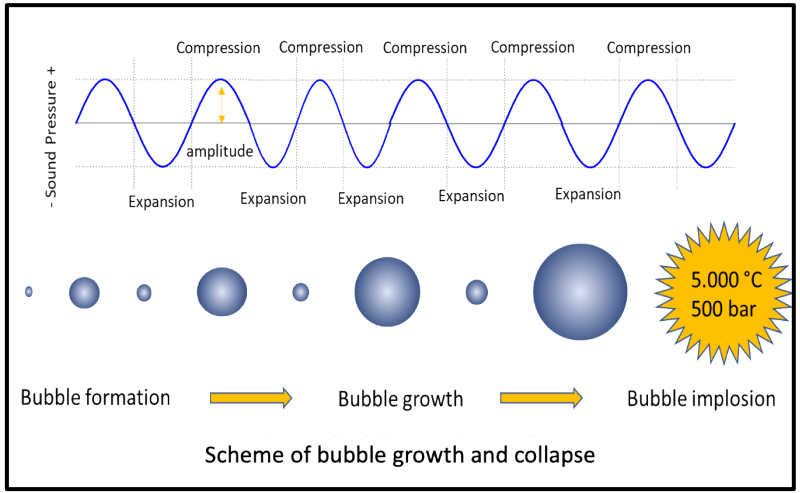
End-Product Formation: F-ISE

- Complete defluorination of PFAS yield in formation of biennial products: $SO_4^{2-}, CO_2, CO,\ and\ F^-$.
- Measure free fluoride ions in aqueous solutions quickly, simply, accurately and economically.



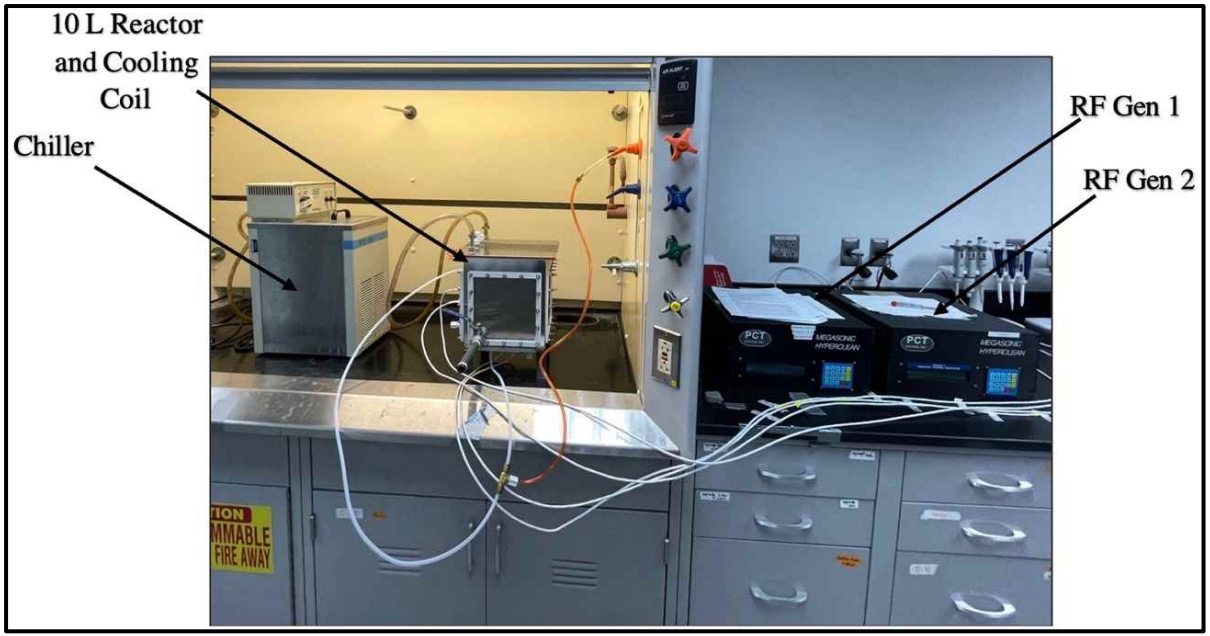
Sonolytic Process

- Acoustic cavitation is a transient process involving the formation, growth, and collapse of micro to nano-sized bubbles (MNBs) in a liquid subjected to intense sound waves
- The extreme conditions created by collapsing cavitation bubbles cause pyrolysis and radical reactions, degrading contaminants



Scheme of bubble growth and collapse

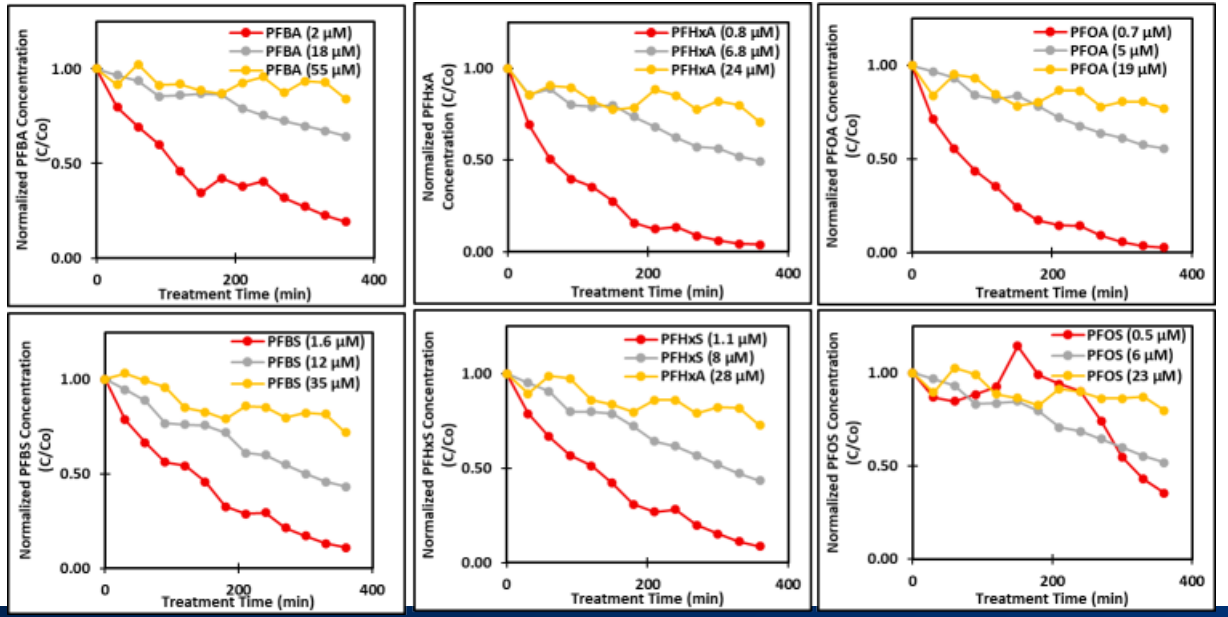
Intermediate scale (10 L) Ultrasonic Reactor



Effect of Initial Concentration PFAS

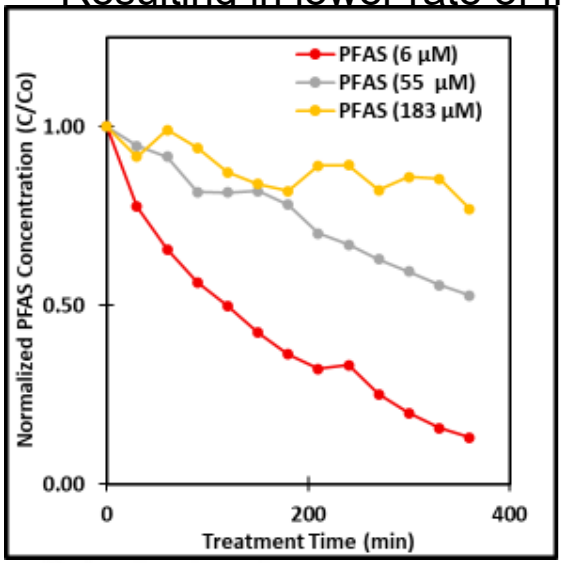
- Long-chain PFAAs, decrease in the concentration faster than short-chain PFAAs
- PFBA presented the slowest removal rate of the PFAAs detected

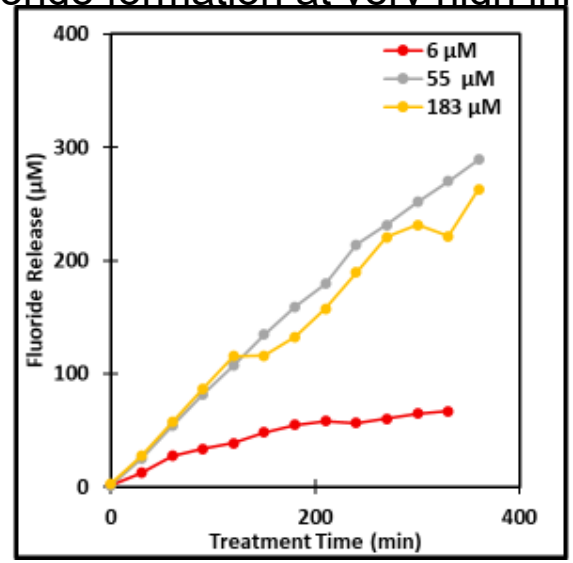
- Although the PFCAs are less hydrophobic and surface active than PFSAs with the same carbon atoms, the carboxylates were degrading faster than sulfonates

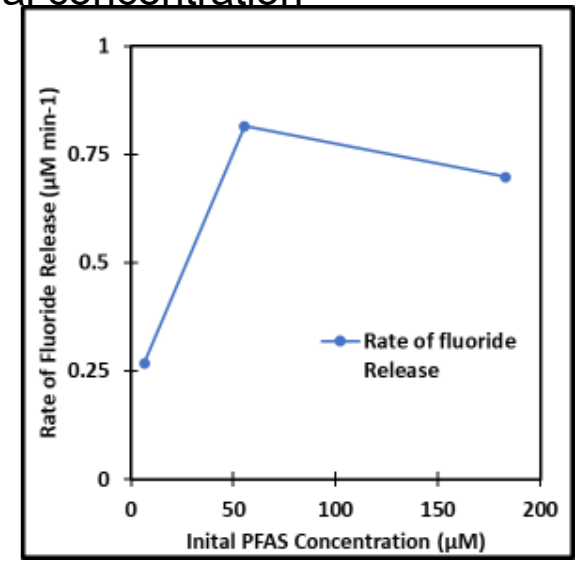


Effect of Initial Concentration PFAS (Cont.)

- Higher concentration, beyond the saturation of the cavitation bubble can exhibited excessive foaming.
- Resulting in lower rate of fluoride formation at very high initial concentration

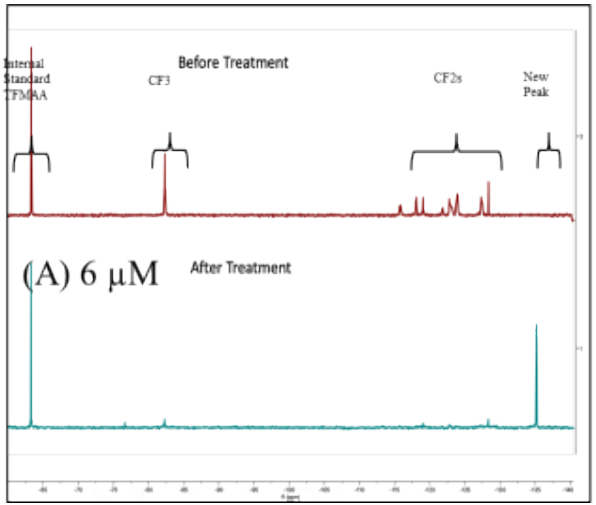


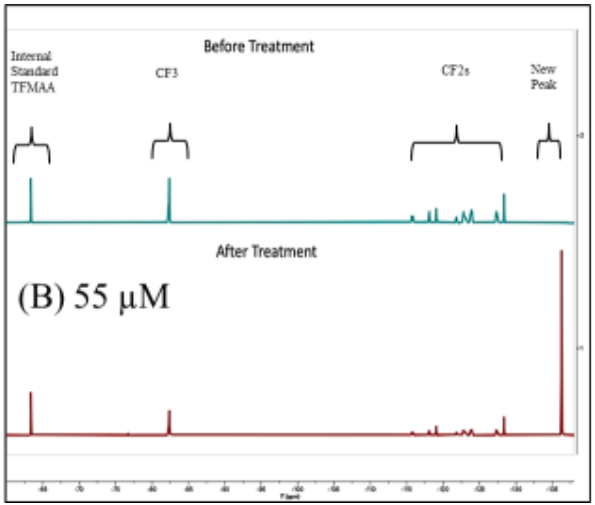


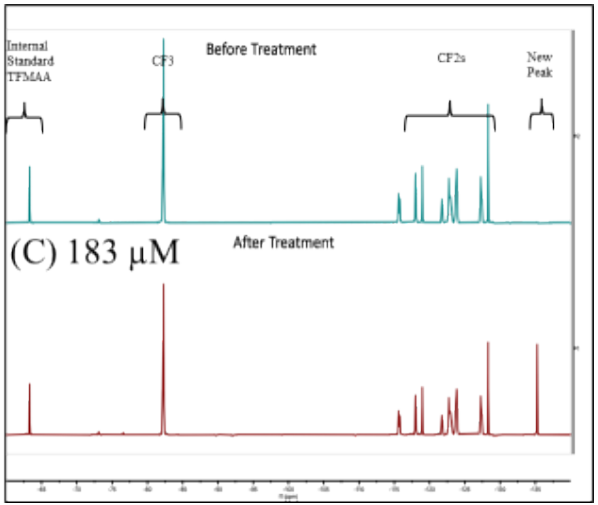


^{19}F NMR to Quantify PFAS Degradation

- The spectrum saw a reduction in the CF3 other CF2 response in terms of peak height and peak area
- The emergence of a signal at -135 ppm after treatment might corresponds to the formation of fluoride

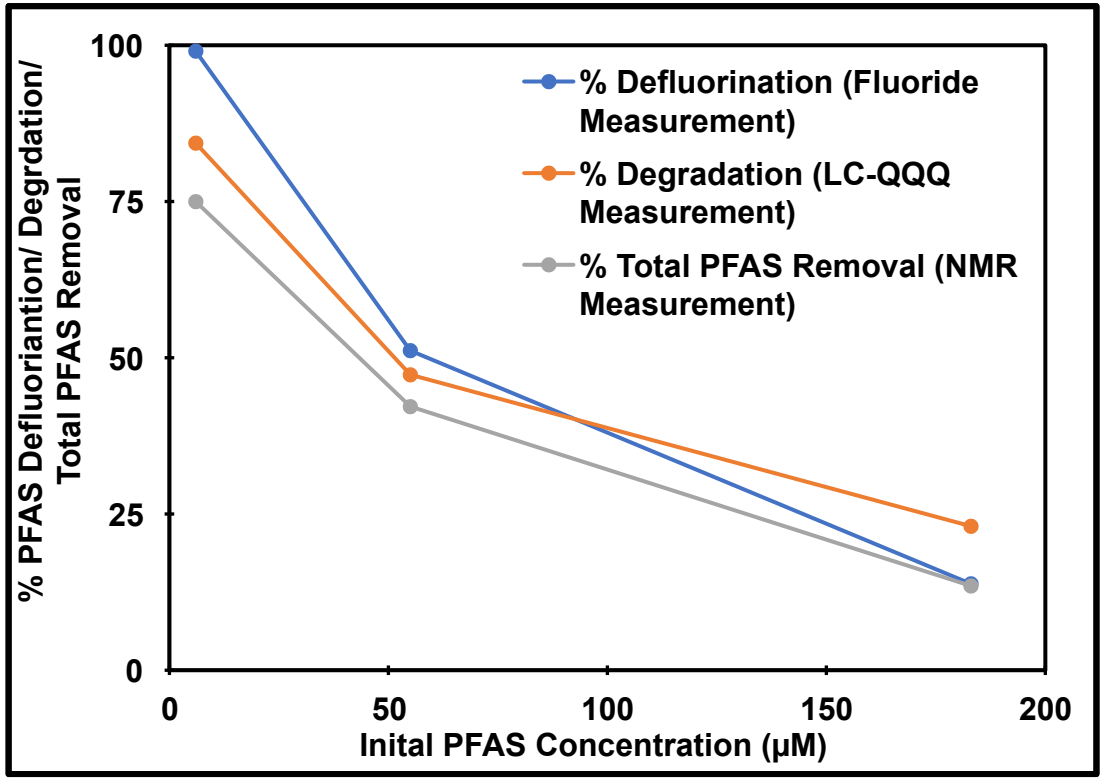






Fluorine Mass Balance

- A near complete mineralization of PFAS in the waste stream, without an increase in the concentration of short-chain PFAS.



Release of Fluoride and Sulfate to Quantify PFAS Degradation

- The measurement of sulfate SO_4^{2-} is not a reliable technique for performing the mass-balance and quantifying the end-product for sonolytic treatment of PFAS.
- Sulfate can exist in different speciation and can also exit the system as sulfur dioxide gas.

	Fluoride Release			Sulfate release		
Initial PFAS Concentration (µM)	Measured Using Ion Chromatography (µM)	Measured Using Ion Selective Electrode(µM)	RPD (%)	Measured Using Ion Chromatography (µM)	Expected Sulfate Release Using LC MS Analysis (µM)	RPD (%)
6	280.72	288.95	2.89	7.39	13.95	61.46
55	244.30	262.00	6.99	6.56	21.13	105.26
183	83.26	106.84	24.81	0.62	2.81	127.27

Summary and Conclusion

- The performance of the intermediate reactor was assessed for treating synthetic high concentration PFAS waste at three different initial concentrations: 6, 55, 183 µM
- NMR can detect **all** organic PFAS and PFAS byproducts
- The mass balance for fluorine was performed using three analytical techniques: triple quadrupole liquid chromatography- mass spectrometry, a fluoride ion selective electrode, and F19-nuclear magnetic resonance
- The result showed near complete mineralization of PFAS in the waste stream, without increase in the concentration short-chain PFAS

Team Member

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Thank You!
Questions?