The future of water purification by electrical discharge plasmas

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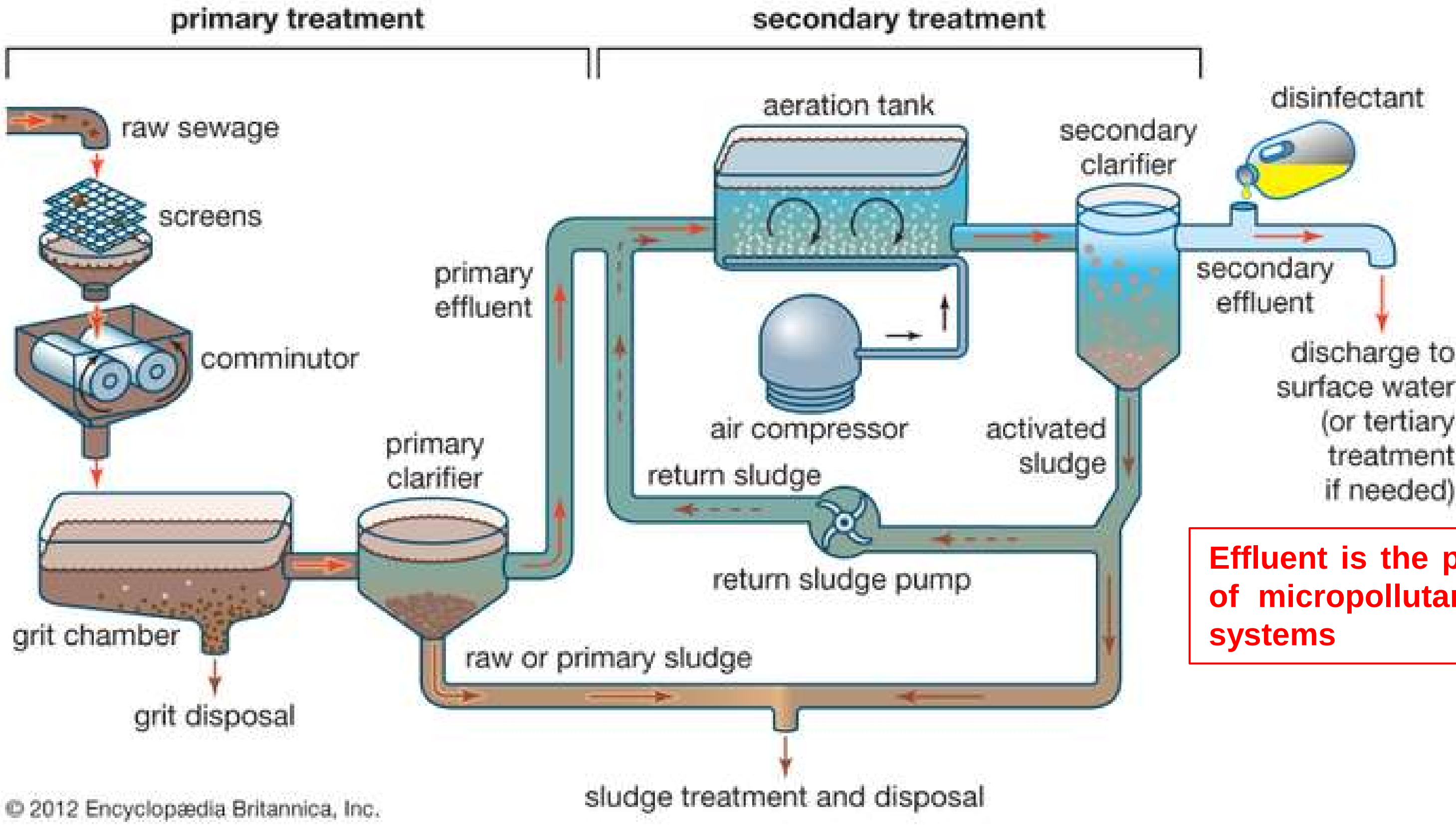
Conventional large scale wastewater treatment



Effluent is the primary source of micropollutants in aquatic systems

- Capacities range between 1 and 100+ million gallon per day

https://www.britannica.com/technology/wastewater-treatment/Primary-treatment

The problem

- Ineffective removal of micropollutants

Solutions:

- Prevention by application of products without micropollutants or only with micropollutants which are easily removed

  Near impossible

- Reassessment and optimization of current treatment processes

  Economically feasible but ineffective towards persistent micropollutants. The removal of those requires additional secondary or tertiary treatment steps.

- Pretreatment of hospital and industrial effluents

  A range of destructive and non-destructive techniques has been investigated.

Vanraes, Patrick *et al*. *Plasma science and technology–progress in physical states and chemical reactions* (2016): 428-478.

Existing and emerging water treatment technologies

- **Non-destructive technologies** (membrane filtration, ultraviolet irradiation, biological filtration, and ion exchange)
- **Destructive technologies** (Advanced Oxidation Processes-AOPs)

	Oxidation potential (V)
Oxygen (O_2)	1.23
Hydroperoxyl radical ($HO_2\cdot$)	1.44
Hydrogen peroxide (H_2O_2)	1.78
Ozone (O_3)	2.07
Atomic oxygen (O)	2.43
Sulfate radical anion ($SO_4^{\cdot -}$)	2.50
OH Radicals ($OH\cdot$)	**2.80**
Fluorine (F_2)	2.87

- Pharmaceuticals
- Industrial Chemicals
- Toxic Compounds
- Pesticides
- Personal Care Products
- Endocrine Disrupting Compounds

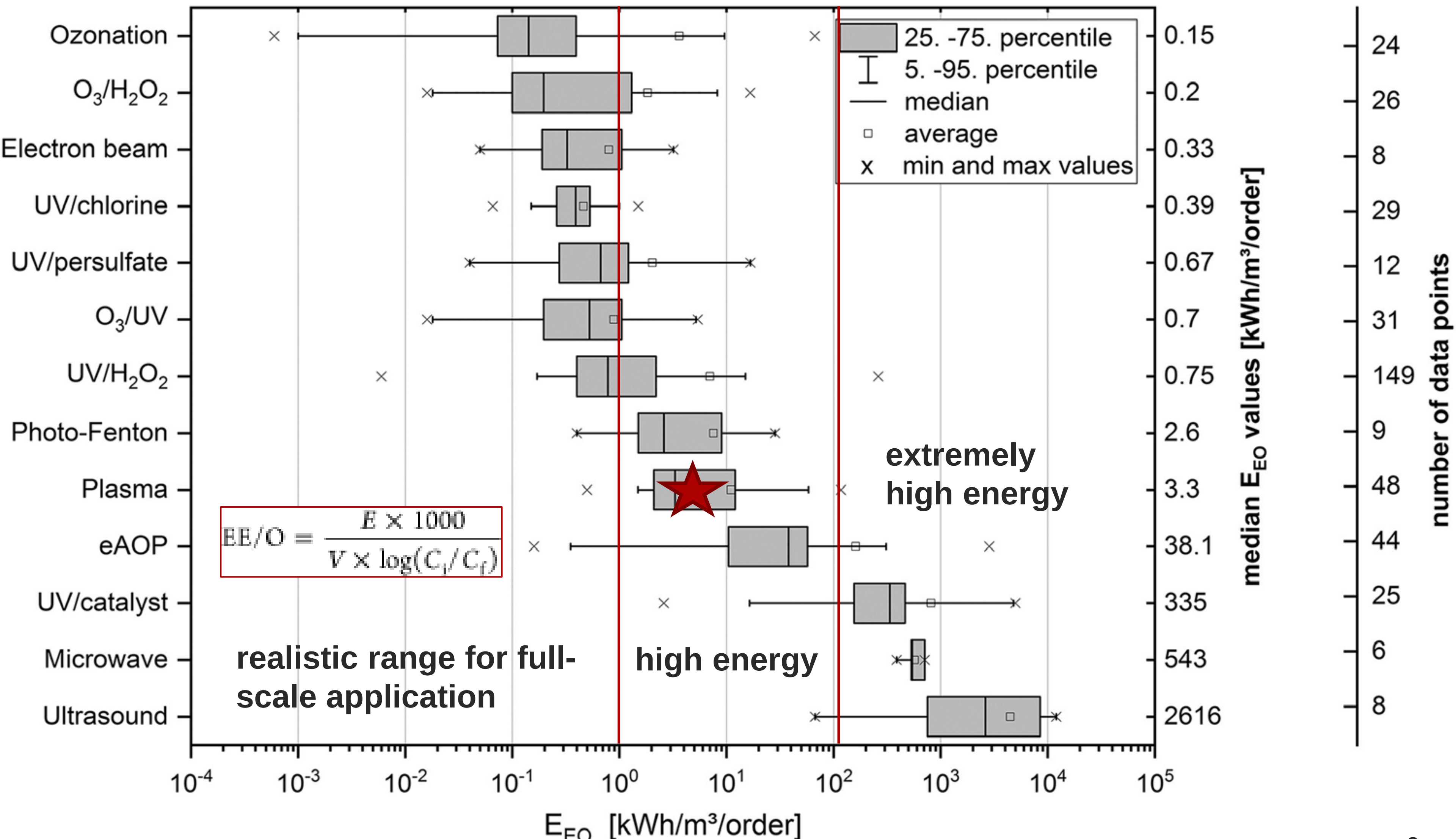
Ultimately, the optimal water treatment technology achieves regulatory effluent limitations at a reasonable cost.

Buthiyappan, A., *et al*. (2016). *Reviews in Chemical Engineering*, *32*(1), 1-47.

Electrical discharge plasma for water treatment

- Wide variety of reactive oxidative species (OH, H_2O_2, O_3).
  - *Also present for other AOPs*
- Existence of reactive reductive species (e.g., e_{aq}^{-}) and ions.
  - *Specific to plasma treatment and advantageous*
- Highly non-selective process.
  - *As is every other AOP*
- Physical effects such as generation of ultraviolet-range radiation (UV), shockwaves capable of inducing cavitation, and in some cases high temperatures capable of thermally decomposing molecules.
  - *No experimental evidence that these processes aid treatment*
- No chemical additives are required.
  - *Many other AOPs also do not require chemicals*

Plasma-based water treatment: comparison with a range of AOPs



Miklos, David B., *et al. Water research* 139 (2018): 118-131.

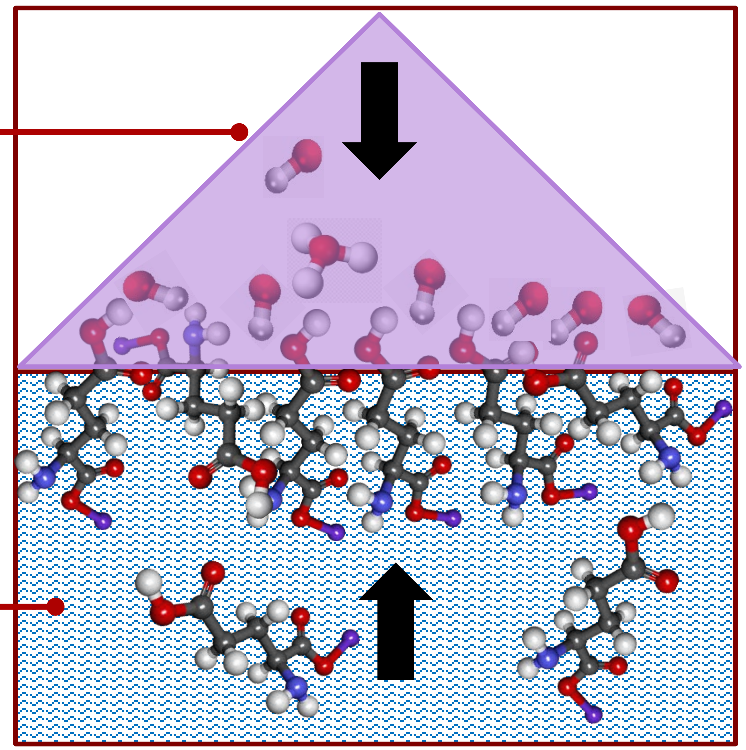
The problem (and the solution) is the heterogeneous nature of the plasma

Plasma area (reactor design)
Operational parameters
Process gas
Types and fluxes of reactive species

Solute-species reactivity

Type of compound
Compound starting concentration
Ionic composition
Means of bulk liquid mass transport (reactor design)

PLASMA SIDE

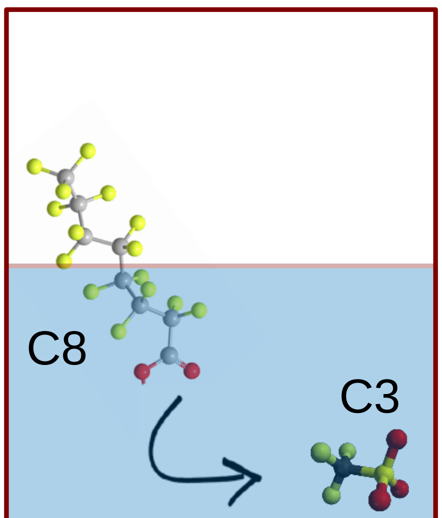


LIQUID SIDE

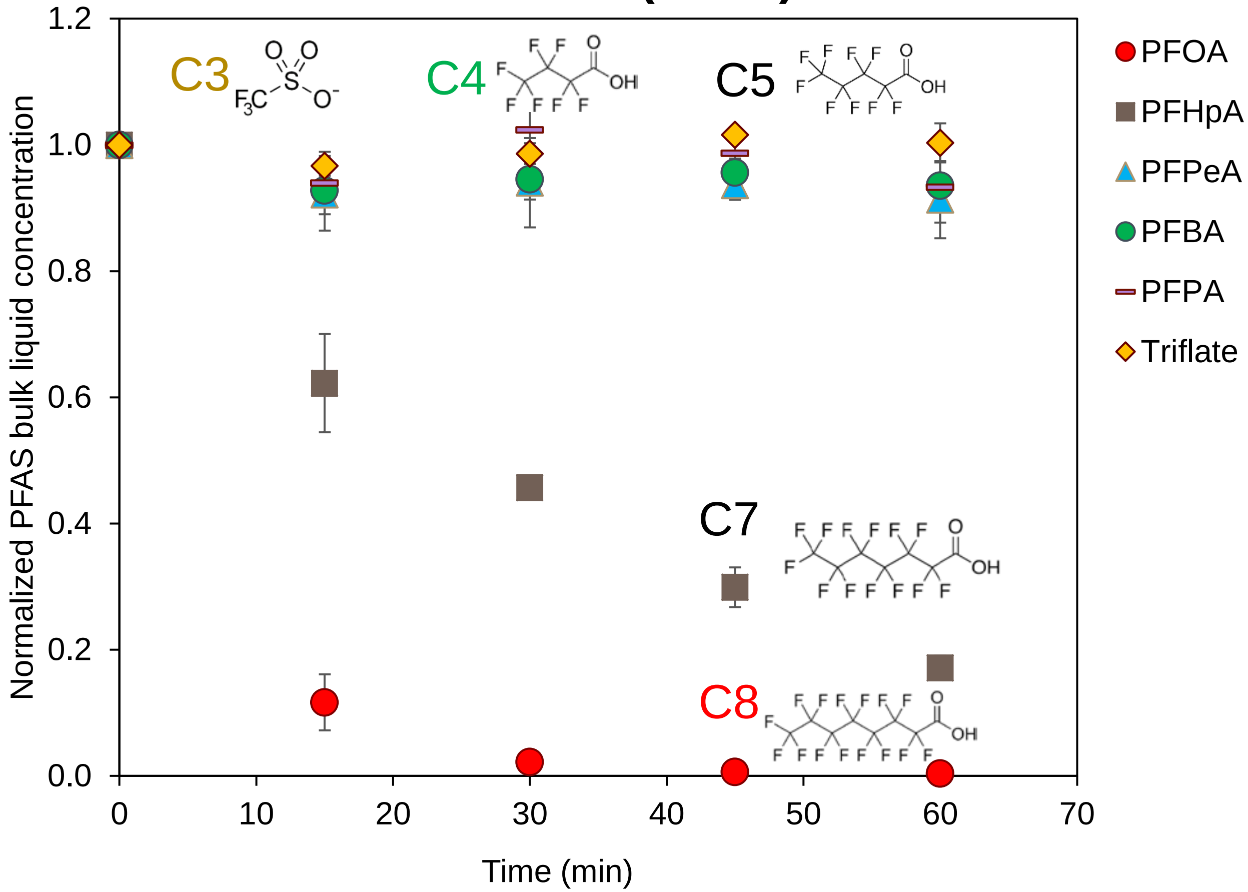
Objective: effectively utilize plasma-generated species by concentrating the contaminants at the plasma-liquid interface over a large surface area.

How do properties of compounds effect plasma reactor performance?

Point-ring reactor with argon bubbling

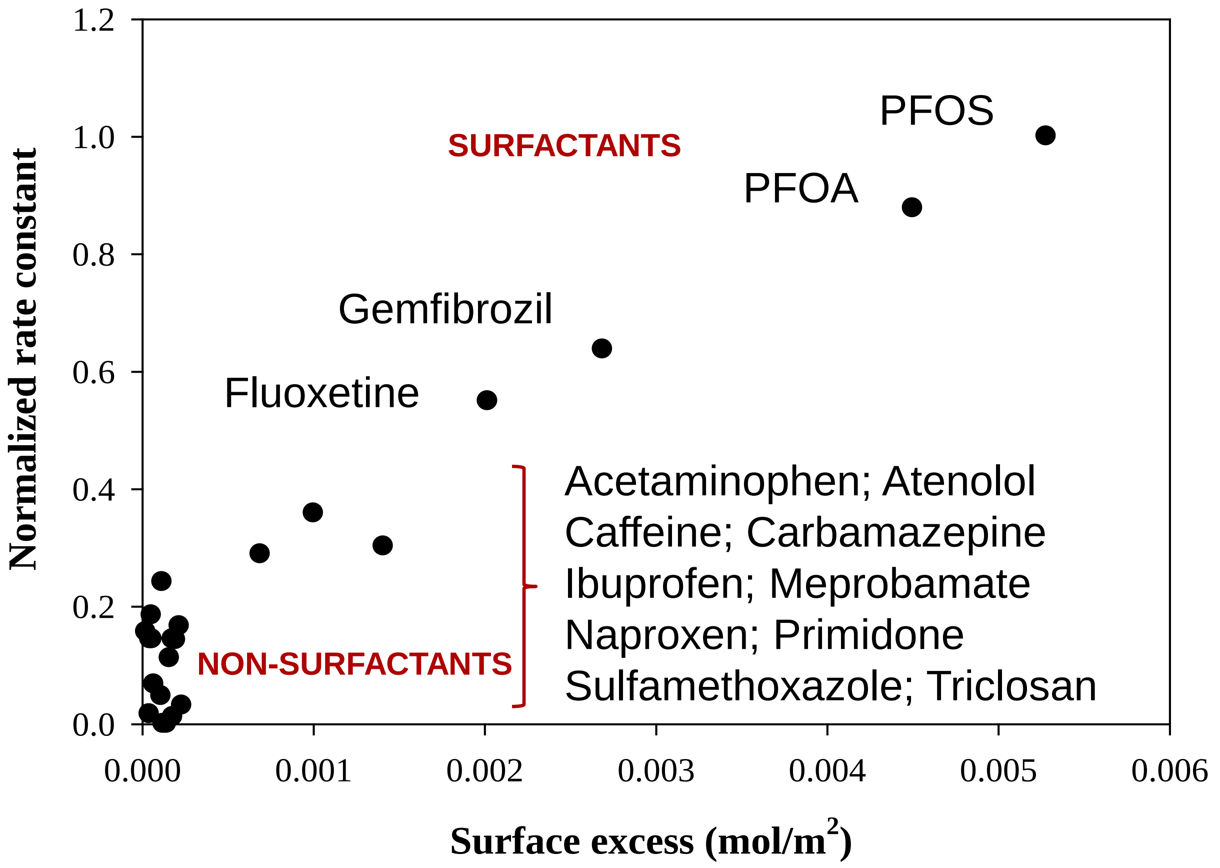


Degradation of Poly- and Perfluoroalkyl substances (PFAS)



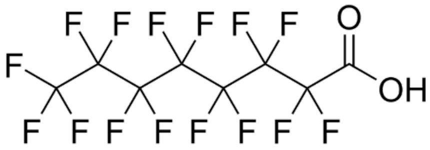
Surfactant-like compounds exhibit a strong tendency for the plasma-liquid interface and are rapidly degraded.

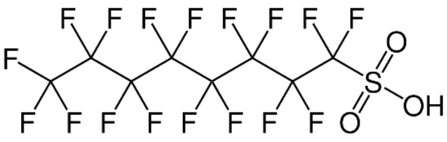
Plasma reactor performance is closely tied to interfacial compound concentration



Our current plasma reactor design(s) are superior for the treatment of surfactants (PFAS and dyes) but are unable to competitively treat non-surfactants.

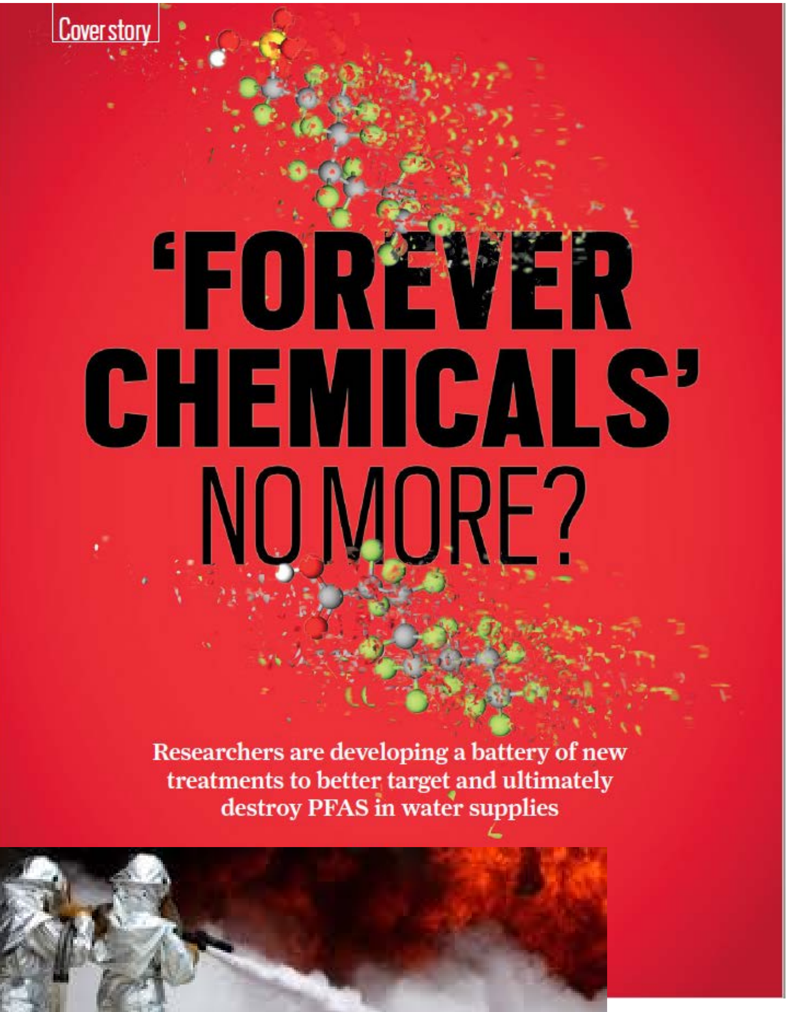
Surfactant treatment: poly- and perfluoroalkyl substances (PFAS) degradation





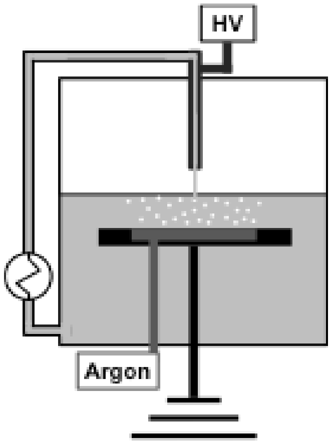
PFOA and PFOS are surfactants!

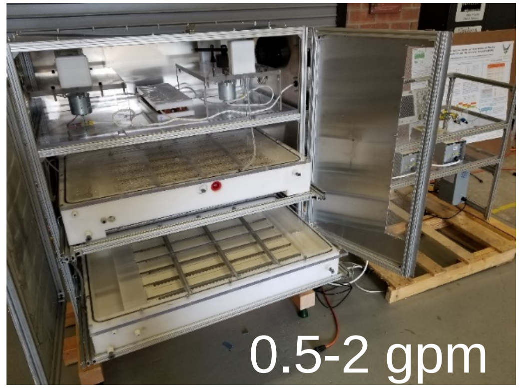
- Sources: military training activities (flame retardants) and manufacturing (non-stick cookware, water resistant clothing, fast food wrappers).
- EPA's health advisory level for PFOA+PFOS in drinking water is at 70 ng/L.
- $12B market
- Plasma is **the most promising treatment technology for the destruction of these compounds**.



Stratton, Gunnar R., *et al*. *Environmental science & technology* 51.3 (2017): 1643-1648.
Nzeribe, Blossom Nwedo, *et al*. *Critical Reviews in Environmental Science and Technology* 49.10 (2019): 866-915.

Plasma reactor scaleup for PFAS degradation





<u>The key reactor design elements</u>:

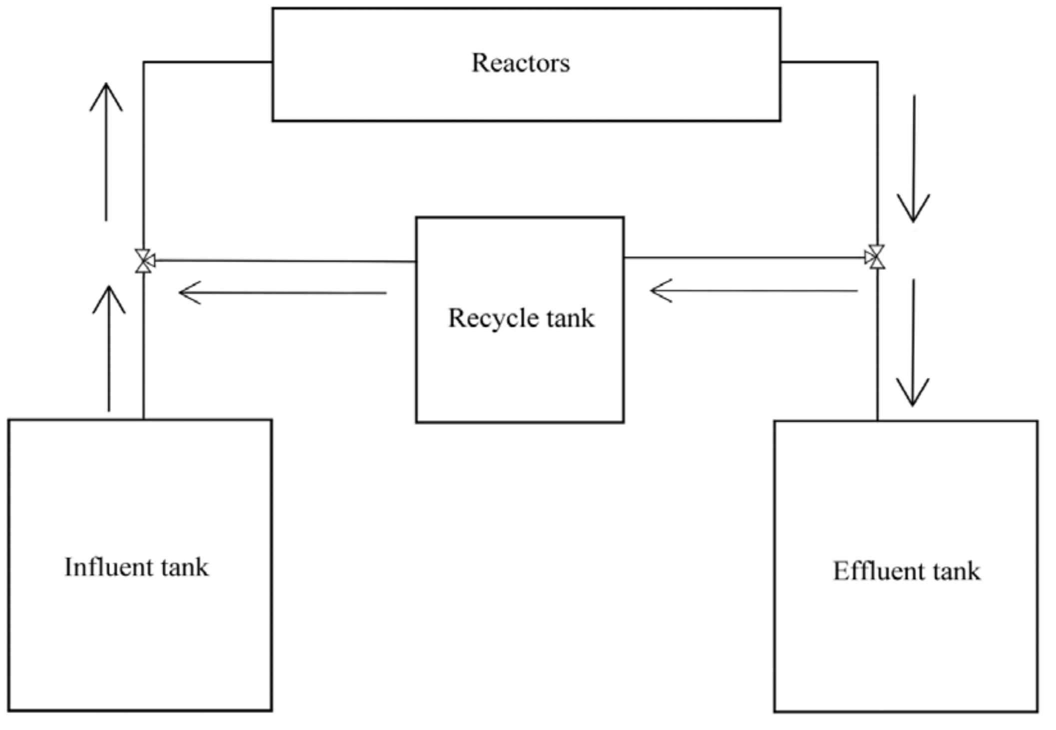
BULK LIQUID MASS TRANSPORT – Bubbling using argon is very effective and the gas can be recycled.

PLASMA AREA – Plasma-generated species must contact the entirety of the gas-liquid interface to maximize the treatment efficacy.

Plasma reactor field demonstration

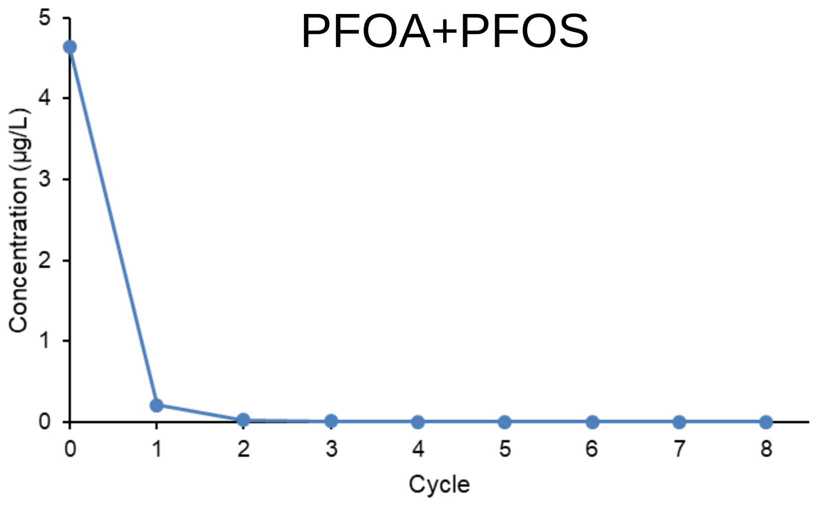
- ~ 2 years effort
- Mobile skid layout, electrical drawings and process flow diagrams
- Trailer integrated system testing at Clarkson before the field demonstration using a generator
- Installation of grounding rods
- Electromagnetic interference testing of plasma reactors
- Equipment and safety training courses
- Development of operation and maintenance manuals
- Base permits, water discharge permits…
- 100s of gallons of water successfully treated over a two-week period at various flowrates up to 2 gpm

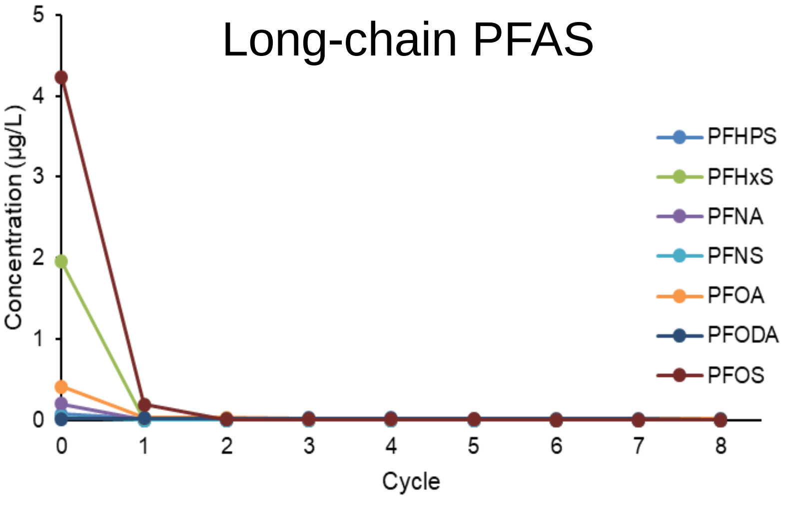
Plasma reactor field demonstration

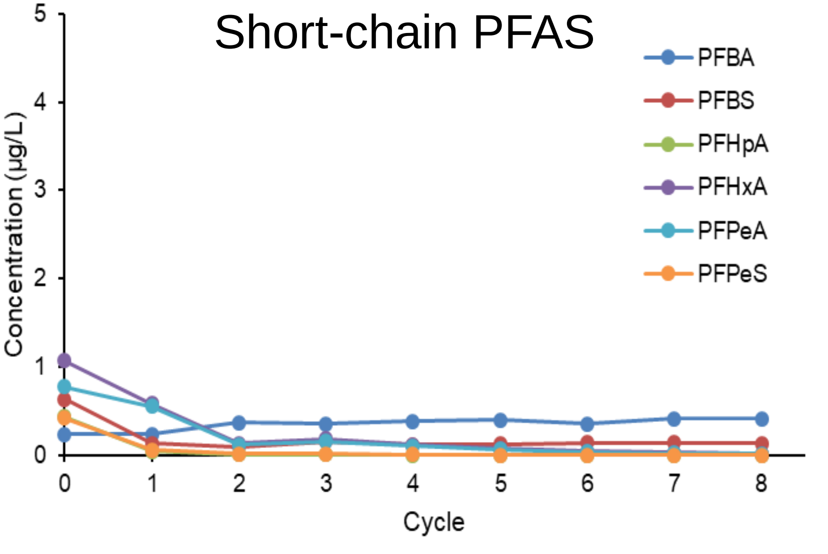


One cycle (18 gallon of water) is defined as a single pass through the reactor from the influent tank.

Field treatment results at 1.5 GPM

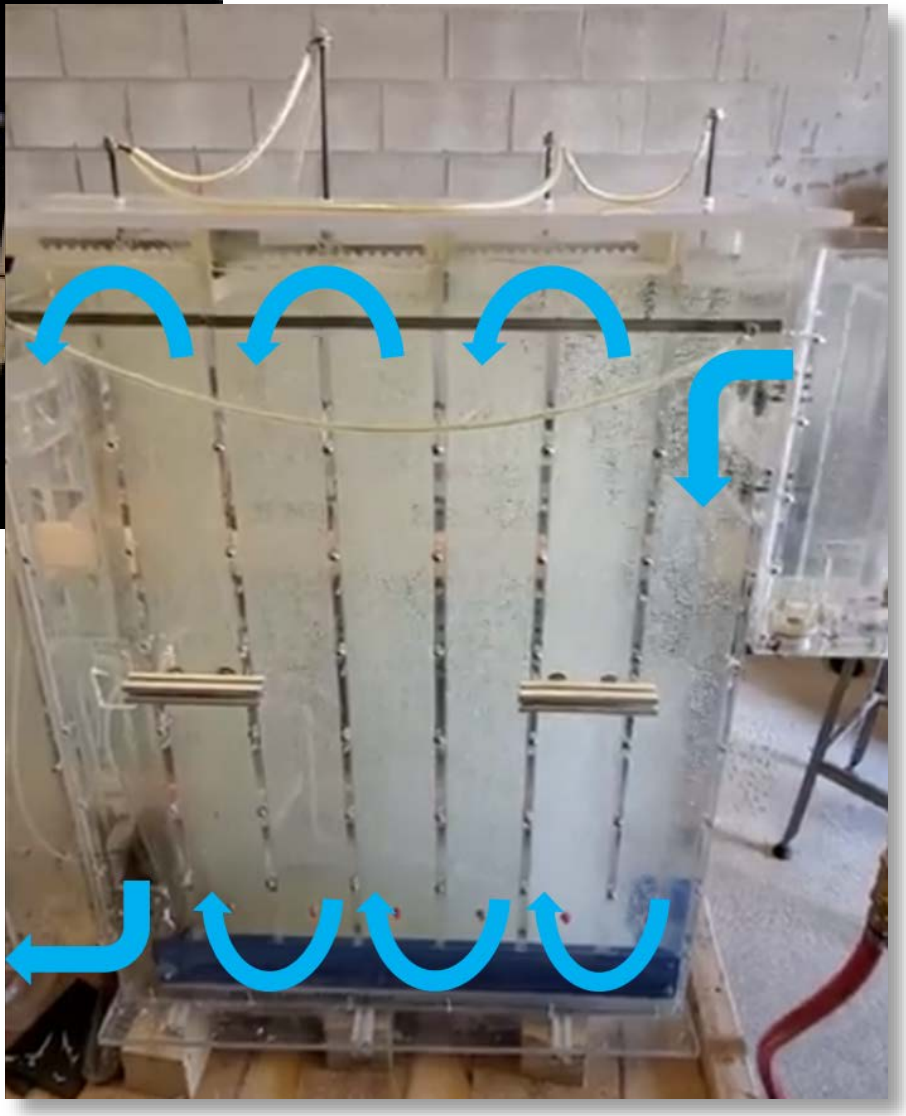






Nau-Hix, Chase, *et al*. *ACS ES&T Water*, accepted, 2021

System throughput increase: 10 gpm



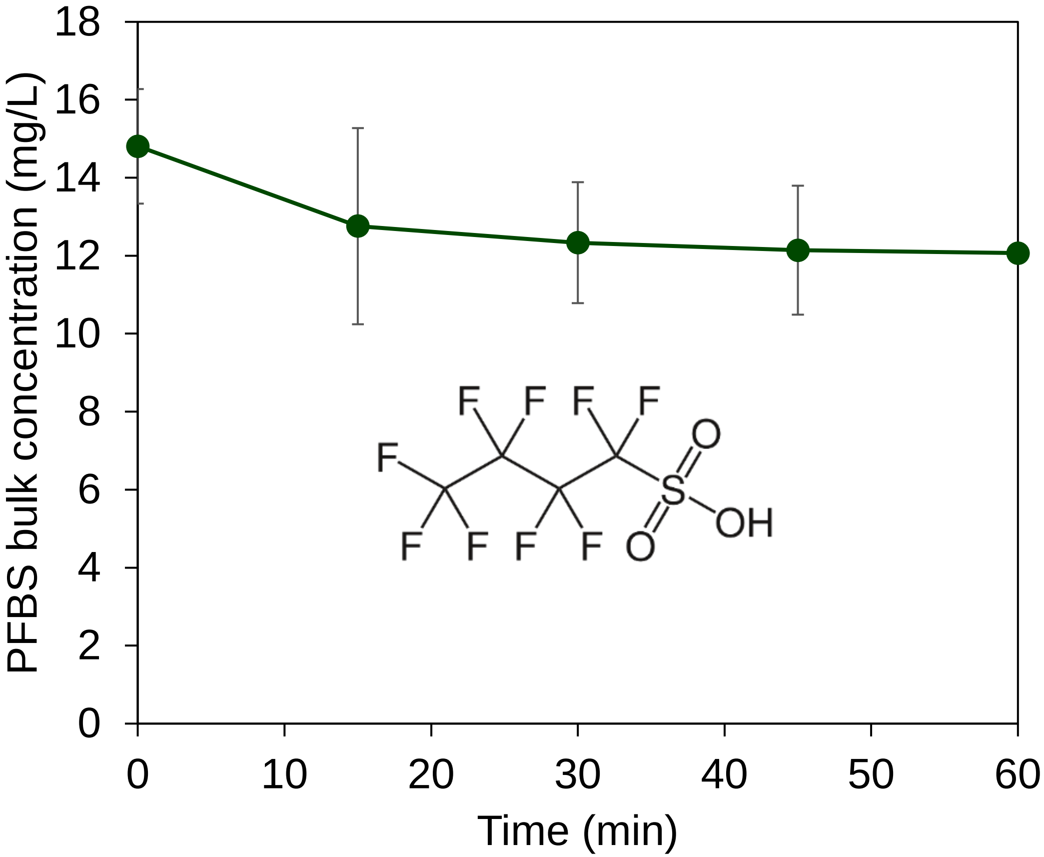
The performance of the 10 gpm system supersedes that of the 2 gpm system due to bulk liquid transport optimization.

Short-chain PFAS treatment: PFBS

Degradation of PFBS (perfluorobutane sulfonate) by a point-ring plasma reactor

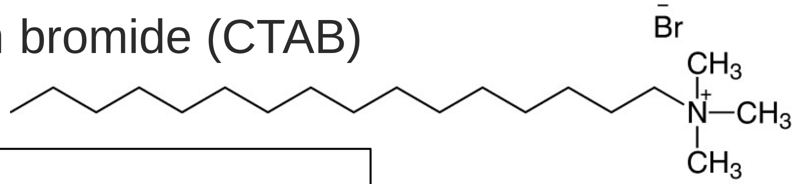
PFBS is the main constituent of semiconductor industry effluents

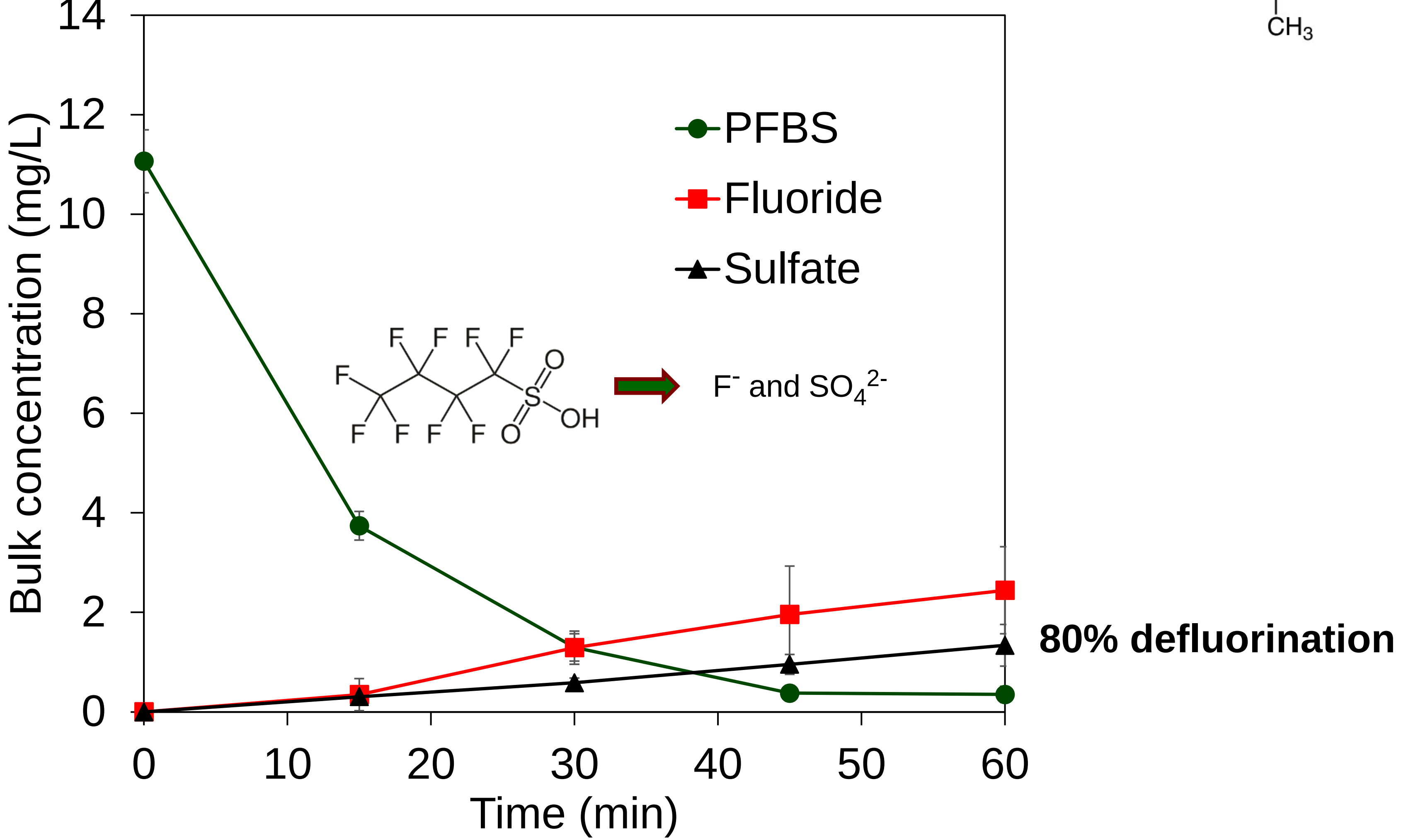
- Low interfacial concentration
- No reactivity with OH
- Low reactivity with e^{-}_{aq}



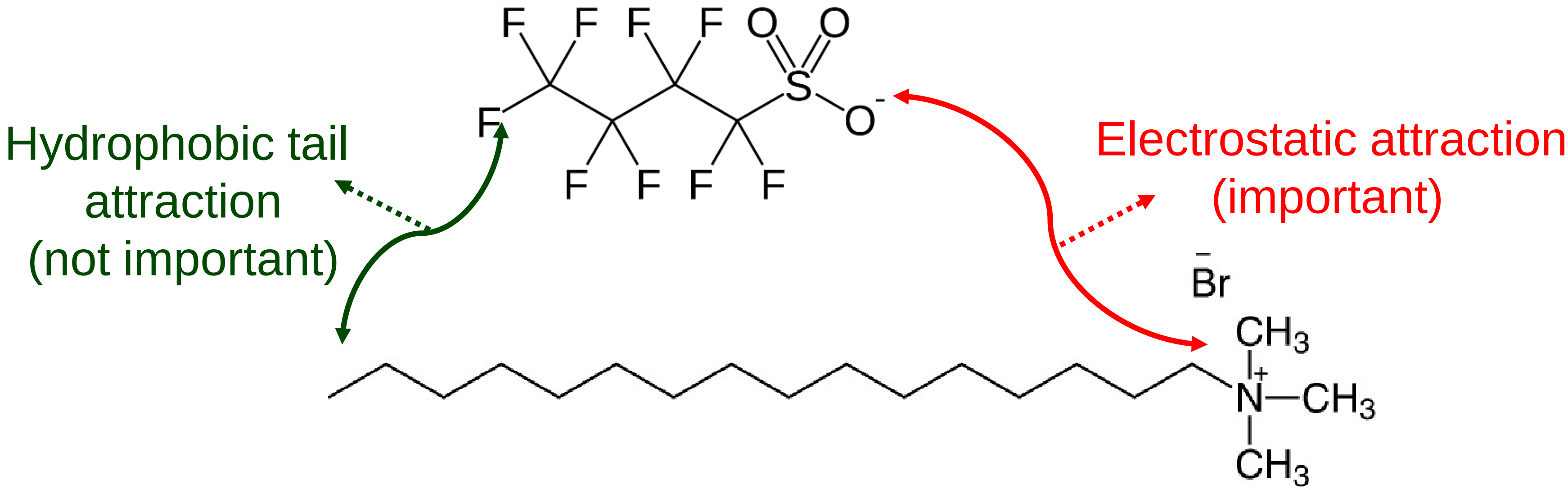
Minimizing bulk liquid mass transport limitations increases the removal rate of PFBS

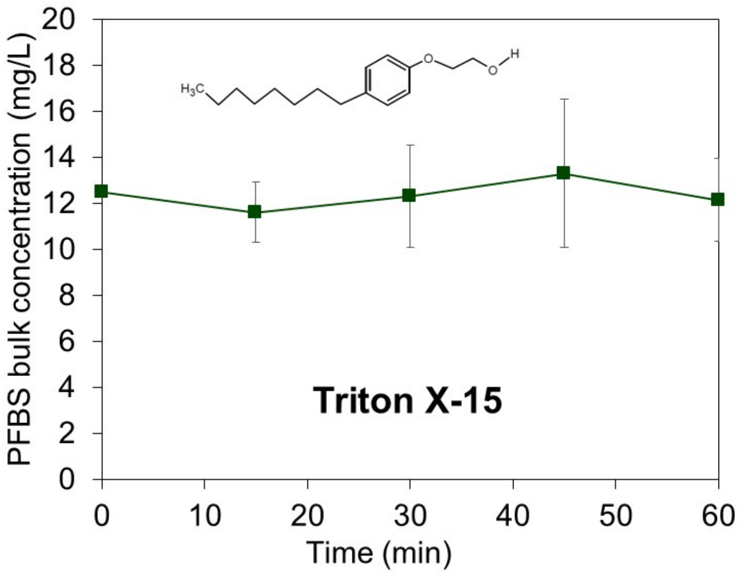
Surfactant: 1.2 mM cetyltrimethylammonium bromide (CTAB)

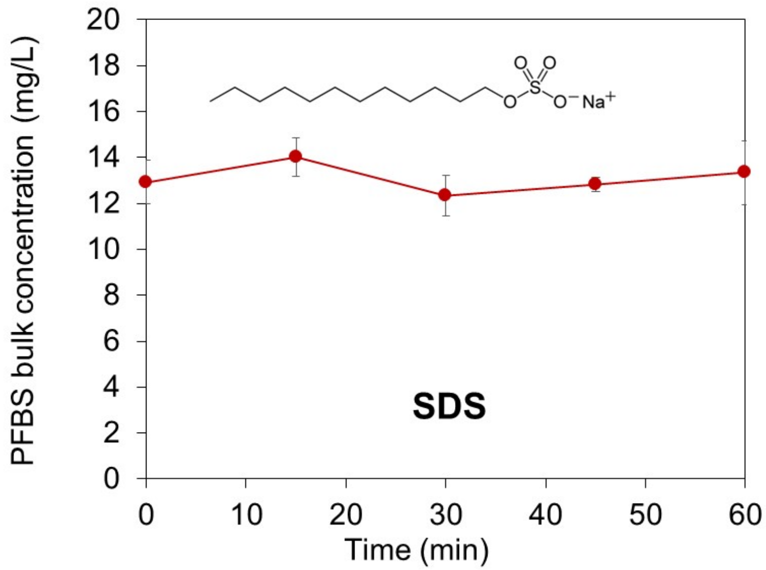




PFBS-CTAB interaction

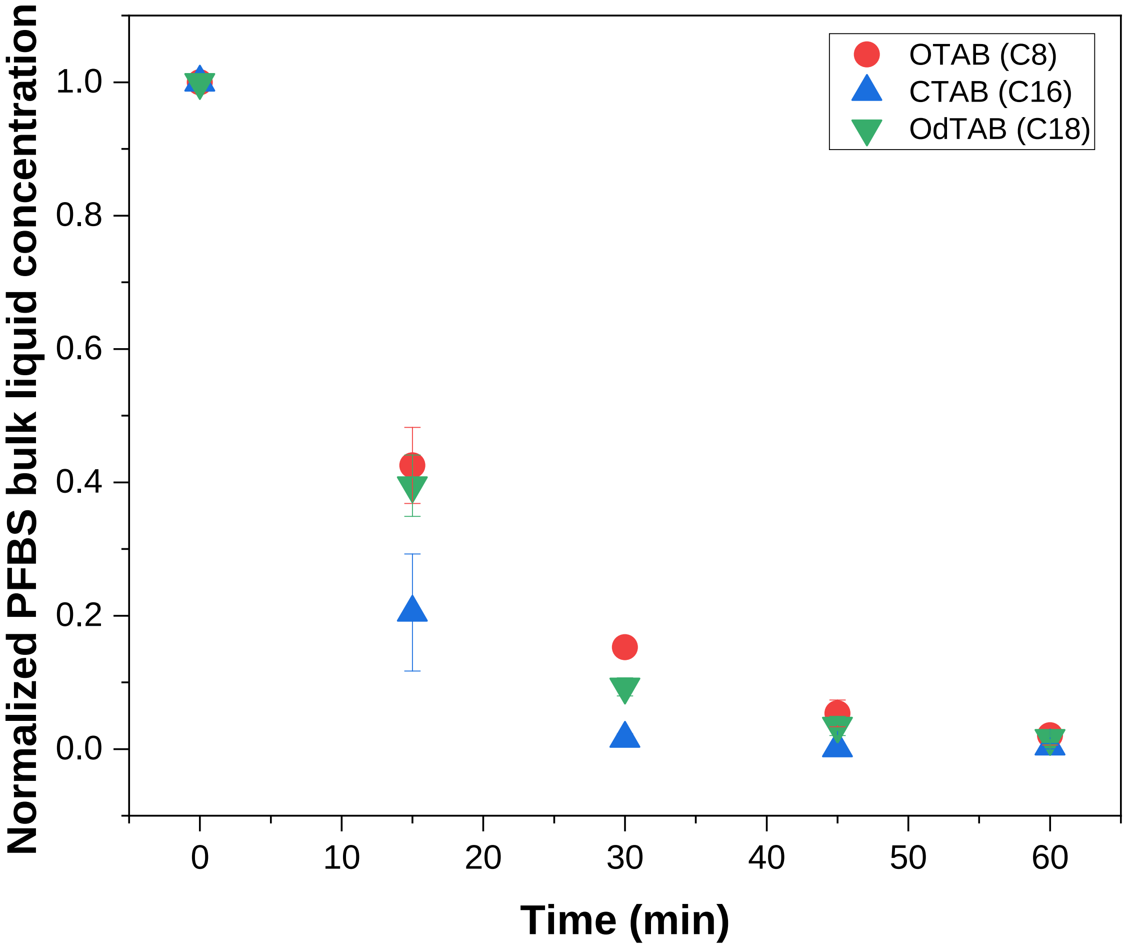




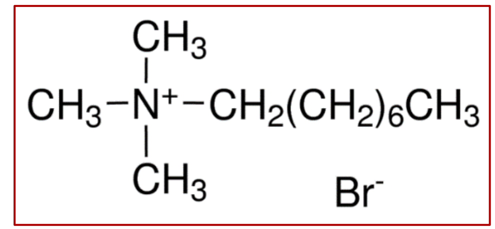


PFBS at the interface

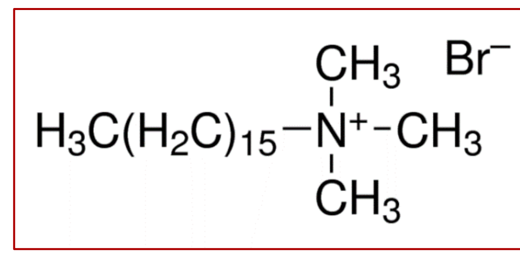
Surfactant (0.2 mM) added every 15 mins



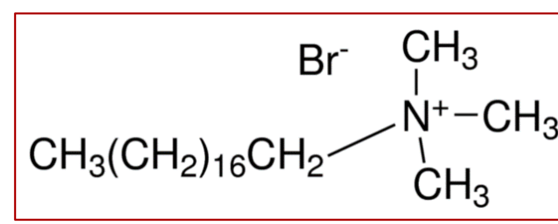
Octyltrimethylammonium bromide (C_8 - OTAB)



Hexadecyltrimethylammonium bromide (C_{16} - CTAB)



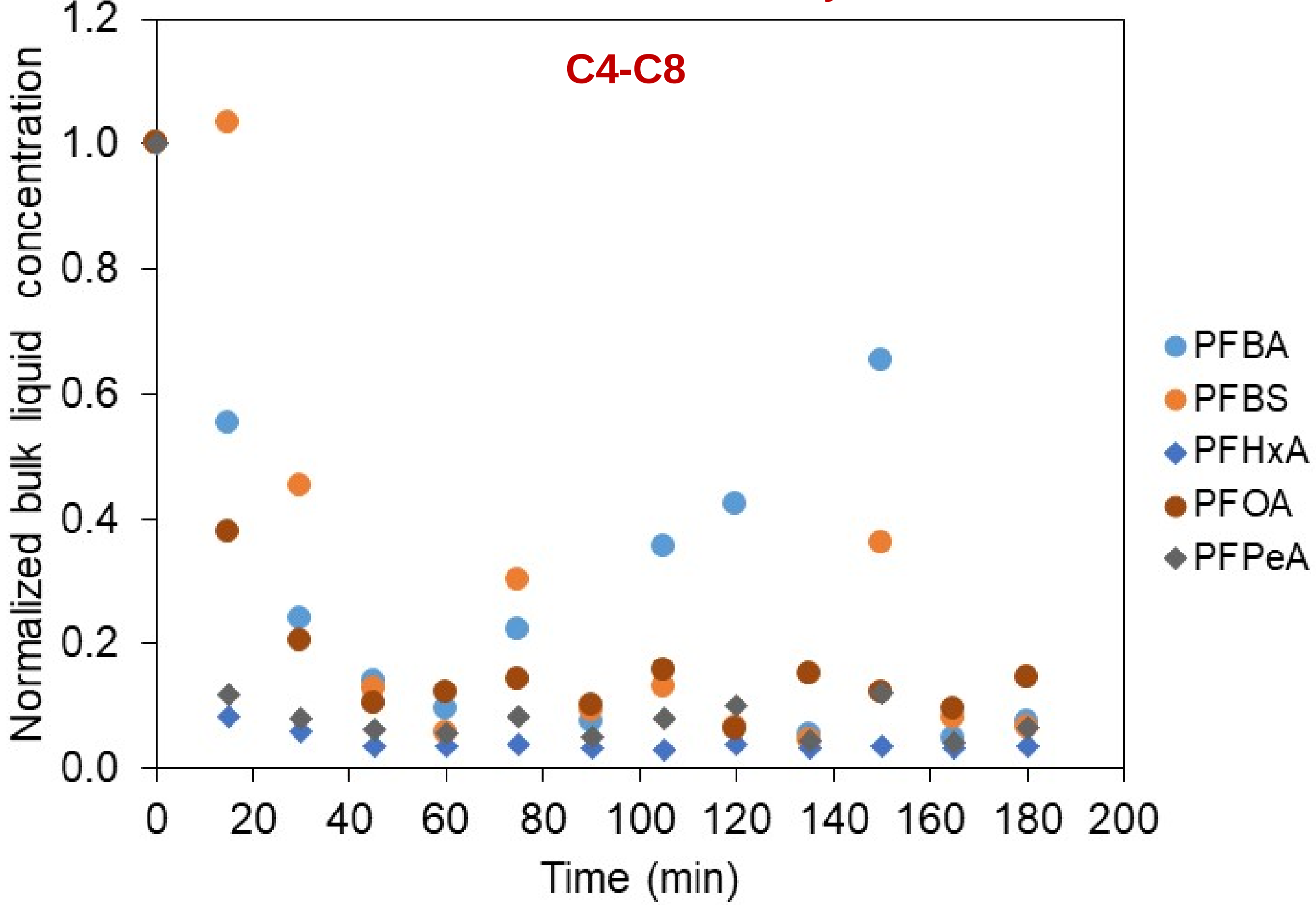
Trimethyloctadecylammonium bromide (C_{18} - OdTAB)



The mechanism of degradation (defluorination) is unknown.

FAB wastewater reverse osmosis PFAS concentrate treatment in the presence of CTAB

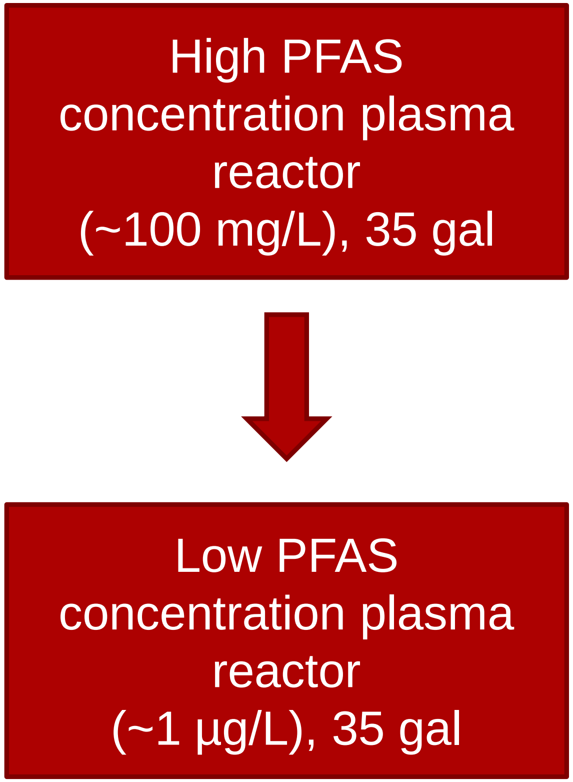
0.2 mM CTAB added every 15 min



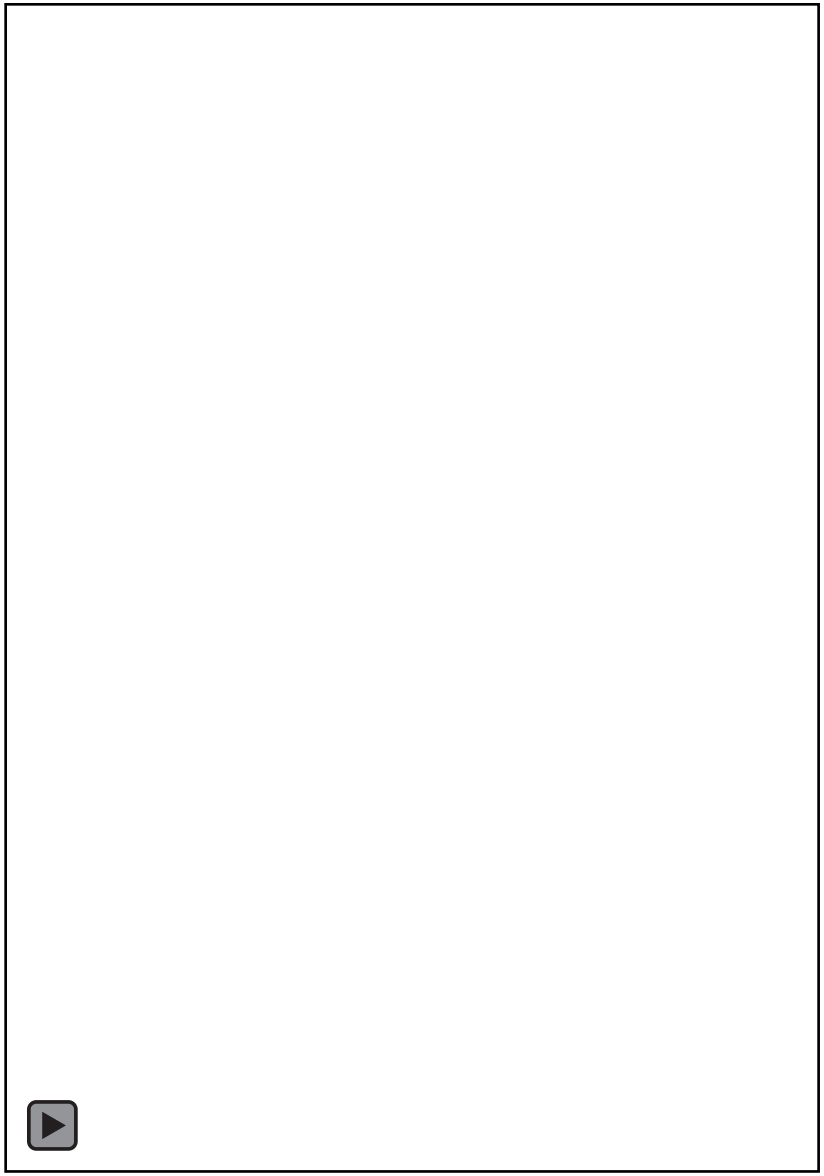
- > 97% degradation of C4-C8 compounds
- C9-C16 compounds removed to below detection limits
- ~70% defluorination

Plasma treatment of Ion Exchange (IX) brine

- **Regenerant brine:** complex and highly concentrated mixture of PFAS, methanol (between 5% and 20%), NaCl (6-7%), and a range of co-contaminants.
- Solution electrical conductivity ~60 mS/cm.

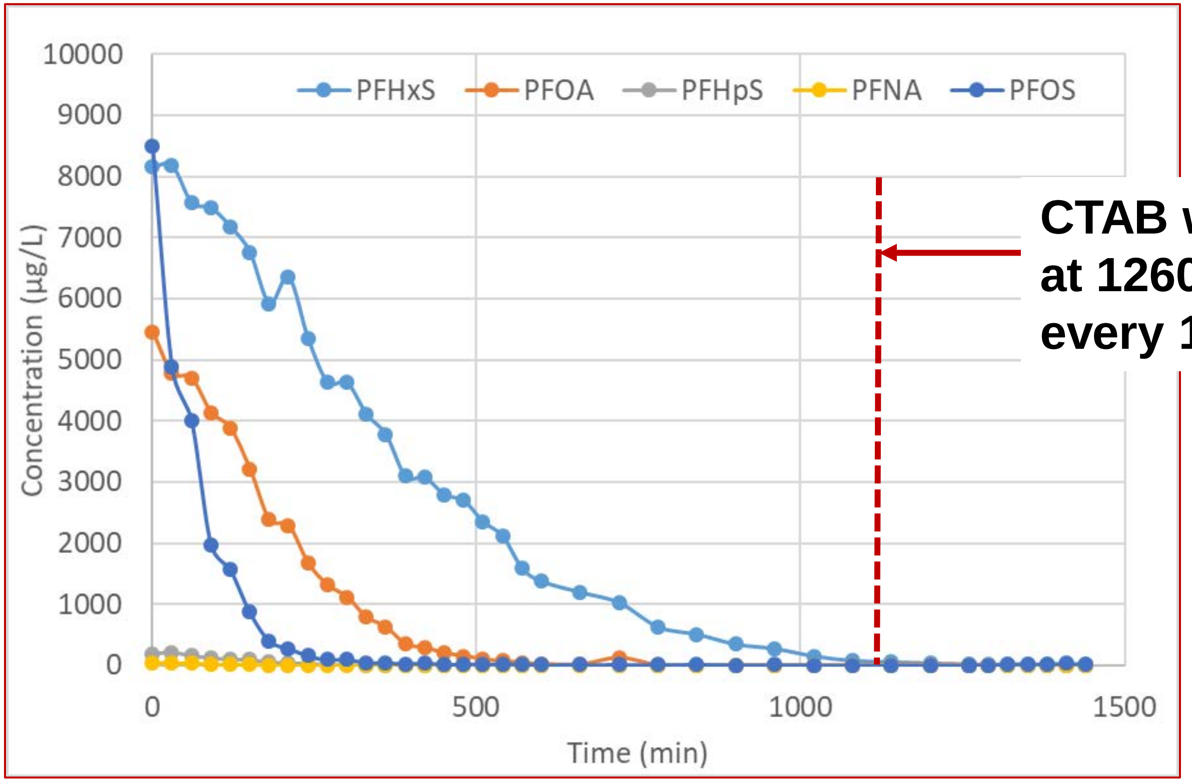


Mobile plasma IX brine treatment system



PFAS removal in high concentration plasma reactor

Long-chain PFAS

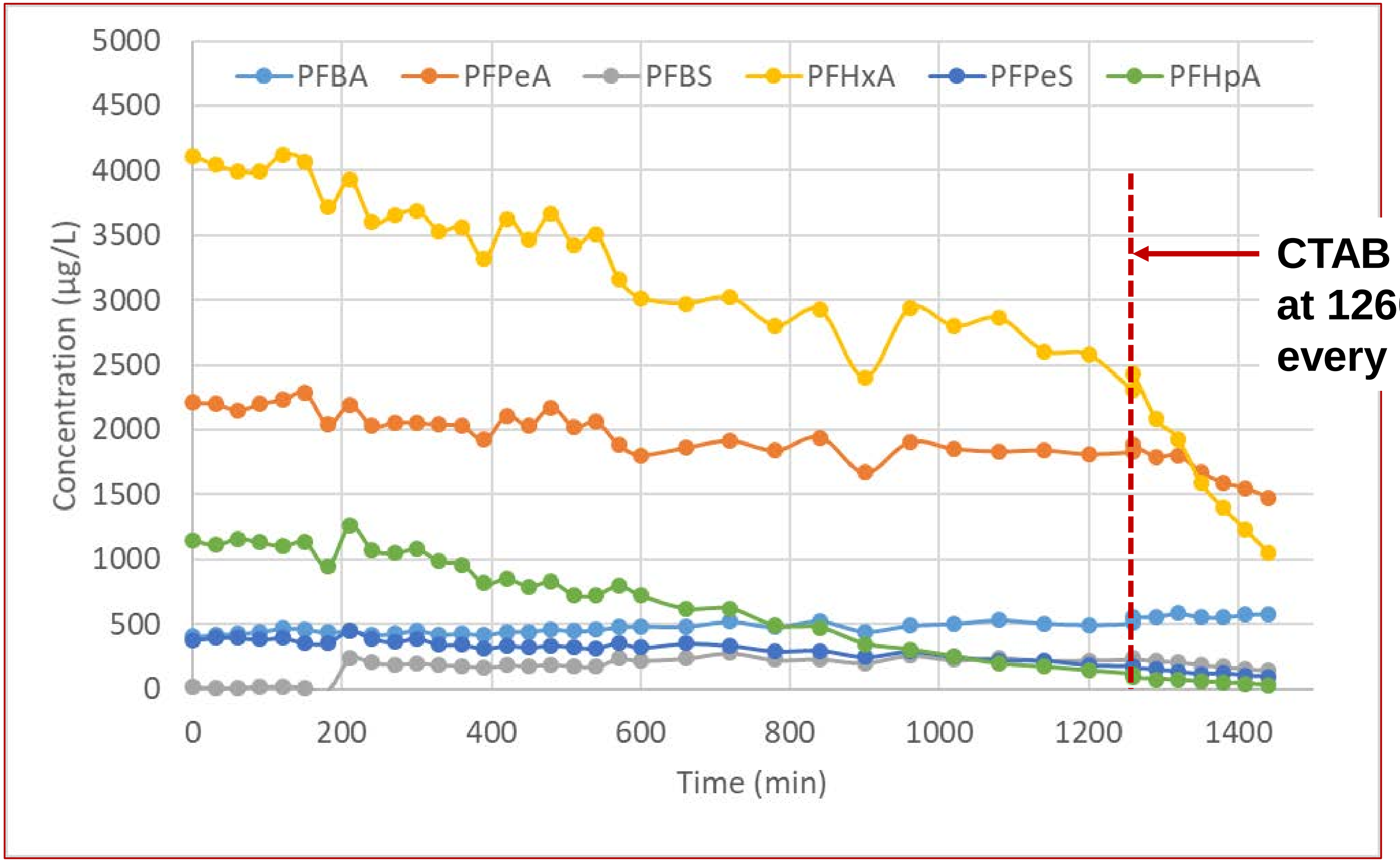


CTAB was added at 1260 min and every 1 hr

Singh, Raj Kamal, *et al*. *Environmental Science & Technology* 54.21 (2020): 13973-13980.

PFAS removal in high concentration plasma reactor

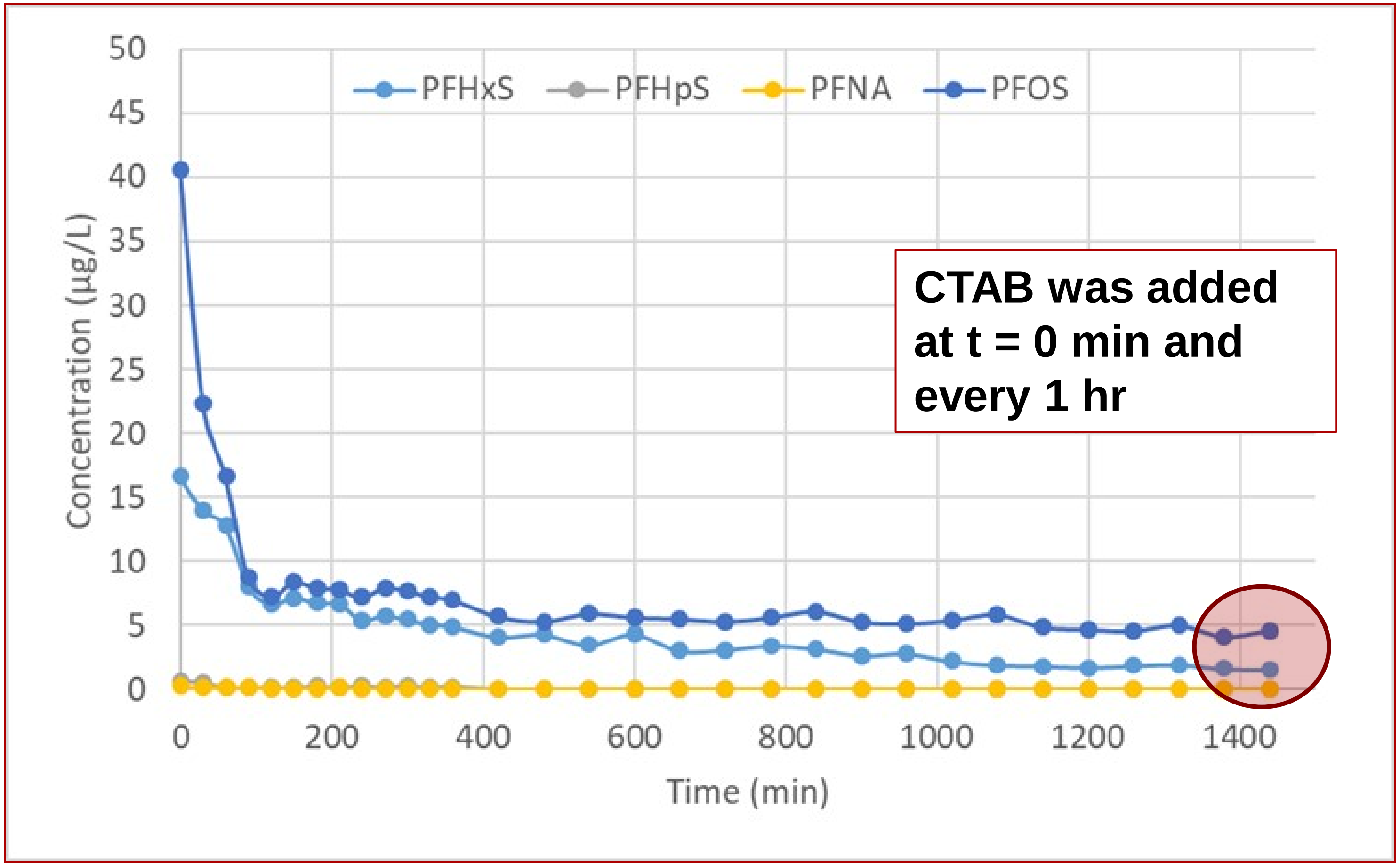
Short-chain PFAS



CTAB was added at 1260 min and every 1 hr

PFAS removal in low concentration plasma reactor

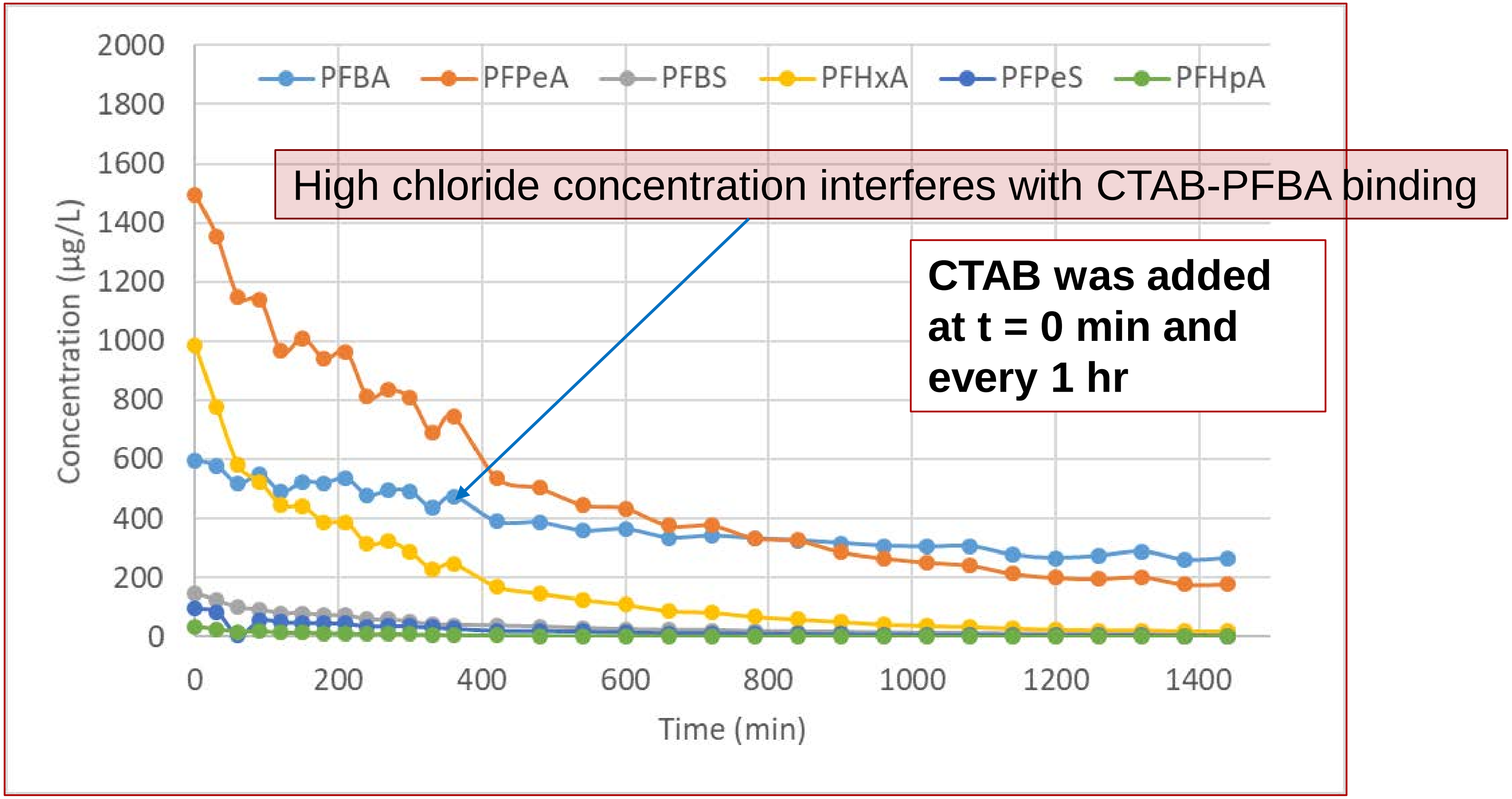
Long-chain PFAS



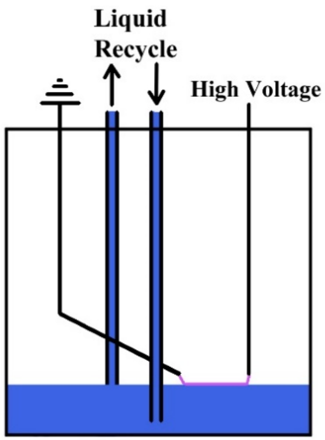
PFAS adsorption-desorption

PFAS removal in low concentration plasma reactor

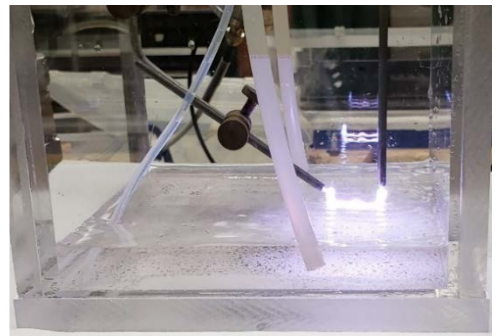
Short-chain PFAS



Inorganic salt effects in highly electrically conductive solutions

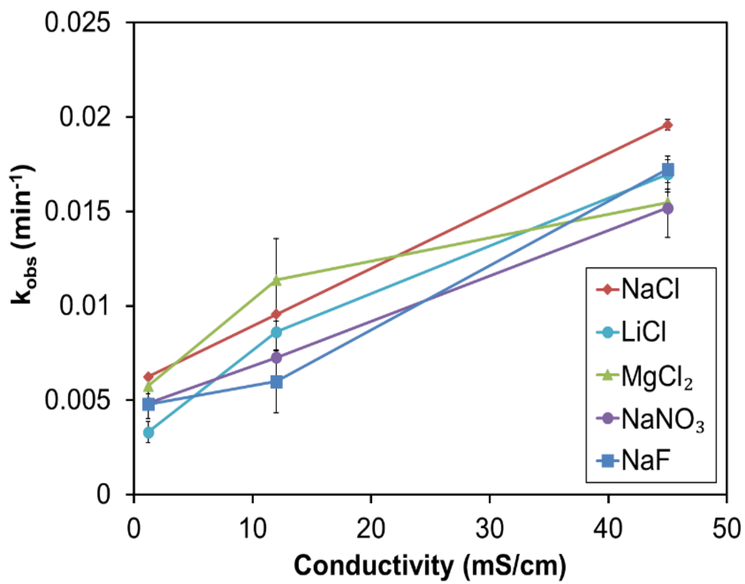


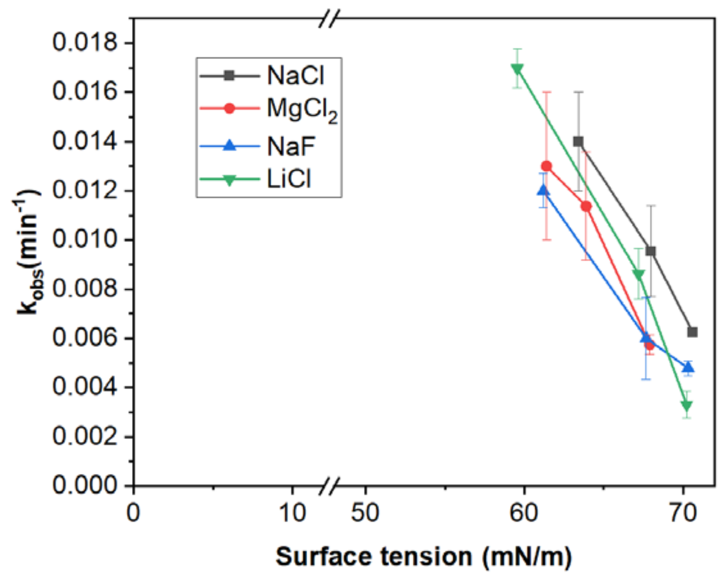
Constant plasma area



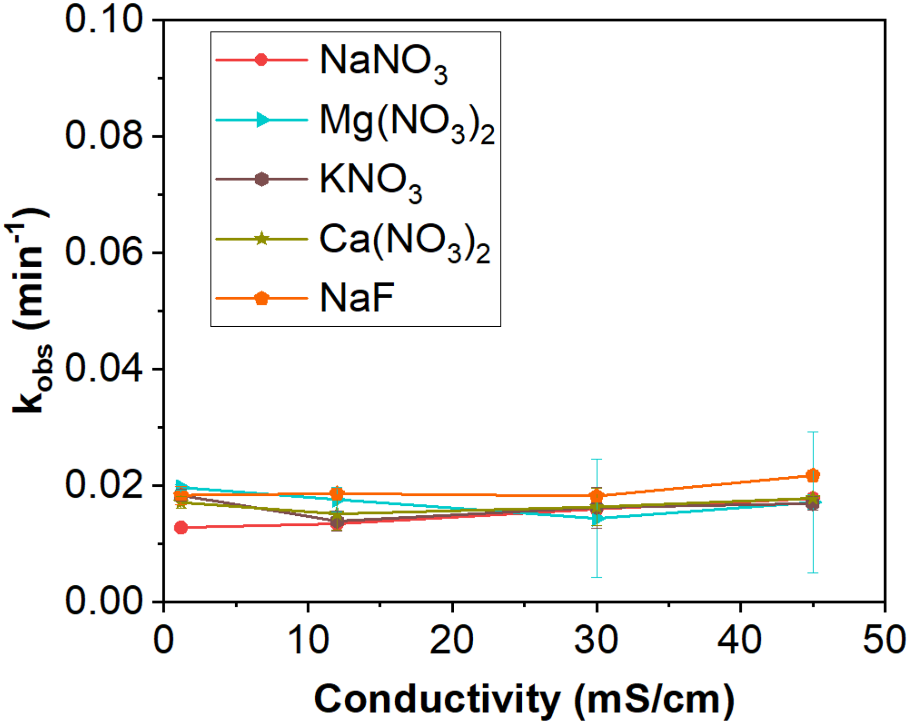
Removal of PFOA and Rhodamine B investigated as a function of solution conductivity up to 45 mS/cm

Degradation of PFOA

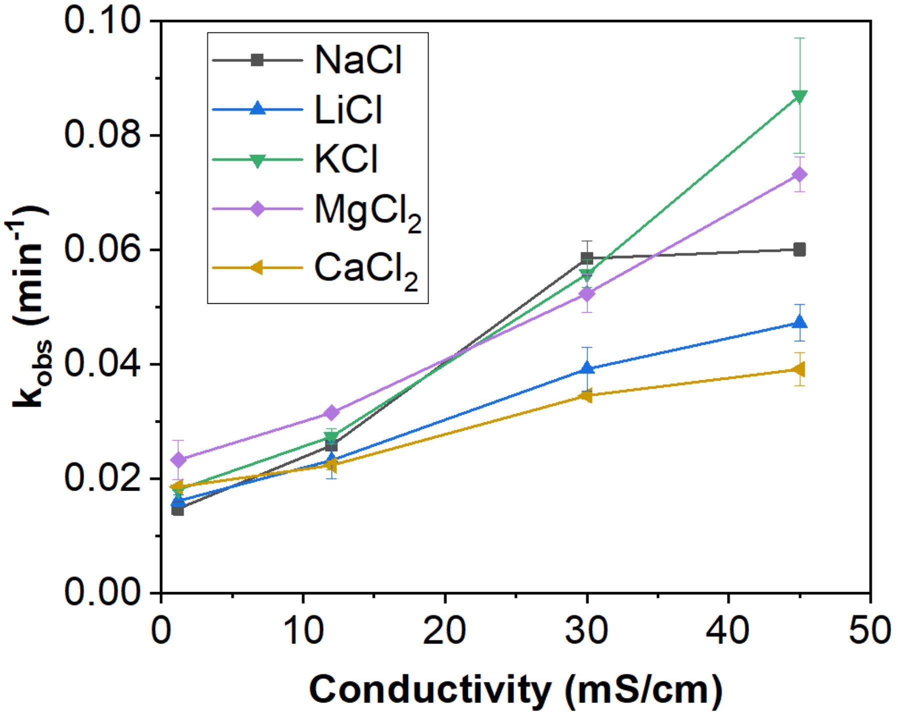




Rhodamine B degradation

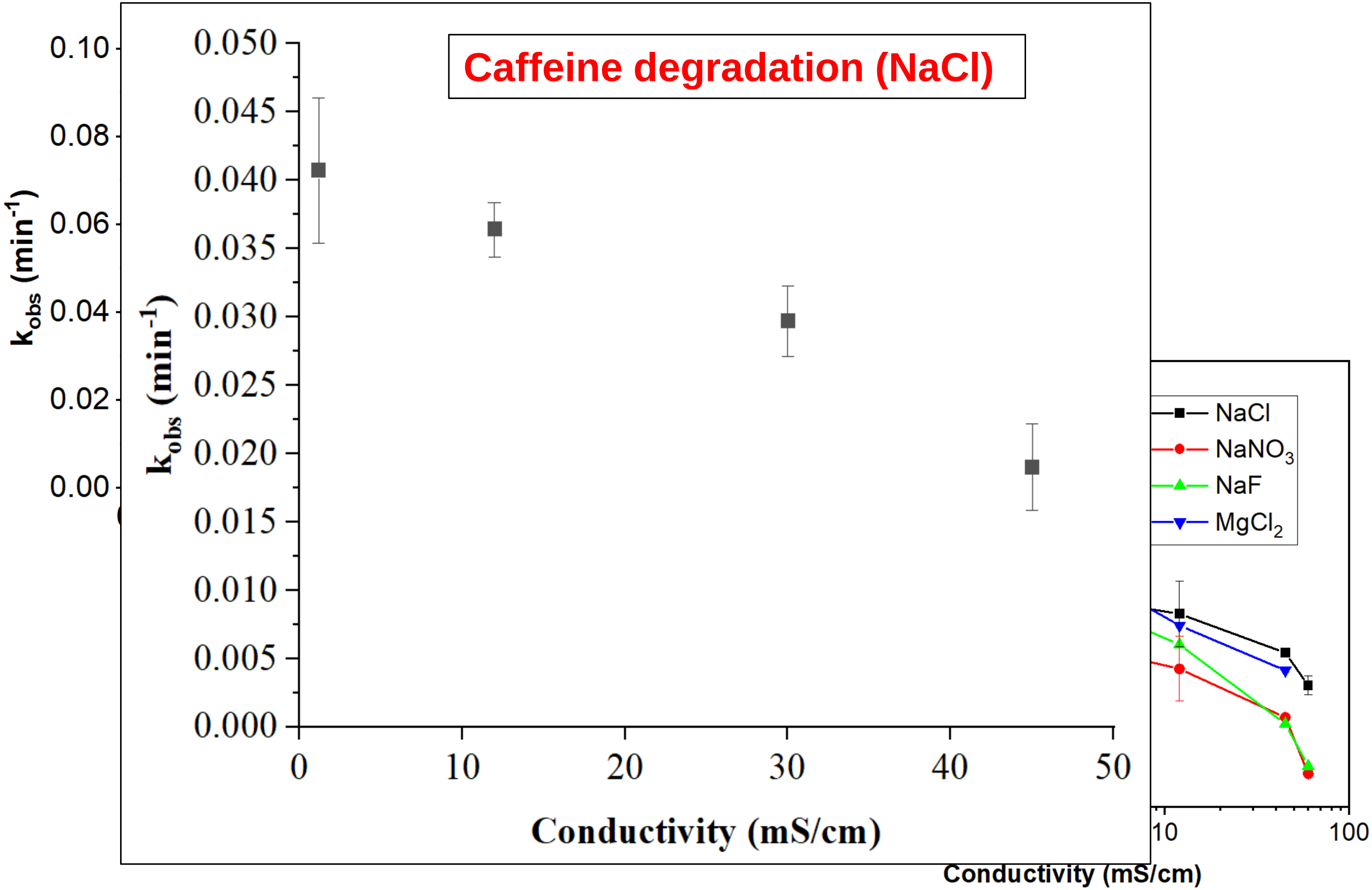


Non-chlorine salts

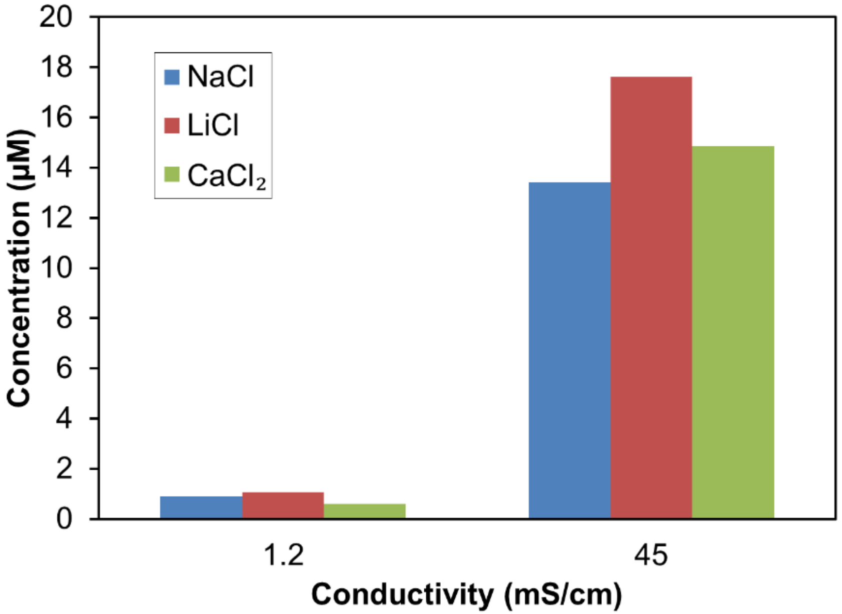


Chlorine salts

Rhodamine B degradation: non-chlorine salts



Chlorine chemistry



Concentration of chlorate (ClO_3^-) formed at 1.2 mS/cm and 45 mS/cm for three chlorine salts

Perchlorate (ClO_4^-) has not been detected

$$Cl^- + {\bullet}OH \rightarrow HOCl^{\bullet -}$$

$$HOCl^{\bullet -} + H^+ \rightarrow Cl{\bullet} + H_2O$$

$$Cl^- + Cl{\bullet} \rightarrow Cl_2^{\bullet -}$$

$$Cl_2^{\bullet -} + Cl_2^{\bullet -} \rightarrow Cl_2 + 2Cl^-$$

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$$

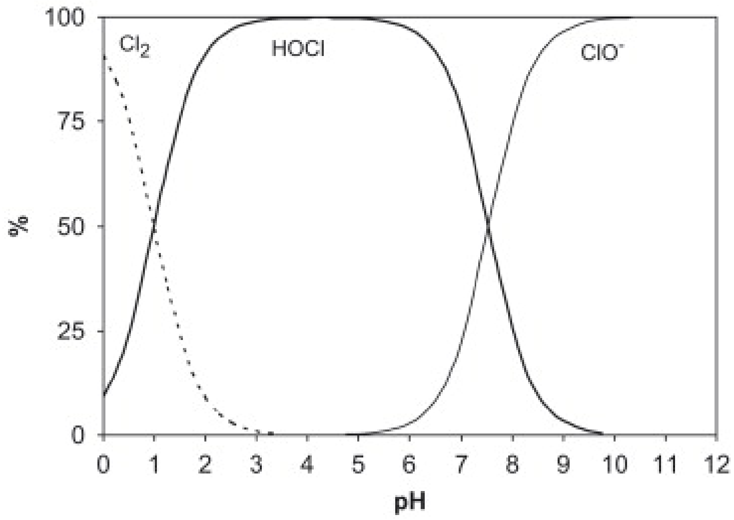
$$HOCl \leftrightarrow H^+ + OCl^-$$

$$OCl^- + {\bullet}OH \rightarrow ClO_2^- + H^+$$

$$ClO_2^- + {\bullet}OH \rightarrow ClO_2^{\bullet} + OH^-$$

$$ClO_2^{\bullet} + {\bullet}OH \rightarrow ClO_3^- + H^+$$

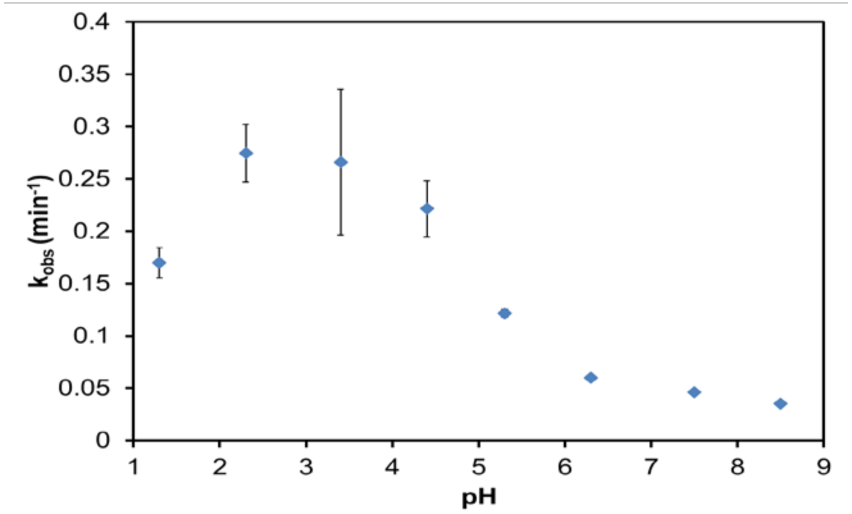
Rhodamine B degradation: HOCl



Chlorine pH-dependent speciation profile

Hypochlorous acid (HOCl) is stable but deprotonates above a pH of ~ 7 to form the relatively inert ClO^- which does not react with RhB.

HOCl degrades RhB and could oxidize various non-PFAS compounds in brine.

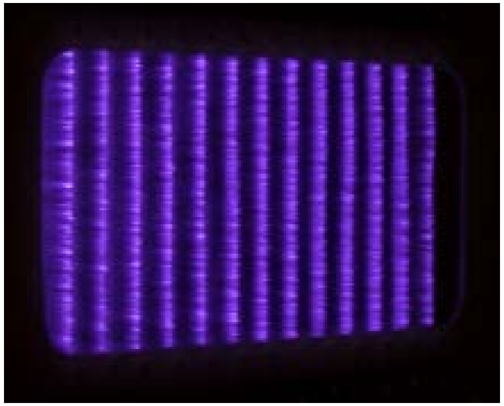


Influence of solution pH on Rh B removal. Conductivity is fixed at 45 mS/cm

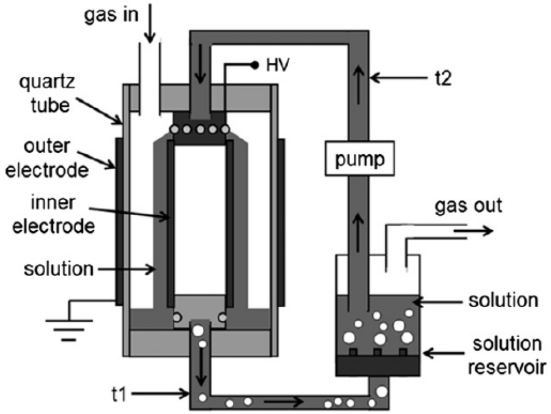
Deborde M, Von Gunten UR. Water research. 2008 Jan 1;42(1-2):13-51.

Non-surfactants

- 100+ reactors available to compare without clear design guidelines.
- For the most effective reactors plasma generated in a gas phase is contacting a thin film of liquid.



Corona above water



DBD with falling liquid film

- **Design points to consider**:

  (1) Ozone chemistry decoupled from OH radical chemistry

  (2) Reasonable treatment volumes

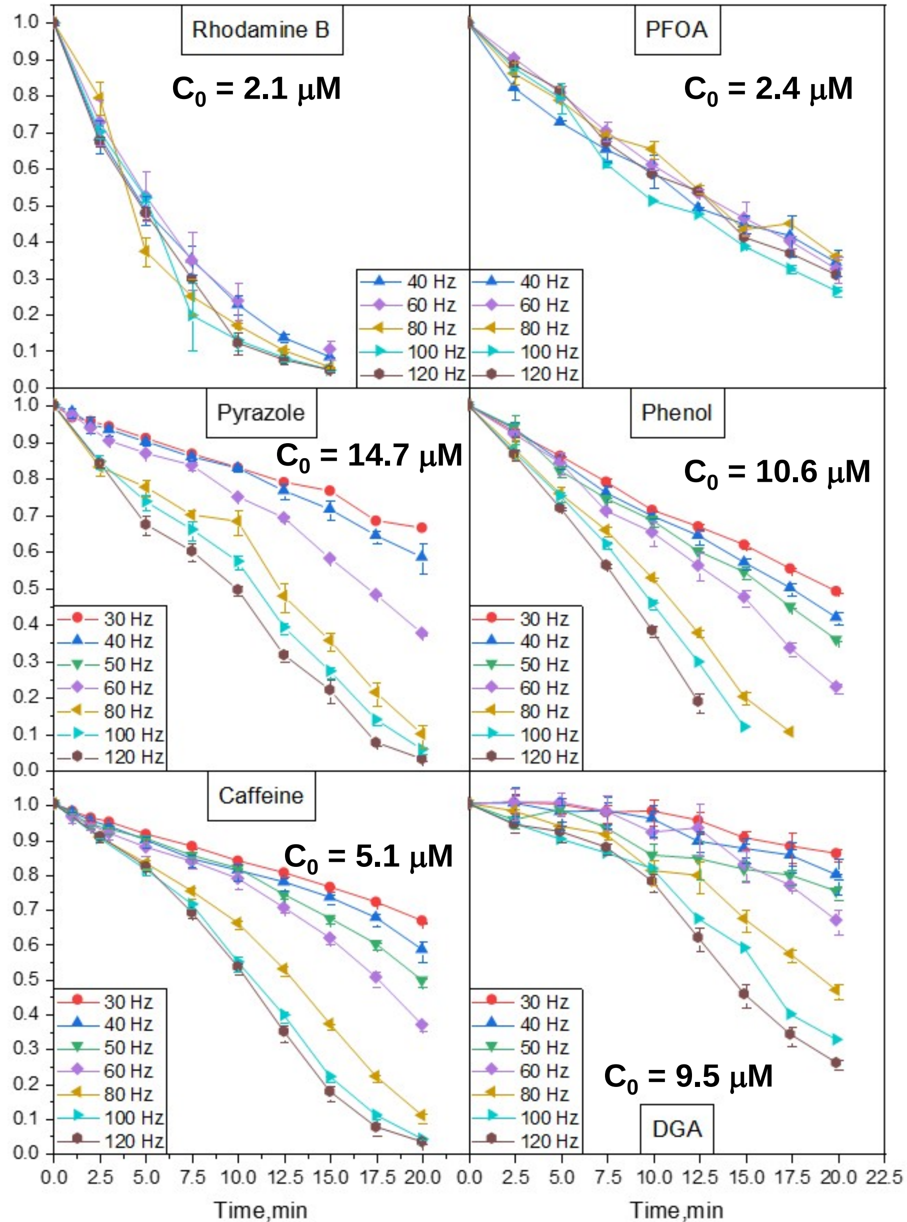
  (3) Environmentally relevant (~µg/L) concentrations of mixtures of compounds

Magureanu, M., et al. *Water research* 45.11 (2011): 3407-3416.
Magureanu, Monica, et al. *Plasma Chemistry and Plasma Processing* 33.1 (2013): 51-64.

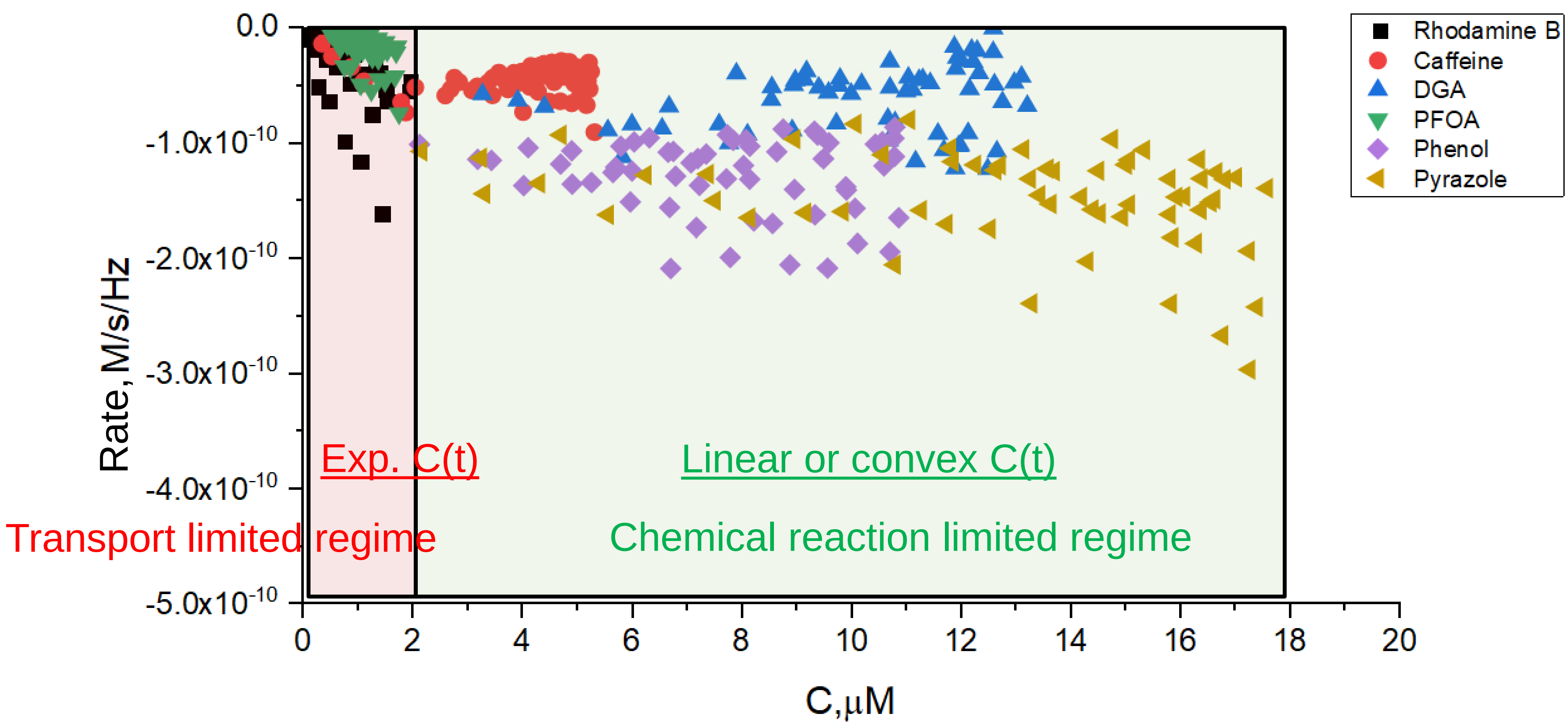
The importance of a compound's initial concentration in its removal

Rail-plate electrode configuration (no external mixing)

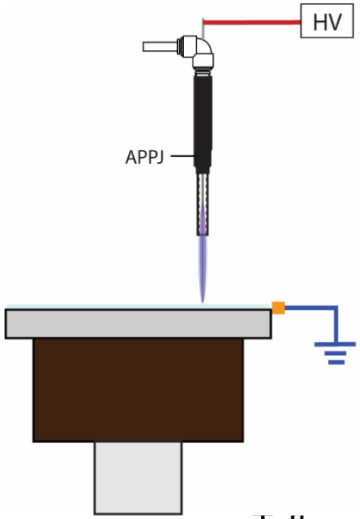
Degradation profiles of six compounds as a function of discharge frequency

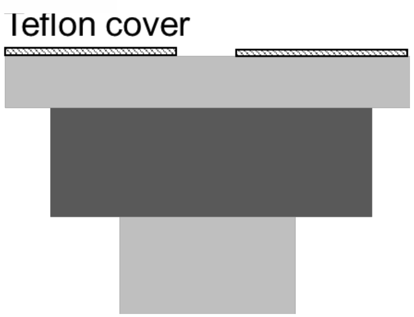


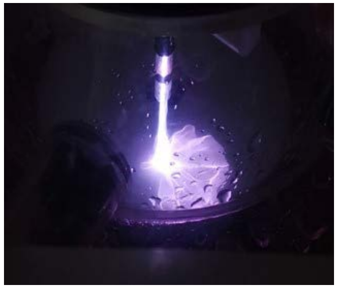
Bulk liquid concentration controls the removal regime



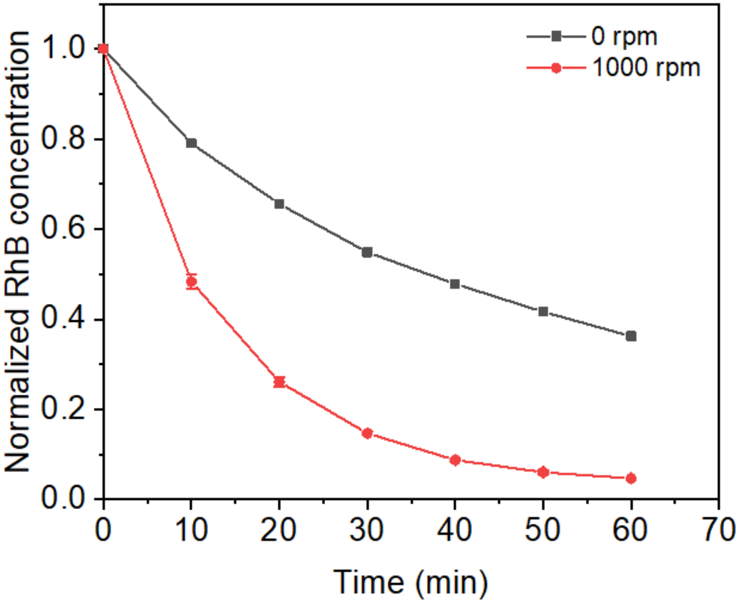
Removal of rhodamine B in a plasma spinning disc reactor

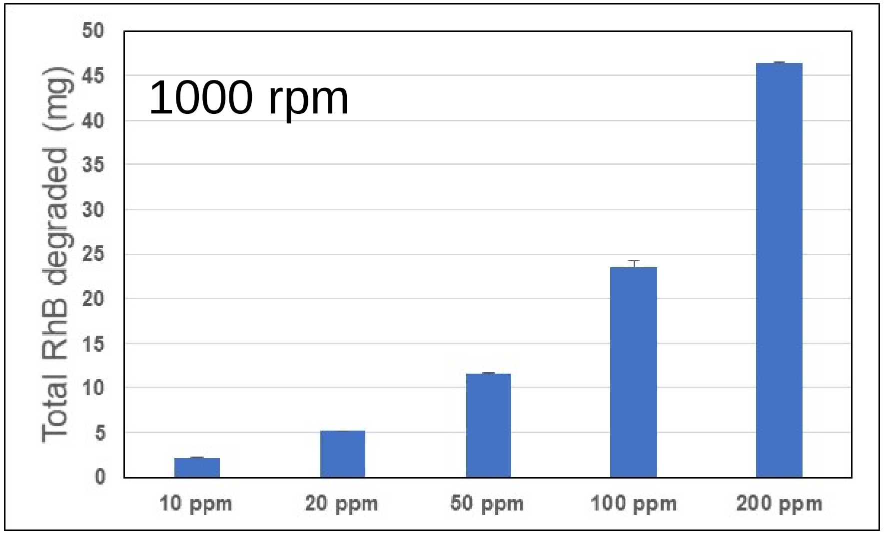






Treatment volume 500 mL

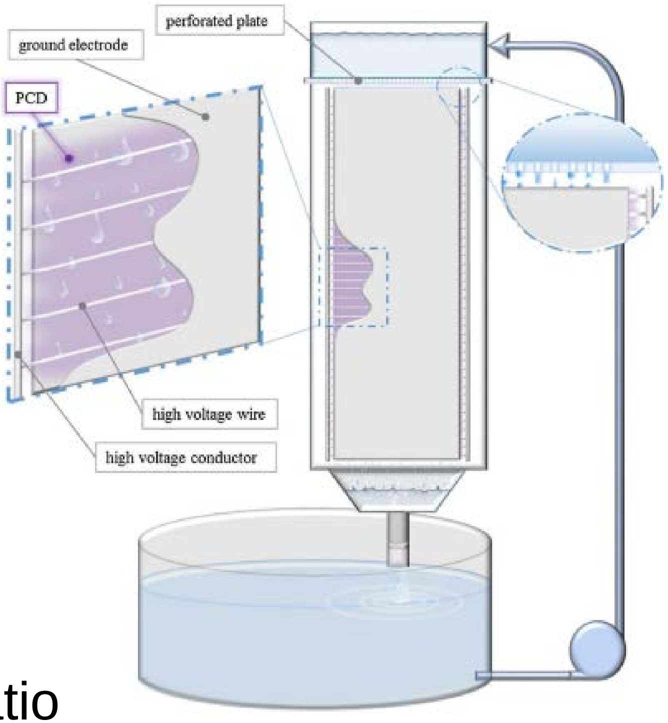




Plasma process (non-PFAS) scaleup

We have promising bench-scale plasma reactors so let's start scaling up!

- 50 L batch hospital effluent treatment
- 27 pharmaceuticals (~1149 µg/L)
- 59 % removal (treatment times not reported)
- Ozone plays a role in the degradation



Pilot scale reactor for pharmaceuticals treatment

Technological challenges:

(1) Ensuring high area-to-volume treatment ratio

(2) Generation of large volume plasma

(3) Power supply scaleup

Ajo, Petri, *et al*. *Journal of Environmental Chemical Engineering* 6.2 (2018): 1569-1577.

Requirements and Recommendations

Reactor design depends on the water characteristics:

- surfactants vs. non-surfactants
- total organic carbon
- solution electrical conductivity

Realistic throughput:

- up to 100 gpm for direct treatment
- up to 20 gpm for concentrate treatment (likely near-future adoption)
  - *Membrane*
  - *Ion exchange*
  - *Adsorption/desorption*

Hypothetical target: Develop a 1 gal 1,4 dioxane treatment system

Dyes should be avoided as they exhibit surfactant-like properties

Performance goal: Rapid removal (minutes timeframe for direct treatment)

Energy considerations not important initially

Requirements and Recommendations

Performance criteria to consider:

- Environmentally relevant concentrations with and without co-contaminants : ~µg/L in groundwater or mg/L post-concentration

  Starting concentrations influence overall kinetics (transport vs. species limited regime)

- Surface-to-volume ratio

  Start with a thin liquid film or a spray (practicality?)

  Filamentary vs. diffuse plasma

- Utilize plasma-generated H_2O_2 to form additional OH in the bulk liquid (?)

>10,000 mg/L of H_2O_2 is required to oxidize organic mater in the groundwater

- Ozone chemistry decoupled from OH radical chemistry
- Air (nitrates!) vs. oxygen vs. argon
- Iron and solid catalysts should be avoided

Summary

- The utilization efficacy of plasma-generated species depends on the proximity of the compound(s) treated to the plasma-liquid interface and the plasma area.
- The process is a competitive AOP for the treatment of a range of compounds and a superior technique for the removal of long-chain PFAS from various aqueous matrices.
- Addition of CTAB facilitates the transport of short-chain PFAS to the plasma liquid interface and enables their removal although chloride ions may interfere with the binding process.
- Chlorine chemistry (HOCl) may significantly contribute to the oxidation of bulk liquid constituents.
- Applications: water reuse (e.g., recycling of wastewater treatment plant effluents) and point source treatment (e.g., industrial and hospital effluents).
- Post-concentration step treatment (plasma treatment train) is the most realistic near-future application of the technology.

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