

A plasma-based process for treatment of perfluoroalkyl substances (PFASs) in ion exchange brine regenerant solution: reactor design challenges and physicochemical processes at the plasma-liquid interface

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Outline

1. Electrical discharge plasmas for water treatment
2. Poly- and Perfluoroalkyl Substances (PFASs)
3. Plasma PFASs treatment
4. Operational parameters influencing the PFAS treatment:
fundamental studies
5. Plasma treatment of PFAS-containing ion exchange brine

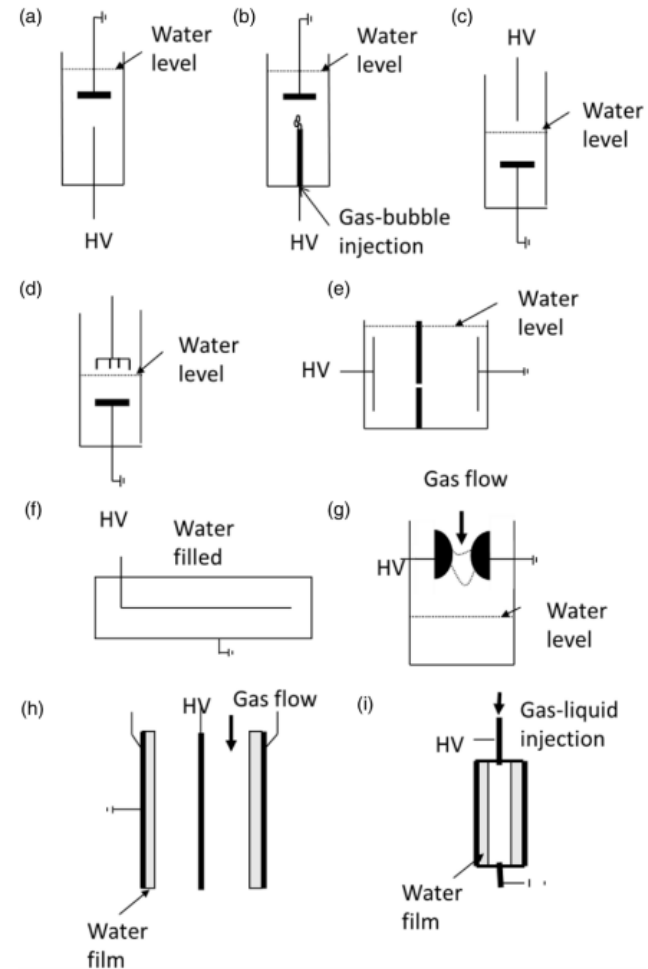
Electrical Discharge Plasmas for Water Treatment

- Plasma processes can be used both **indirectly** (to generate ozone) and **directly** to treat contaminated water.
- Direct treatment: OH, H, e⁻, H₂O₂, etc.
- Plasma processes tested on numerous model compounds (e.g., phenol, dyes, pharmaceuticals and personal care products, etc.) at **energy yields of similar magnitude to conventional and emerging AOPs**.
- Widespread skepticism towards plasmas for water treatment.

Plasma Reactors for Water Treatment

Research indicates that **the best performing plasma reactors** feature the following characteristics:

1. Gas discharge is contacting the liquid as a spray and/or jet. Alternatively, gas bubbles are present in the liquid.
2. Argon and/or oxygen are used as processing gases.
3. Thin layers of water are being treated.



Performance of Plasma Reactors for Water Treatment

The performance of a plasma reactor will depend on:

1. PLASMA AREA

- electrode geometry
- discharge phase (gas vs. liquid)
- input power
- means of power delivery

Concentrations of
reactive species

2. VOLUME OF THE TREATED LIQUID

3. THE TYPE AND INITIAL COMPOUND CONCENTRATION

- the plasma technology appears to be superior for the treatment of molecules that exhibit surfactant-like behavior and competitive for the removal of trace organic contaminants.

Present and Future of Plasma-based Water Treatment

- Plasma reactors **cannot competitively** treat all types of compounds.
- The technology will **not be able to compete** with homogeneous processes UNTIL the contact between the plasma and the treated liquid is maximized in an efficient manner. **We were able to accomplish that for surfactants.**
- Demonstrate the **superiority of the plasma technology** for the treatment of surfactant-like molecules:
 - Promote plasma-based water treatment
 - Help overcome the widespread skepticism regarding the technology
 - Demonstrate the importance of the informed plasma reactor design

Poly- and Perfluoroalkyl Substances (PFASs)

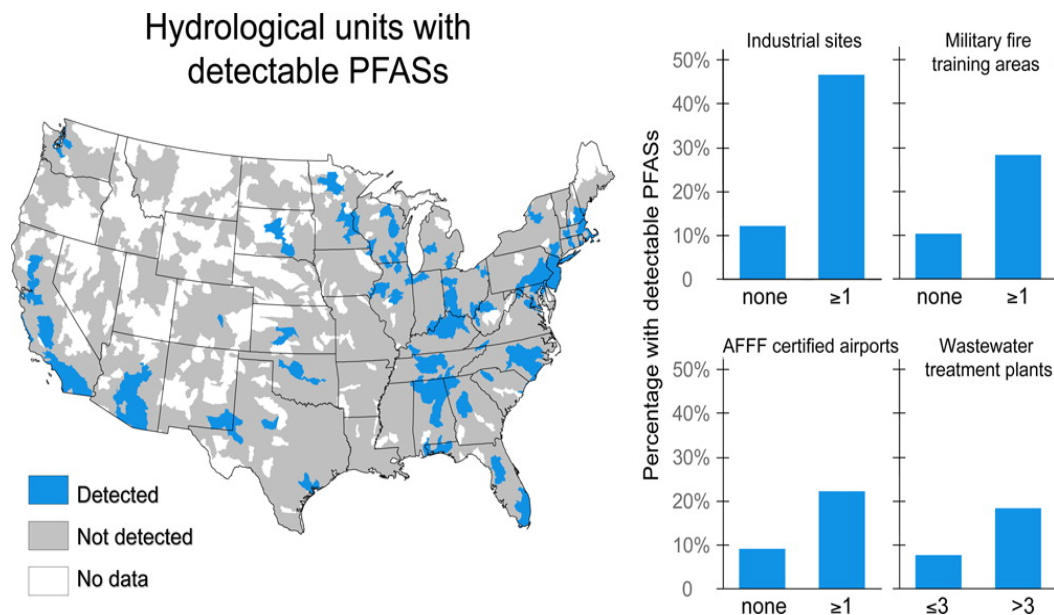
Magnitude of the problem:

billions of gallons of water contaminated with PFASs.

Sources:

military training activities (flame retardants), manufacturing (non-stick cookware, water resistant clothing, fast food wrappers),...

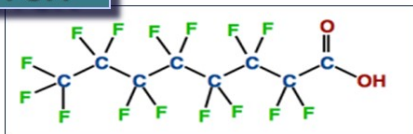
Health effects: fetus development, cancer...



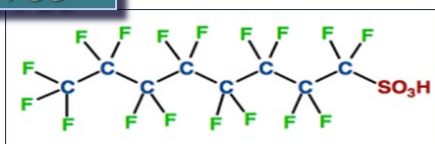
Areas with detectable levels of poly- and perfluoroalkyl substances (PFASs) and their proximity relationship to industrial sites, military fire training sites, airports and wastewater treatment plants. Image by Hu XC et al., Environmental Science & Technology Letters, 2016

Poly- and Perfluoroalkyl Substances

PFOA



PFOS



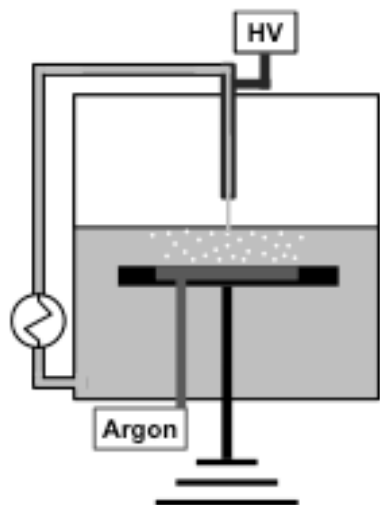
PFOA=perfluorooctanoic acid

PFOA=perfluorooctanesulfonic acid

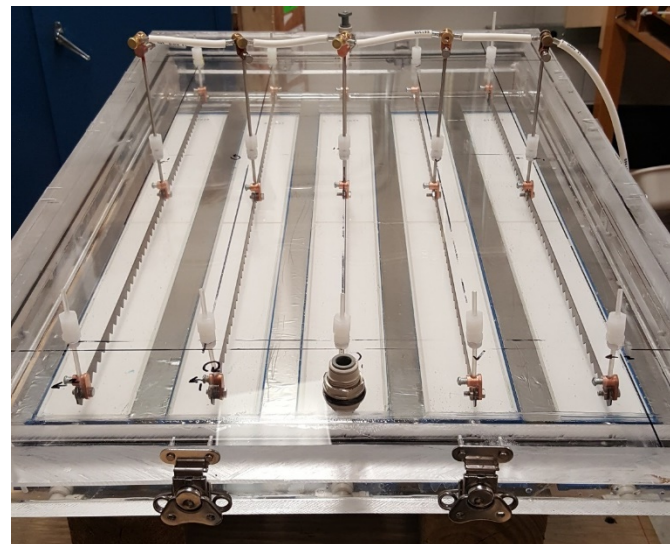
- ✓ highly soluble in water
- ✓ non-volatile
- ✓ surfactant properties

- EPA's health advisory levels for PFOA and PFOS in drinking water are at 70 ng/L.
- PFASs cannot be oxidized (C-F bond).
- Current solution: adsorption by activated carbon followed by incineration.
- Air Force alone is expecting to spend \$2 billion for cleanup of PFAS-contaminated sites.

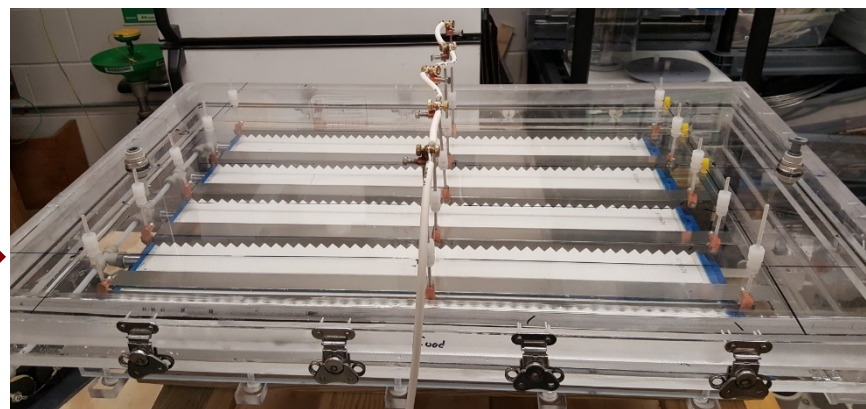
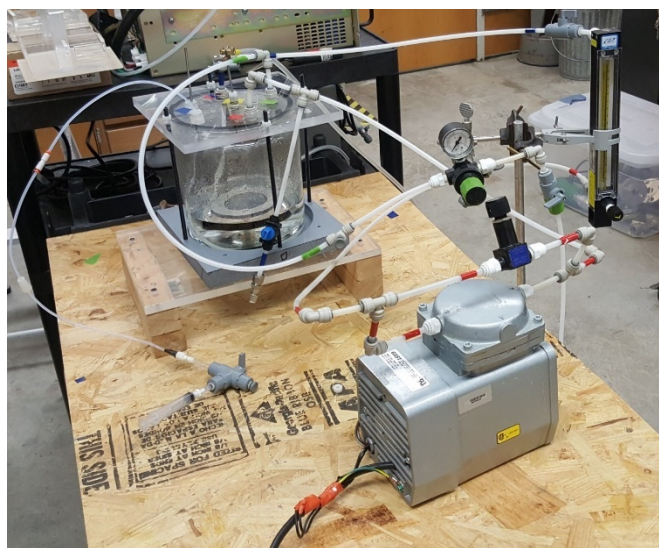
Plasma Reactor(s) for PFASs Degradation



Bench scale, 0.5 L, batch

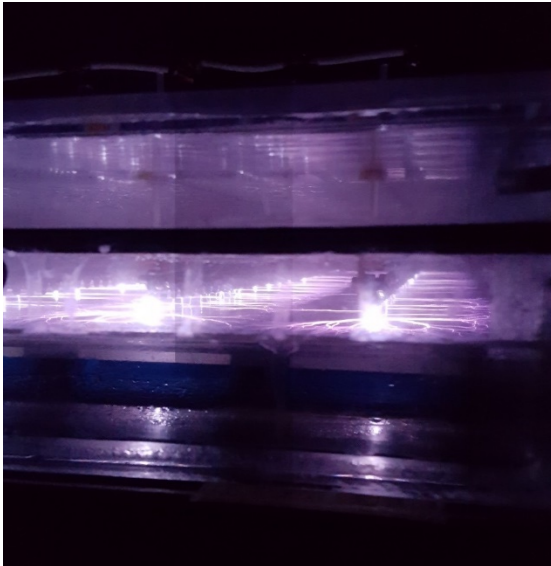
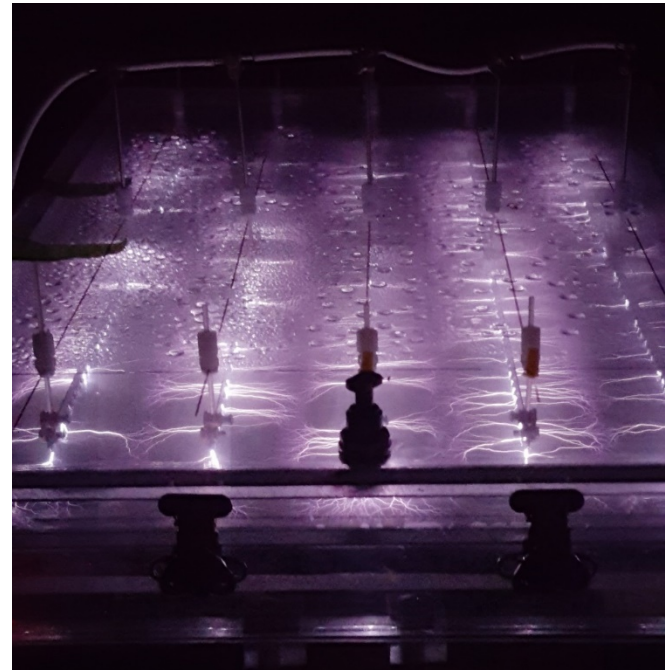
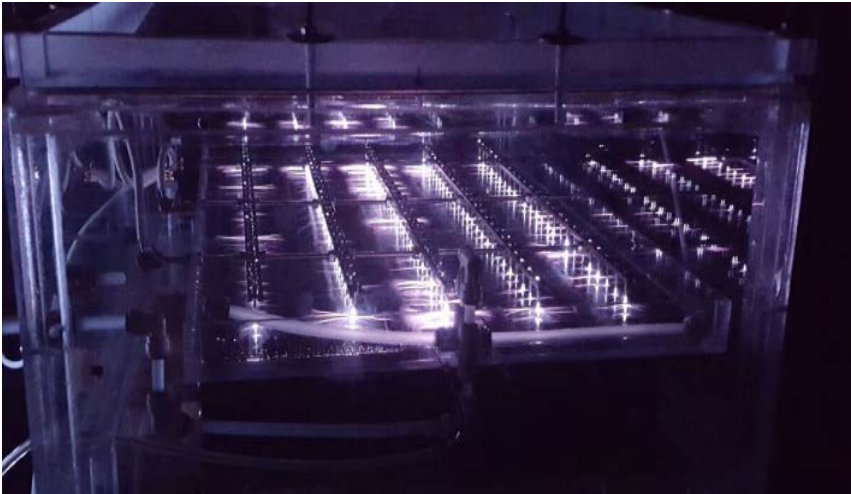


Scaled-up unit, 0.1-2 gpm, flow-through



- Submerged gas diffusers
- Recirculation of the process gas (argon)

Scaled Up Plasma Reactor



Demonstrating the Plasma Reactor in the Field

Evaluation of PFAS Samples for Site Selection: Bench-scale testing of IDW (Investigation-Derived Waste) purge water. Water from 10 Air Force sites has been treated.



Design Optimization: Limited laboratory testing of the prototype plasma reactor to optimize operational characteristics with respect to site-specific groundwater quality.



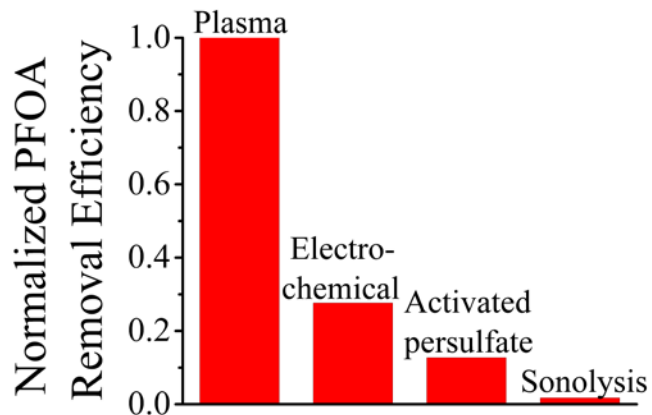
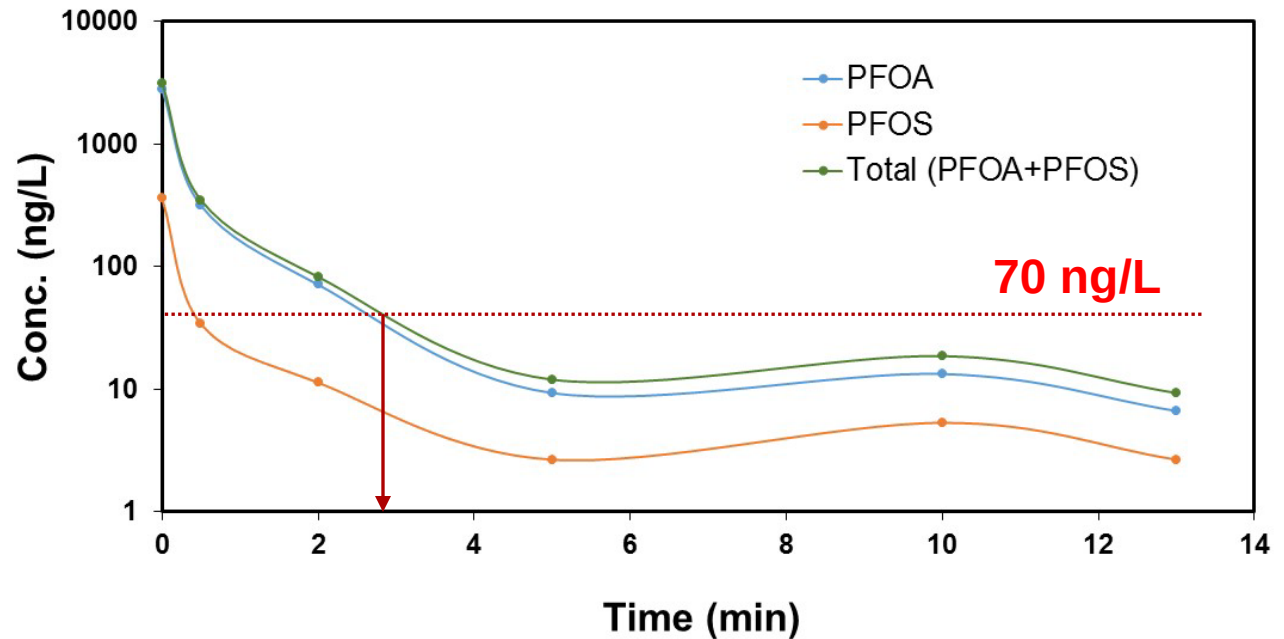
Not a straightforward task

Field Demonstration: Design, construction and operation of the plasma reactor skid at an Air Force site. **Summer 2018.**

Evaluation of PFASs Samples for Site Selection

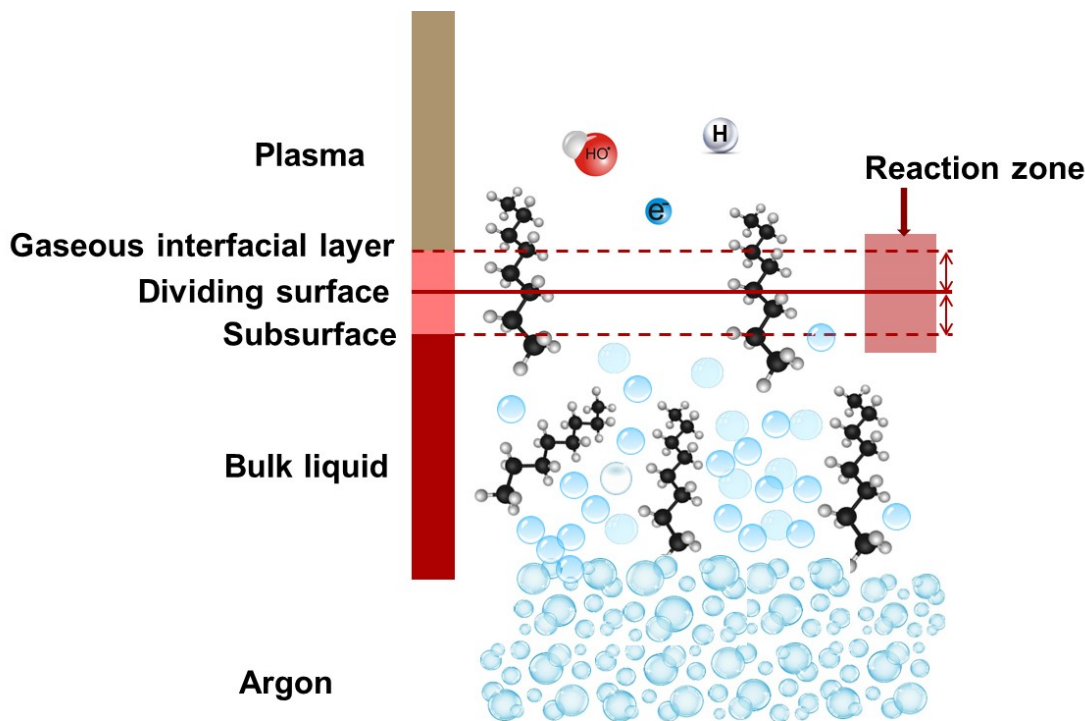


Joint Base San Antonio Air Force Base



Process	Contaminant	Treatment costs (\$/m ³)
Activated carbon	PFOA	0.39
	PFOS	0.45
Plasma	PFOA	0.19
	PFOS	0.11
Sonolysis	PFOA	13.5
	PFOS	32.7

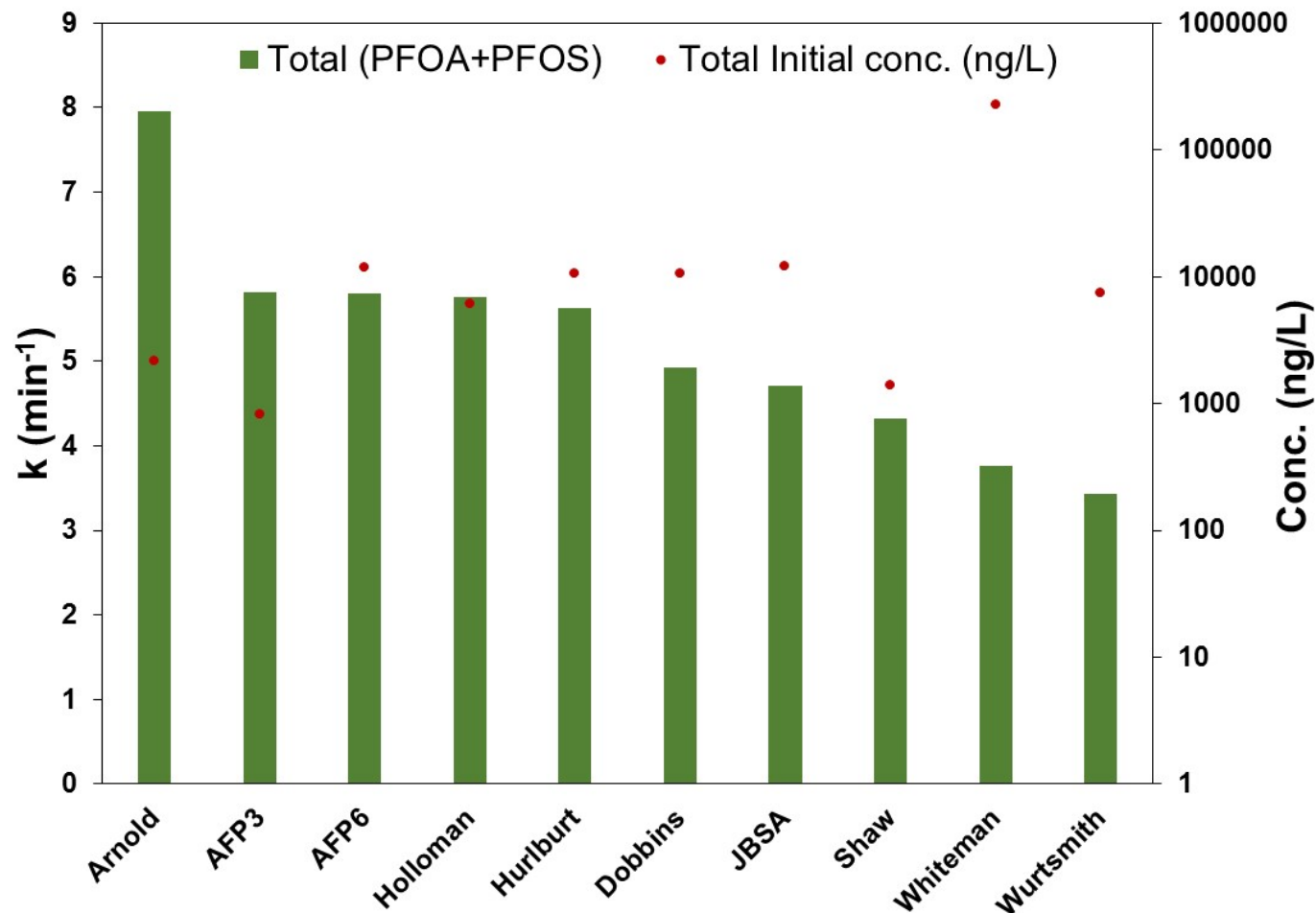
Mechanism of Degradation and Products



- ~~Radical-oxidative~~
- Radical-reductive (?)
- Electron-reductive (~15%)
- Collisions with Ar ions (?)
- Thermal (?)

- 60% of the starting PFOA solution is mineralized to fluoride ions.
- Very small amounts (~10%) of shorter chain PFASs are formed and degraded.
- Large quantities of short-chain fluorocarbon gases are formed and degraded over time. Cannot be identified/quantified yet.

Treatment Rates and Water Quality Parameters



Treatment rates **depend on the initial PFASs concentrations**. They appear not to be affected by the presence of co-contaminants or solution conductivity (if $<1000 \mu\text{S/cm}$).

Predicting the Effectiveness of the Treatment

- Geochemical characteristics of water vary from sample to sample.
- How to ensure continuous success of the treatment?

Fixed:

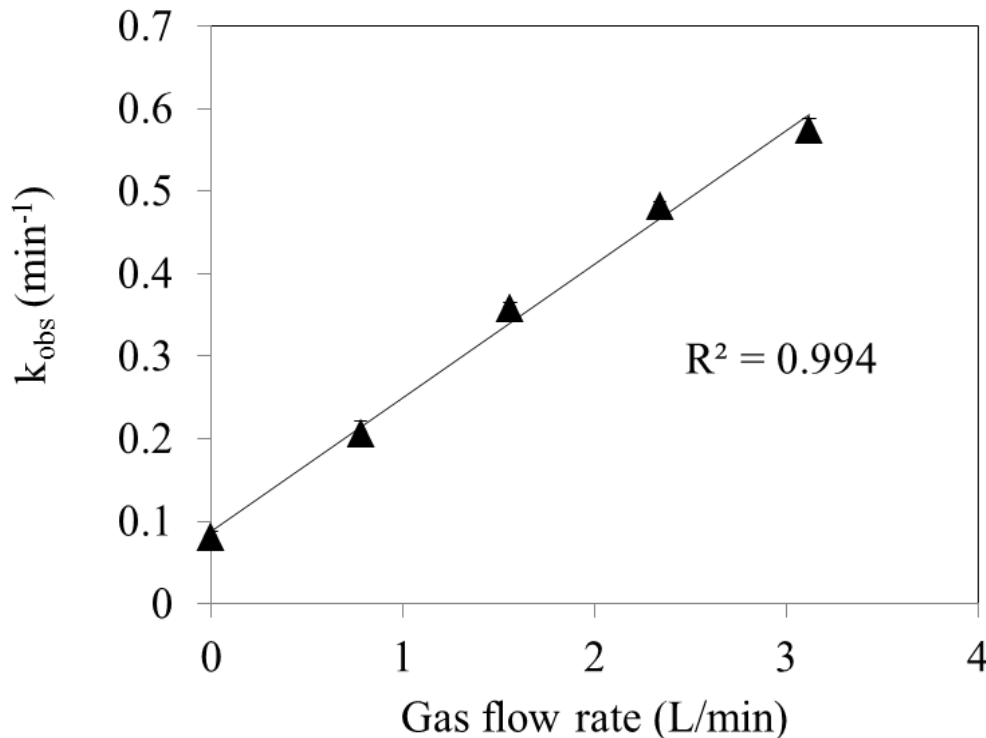
- Reactor design
- Input power

Variable:

- Argon flowrate
 - Retention time of the water in the reactor
 - Discharge frequency
 - Water composition: initial concentration of the compounds
-

Argon Bubbling Rate and the Removal Rate of Rhodamine B (RhB)

Rhodamine B: easy to analyze model surfactant compound



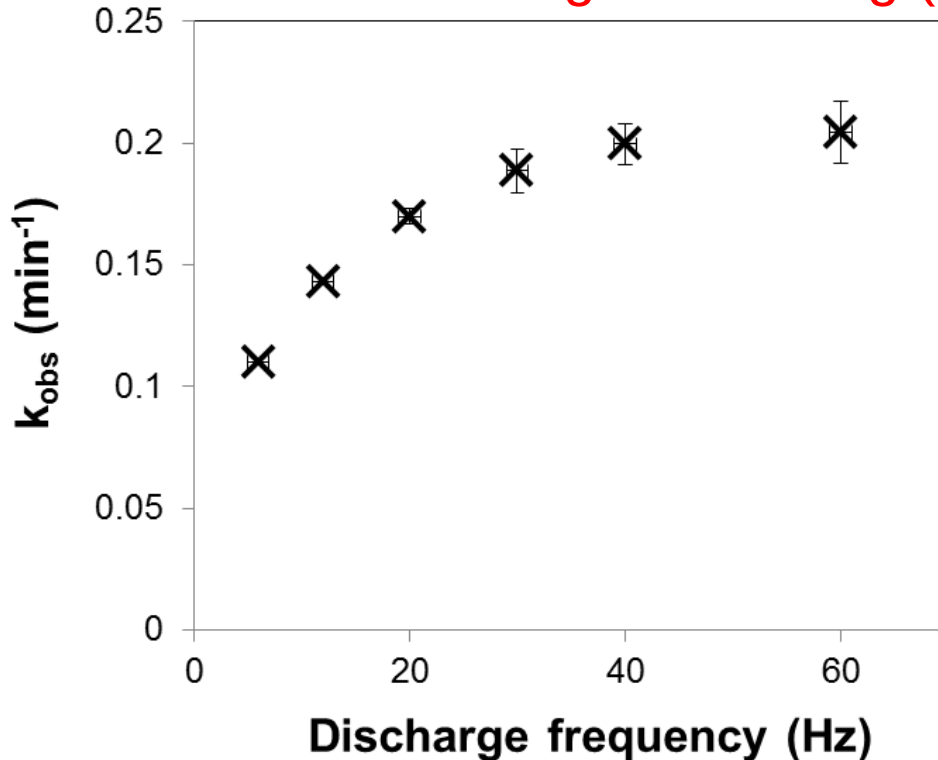
Removal increases due to increased surface density and surface renewal rate.

The optimum bubbling rate is simply the highest that can be achieved for a given system.

PFAS treatment: gas flux of 17 mL/cm²s which corresponds to the maximum bubbling rate of 3.8 L/min per diffuser.

Discharge Frequency and the Removal Rate of Rhodamine B

No argon bubbling (system complexity)



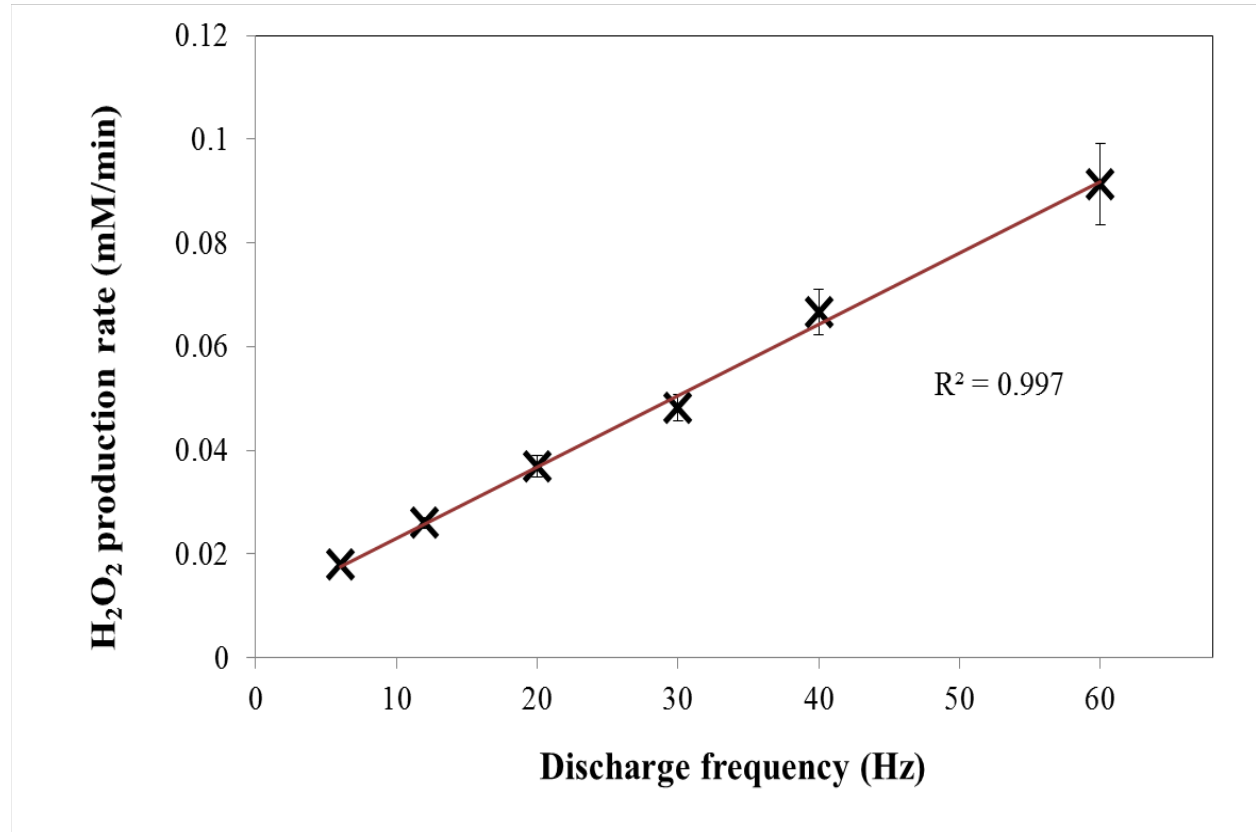
Rate constant increases/plateaus while the efficiency of the treatment is reduced with increased frequency.

Each individual discharge is having less of an effect as the frequency increases. This could be due to:

- (a) Changes in the production rates of the reactive species
- (b) Changes in the qualities of the treated solution

Discharge Frequency and the Removal Rate of Rhodamine B: production rate of reactive species

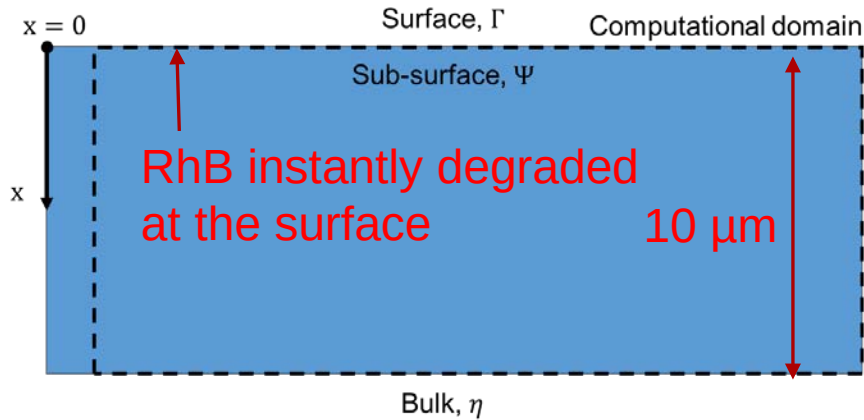
H_2O_2 production rate = surrogate for the quantities of reactive species generated by the plasma



Strong linear correlation = no significant variation in the quantities of reactive species generated by each discharge at different frequencies.

Exploring the Dependence of the Removal Rate on Discharge Frequency

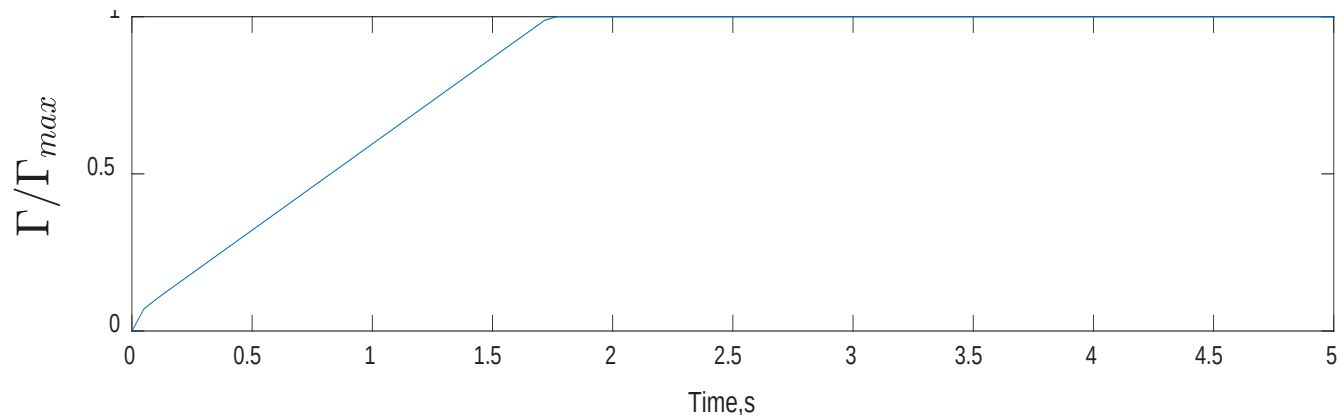
1D Langmuir-Hinshelwood adsorption kinetic model



Γ_{max} = maximum (equilibrium) surface dye concentration

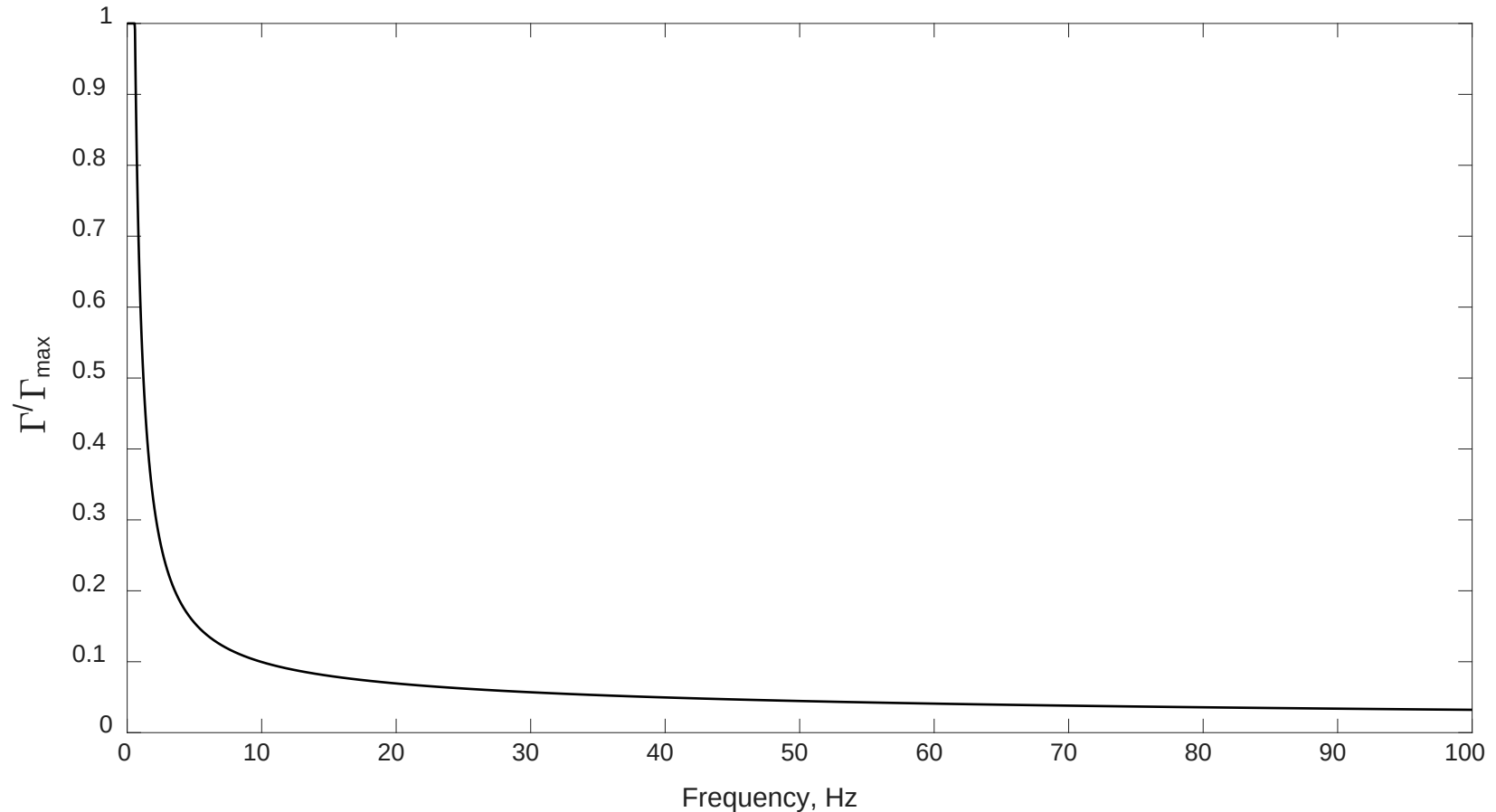
$\Gamma(t)$ = instantaneous surface dye concentration

completely back-mixed



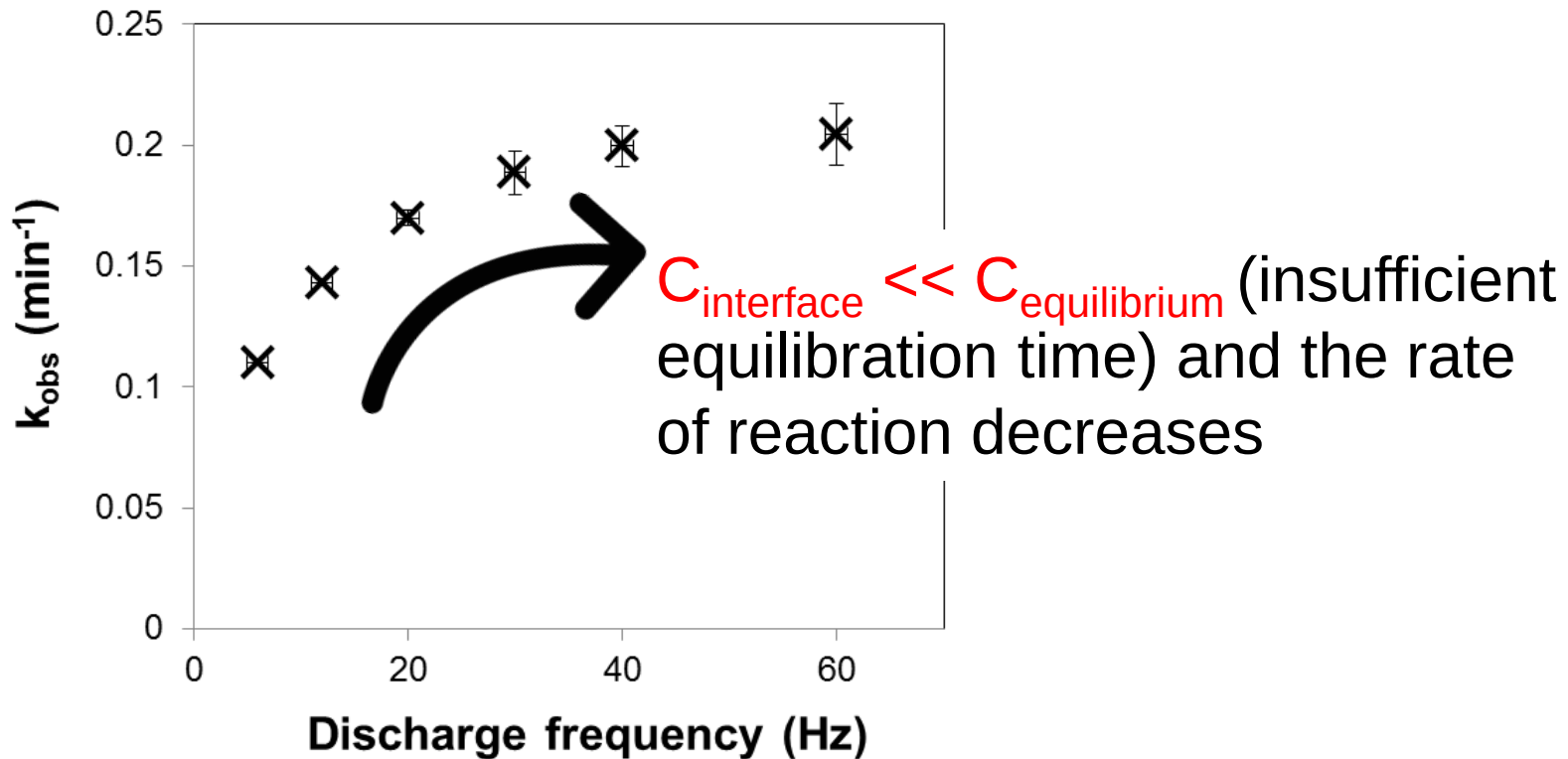
Equilibration time for RhB is ~ 2 s.

Exploring the Dependence of the Removal Rate on Discharge Frequency



As the frequency increases, the discharge period decreases and the surface concentration of the dye decreases.

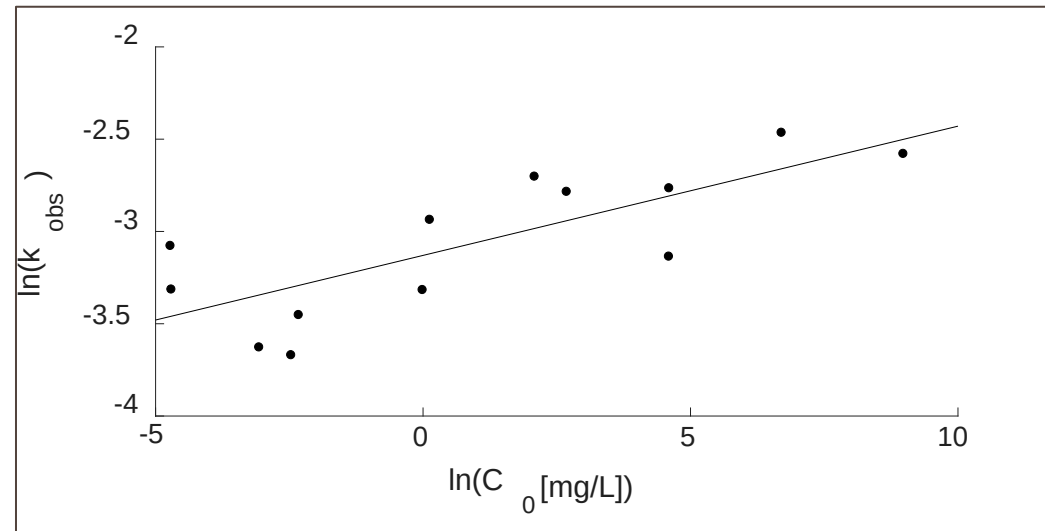
Exploring the Dependence of the Removal Rate on Discharge Frequency



PFAS treatment: using a lower frequency will increase treatment efficiency, but necessitate a larger system to attain a given capacity. The optimum frequency for the treatment of PFASs was determined to be 40 Hz.

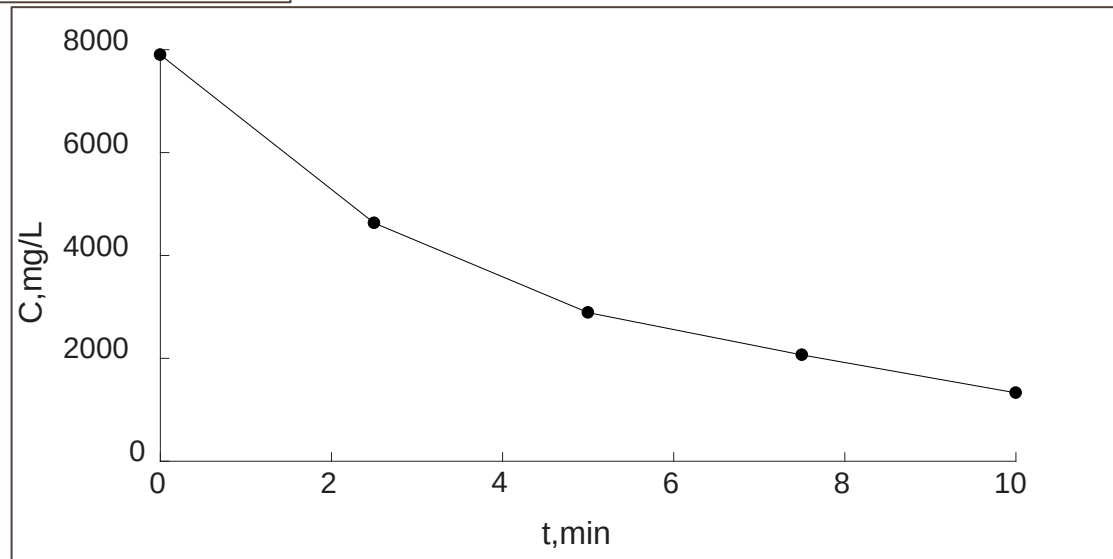
Removal Rate of Rhodamine B: Influence of the Initial Concentration of the Dye

No argon bubbling (system complexity)



Removal increases with an increase in the initial concentration

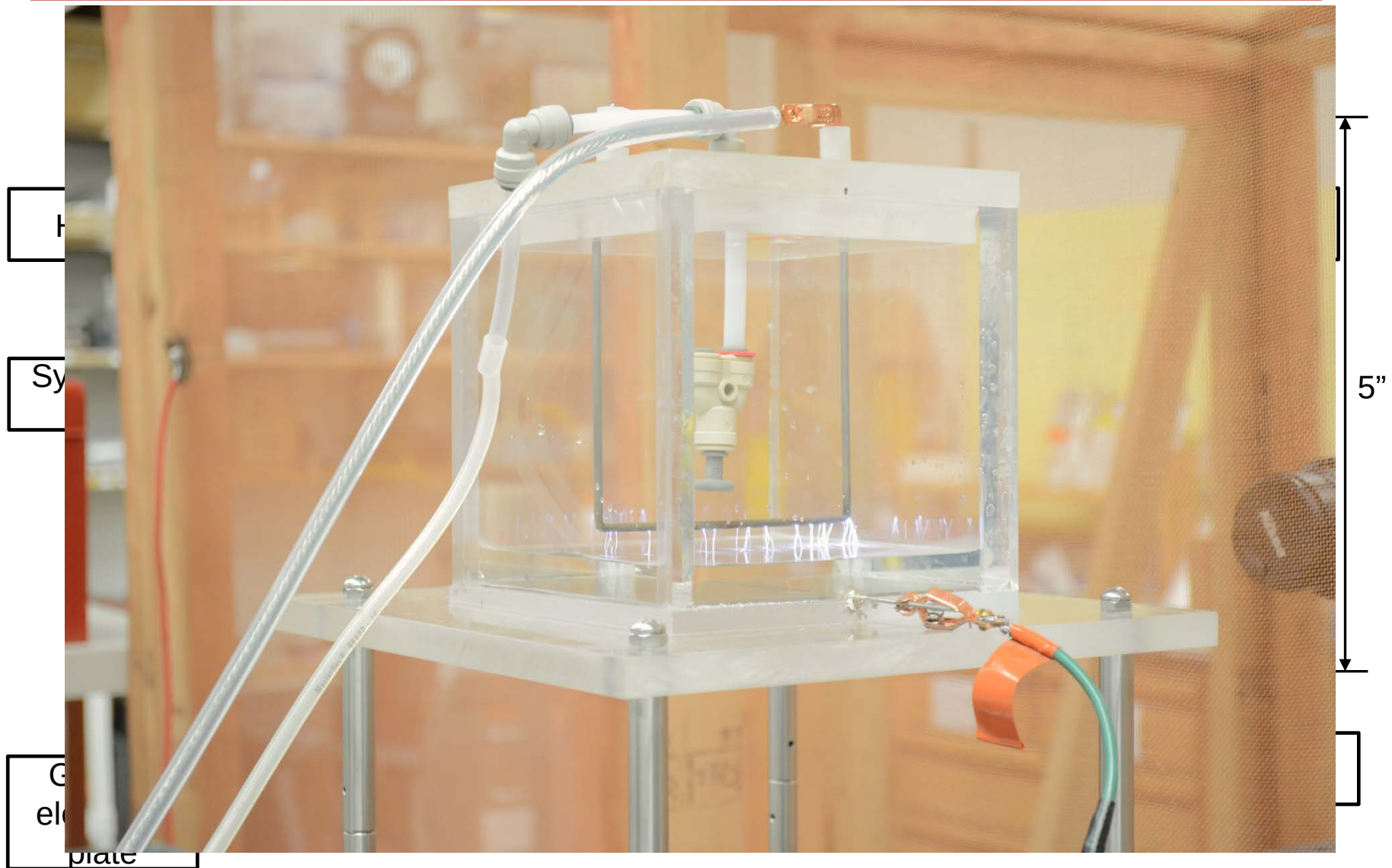
Kinetics follows first order for all bulk liquid concentrations



Bulk Liquid Transport vs. Reaction: Research Objectives

1. For a fixed bulk liquid concentration, explain the relative importance of diffusion, convection and reaction in the dye removal. **Base case: Rhodamine B without bubbling.**
2. Explain the effect of the bulk liquid concentration on the dye removal.
 - o For PFAS removal, the rate constant decreases with an increase in bulk liquid concentration when argon is bubbled through the solution.
 - o Even for Rhodamine B, the inclusion of bubbling reverses the trend and the removal decreases with an increase in concentration.

Bulk Liquid Transport vs. Reaction: Development of a 2-D Transport Model



The 2-D Model and the Transport Equation



$$\frac{\partial C}{\partial t} = \nabla \cdot (-D \nabla C) + \nabla \cdot (\mathbf{U}C) + S_{\text{Reaction}}$$

Convective Term: Time Evolution of the Flow Field for the Base Case

Aqueous NaCl solution at 300 $\mu\text{S}/\text{cm}$, $f=40$ Hz, $V=(+)$ 25 kV

Argon is the gas headspace (no flow)

Discharge location



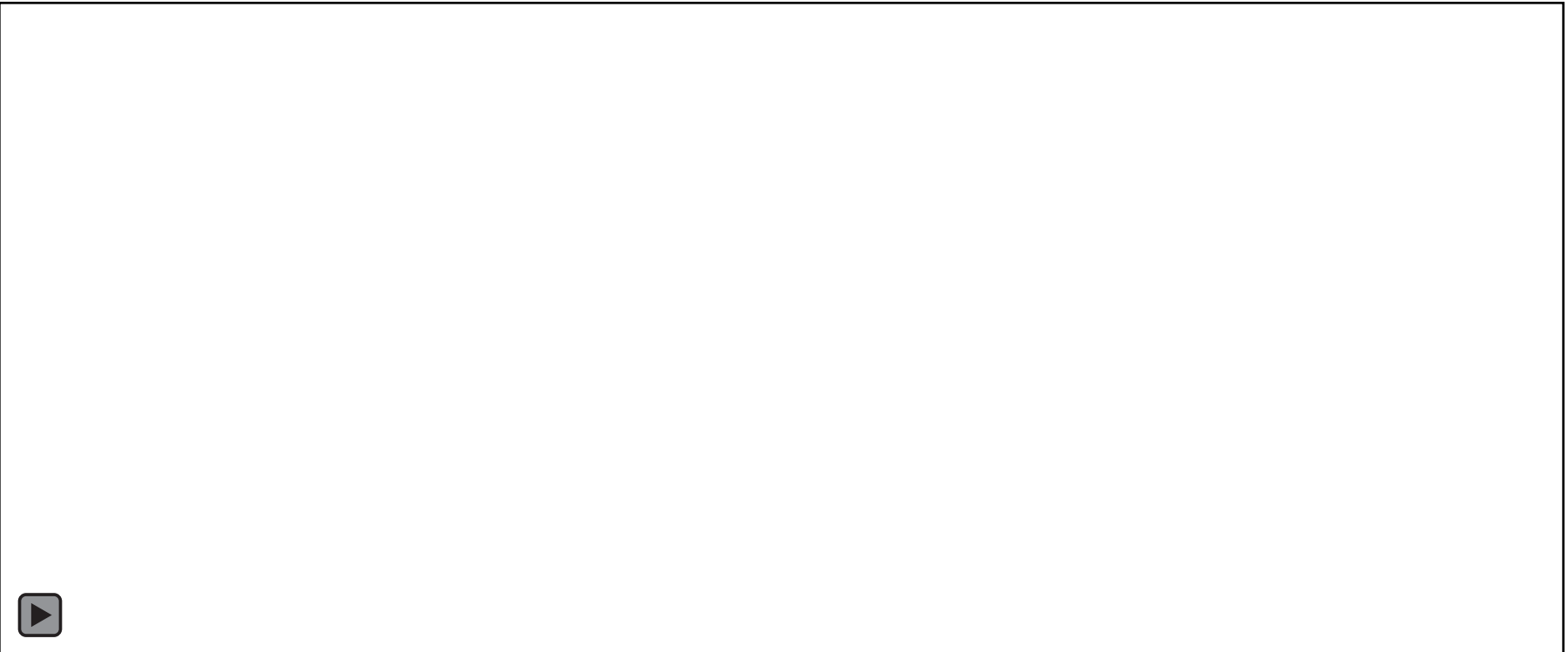
Convective Term: Time Evolution of the Flow Field for Rhodamine B

Aqueous NaCl solution at 300 $\mu\text{S}/\text{cm}$, $f=40$ Hz, $V= (+)$ 25 kV

Argon is the gas headspace (no flow)

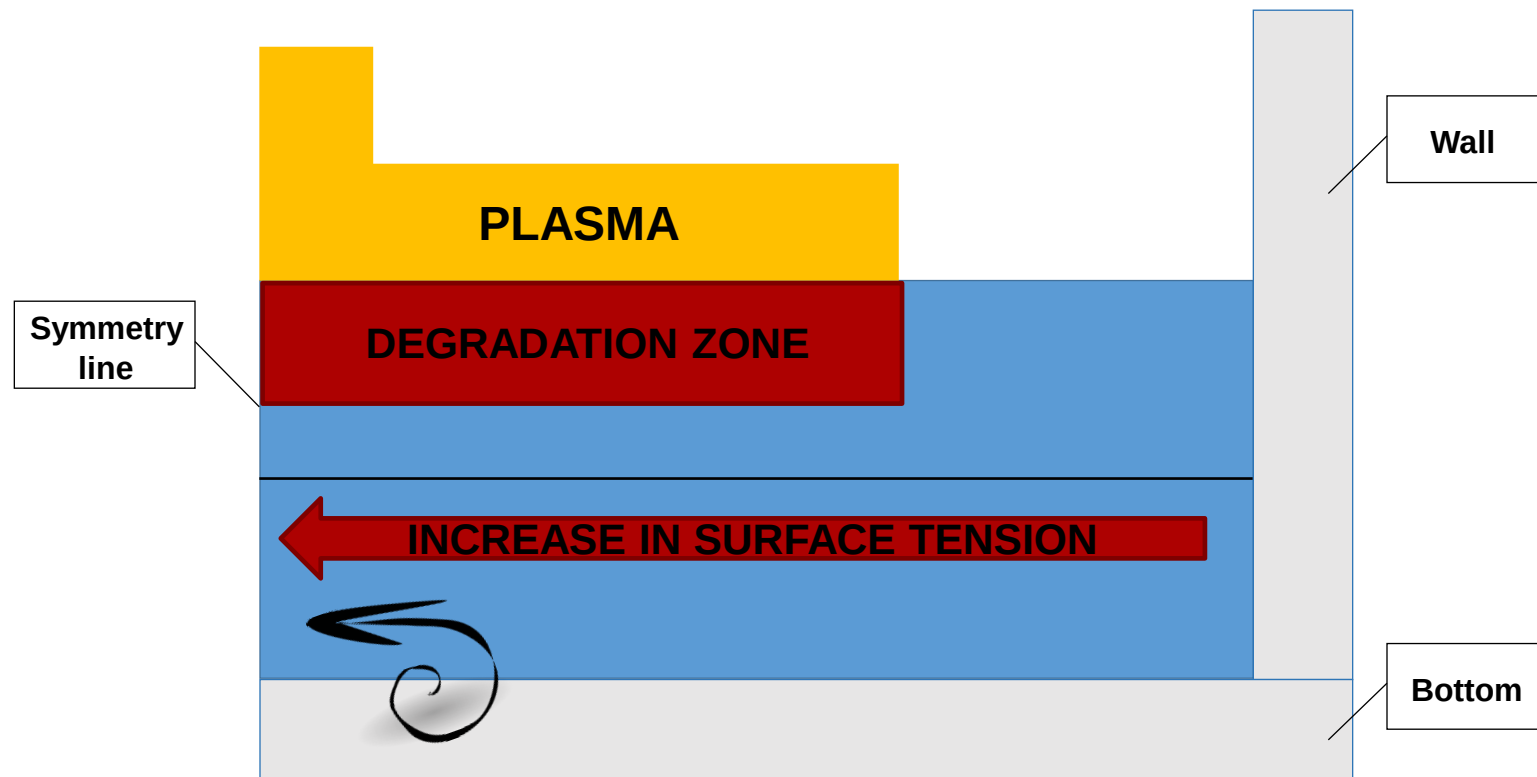
1 mg/L RhB dye

Discharge location

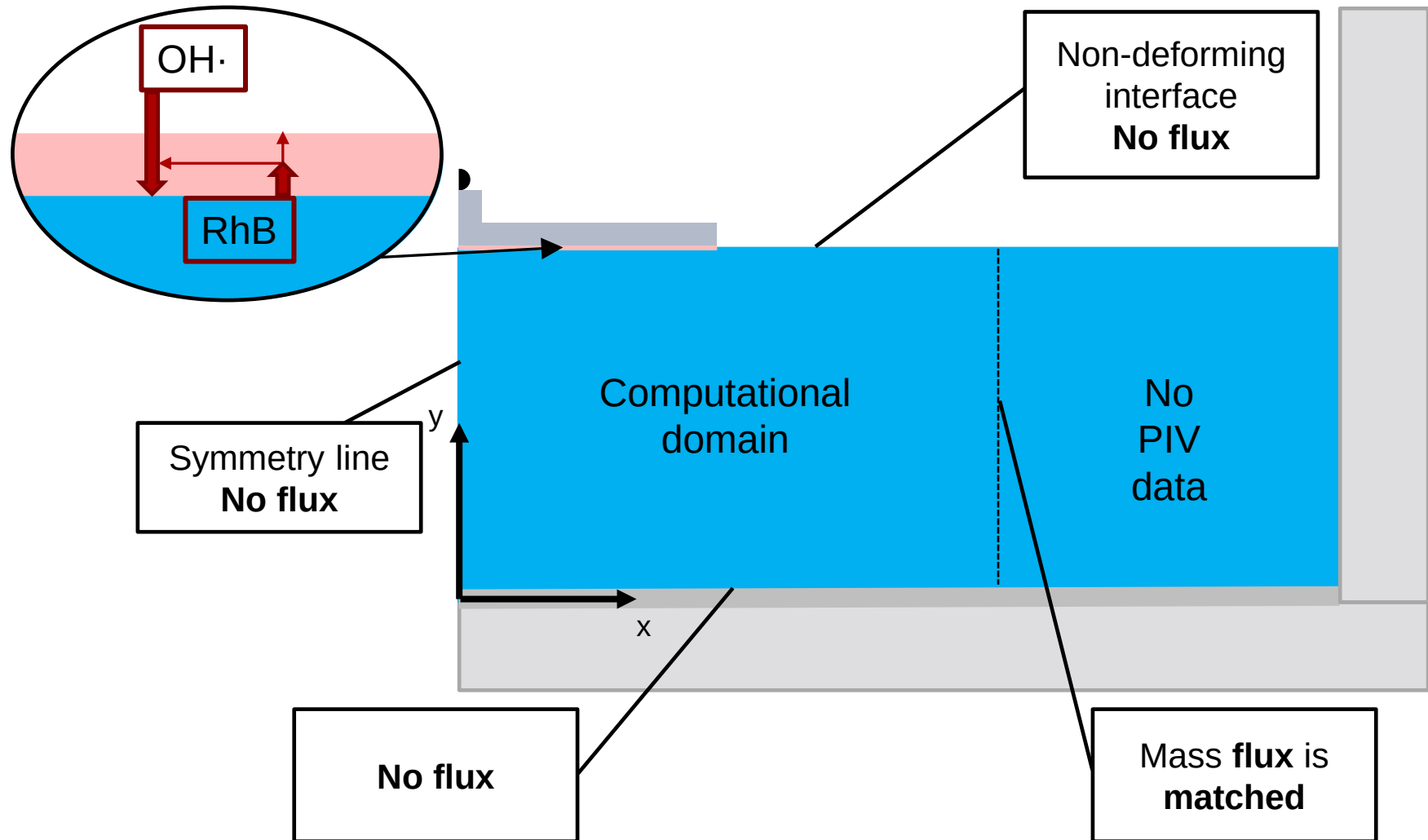


The Flow Reversal and the Concentration Gradient Driven Marangoni Flow

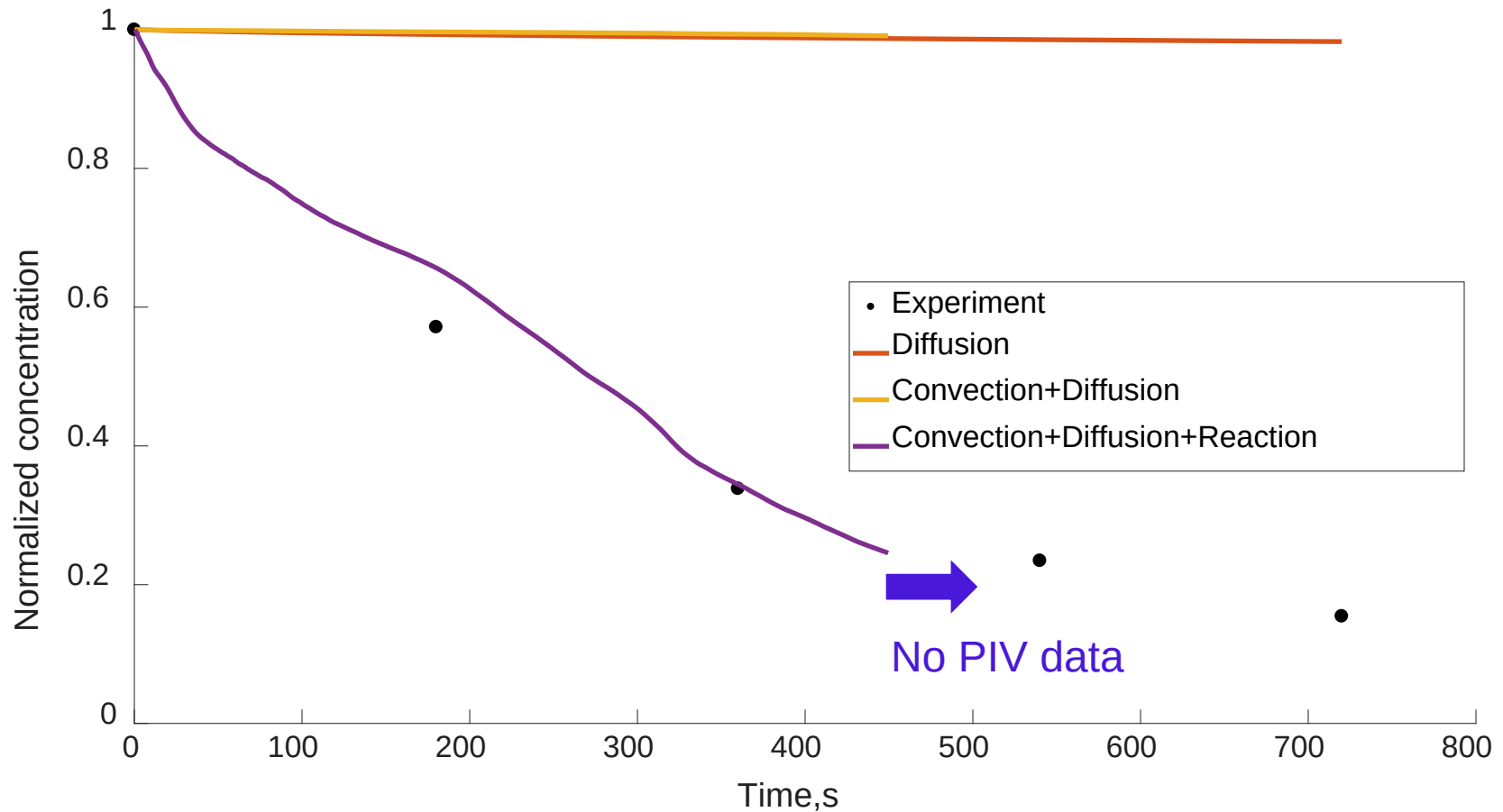
Strong surfactants reverse the flow but only for a certain period of time; as they degrade, flow returns to “normal”.



Transport Equation: Boundary Conditions



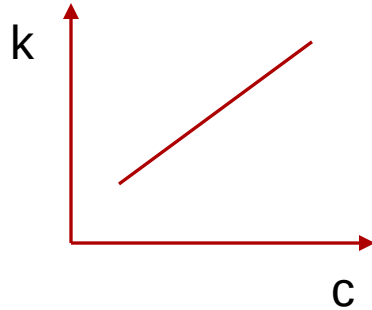
The Relative Importance of Diffusion, Convection and Reaction in the Dye Removal



The importance of the bulk liquid transport in the removal must be verified for all liquid concentrations investigated.

Dye Removal: Bubbling vs. No Bubbling

No bubbling / no mixing:

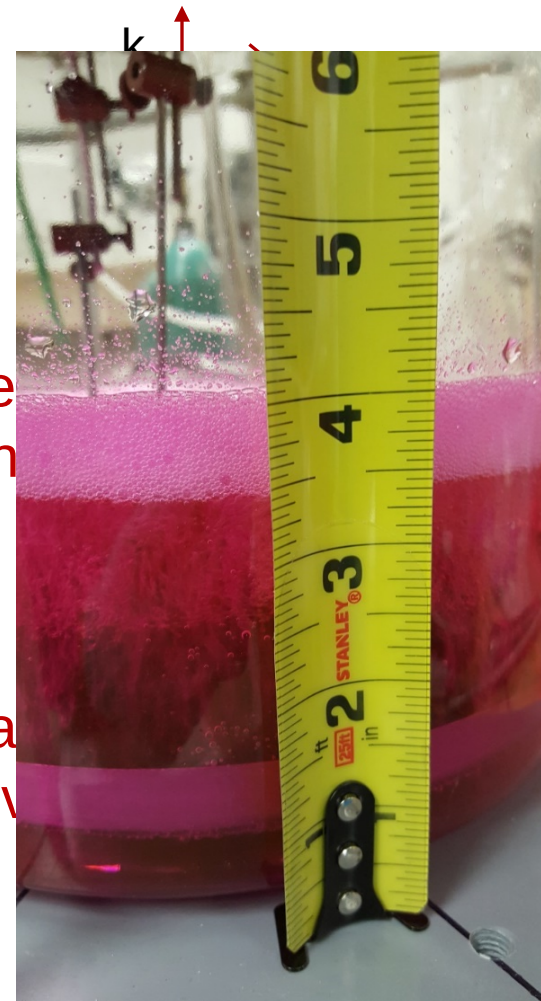


Magnitude of the velocity field increases with dye concentration (surface tension driven flow)



Surface renewal rate increases with velocity and so does the removal rate

Bubbling:



The magnitude of the velocity field increases with dye concentration.

Foam formation prevents the dye from reaching the surface.

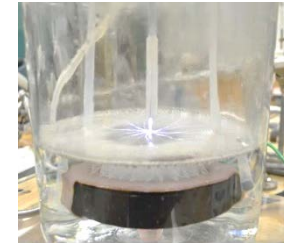
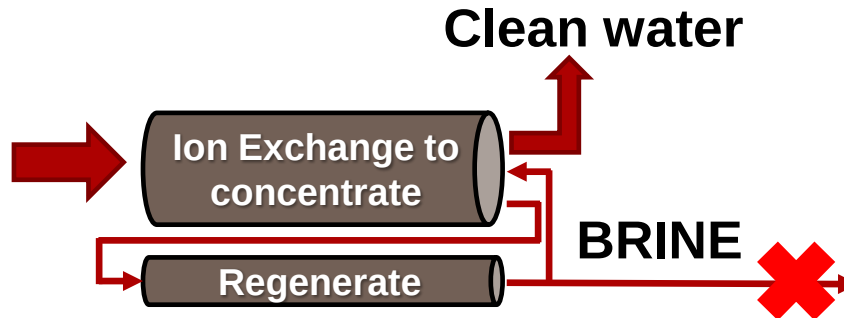
PFAS removal: decrease bubbling rates at higher initial concentrations.

Outline

1. Electrical discharge plasmas for water treatment
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fundamental studies
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Plasma Treatment of Ion Exchange Brine

- High volume
- Low concentration
- **1000+ contaminated groundwater sites**



Challenges

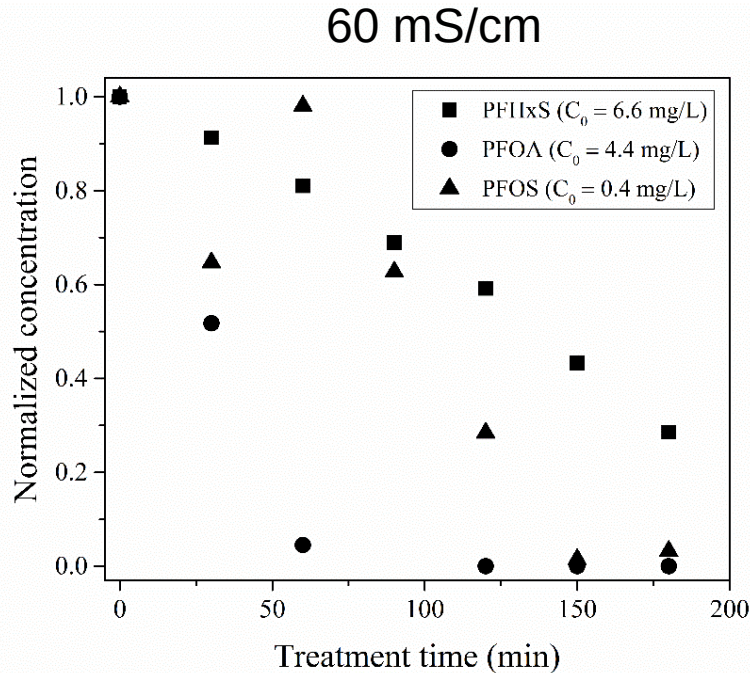
- Low treatment surface area
- Foaming

IX resin regeneration:

- (1) mixing an alcohol-based regenerant solution with the PFASs-saturated resin to desorb PFASs;
- (2) draining;
- (3) rinsing the resin.

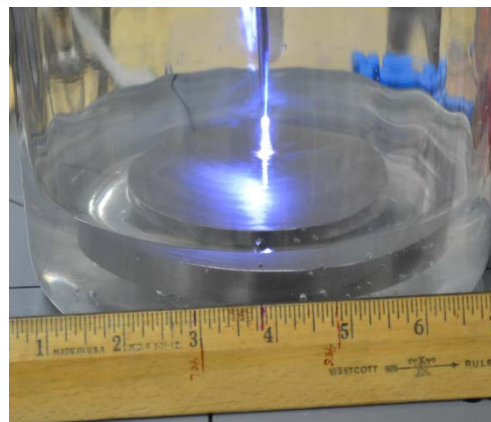
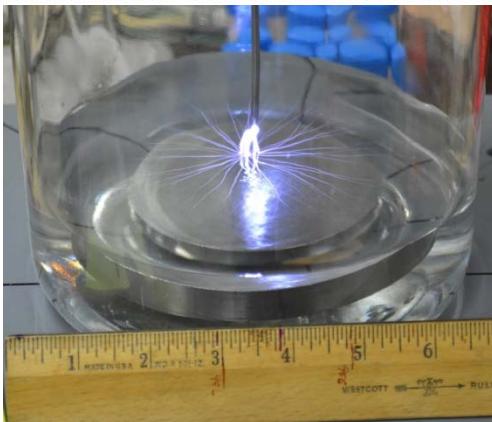
The regenerant solution is then distilled to recover some of the alcohol (typically methanol). **The leftover solution (regenerant brine) is a complex and highly concentrated mixture of PFASs, methanol (between 5% and 20%), NaCl (6-7%), and a range of co-contaminants.**

Plasma Treatment of Ion Exchange Brine: Reactor Performance



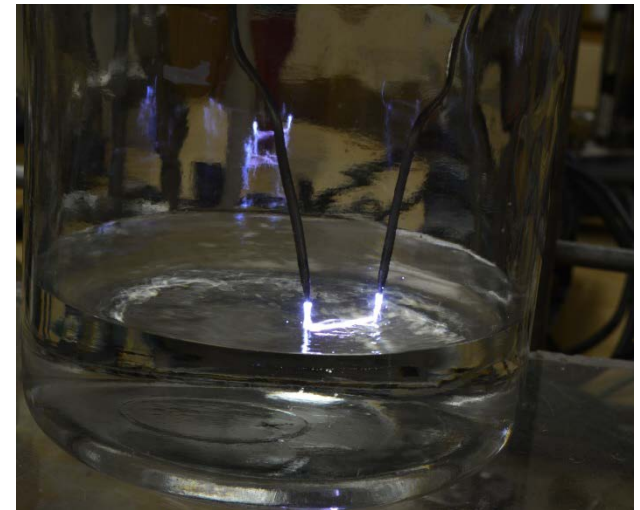
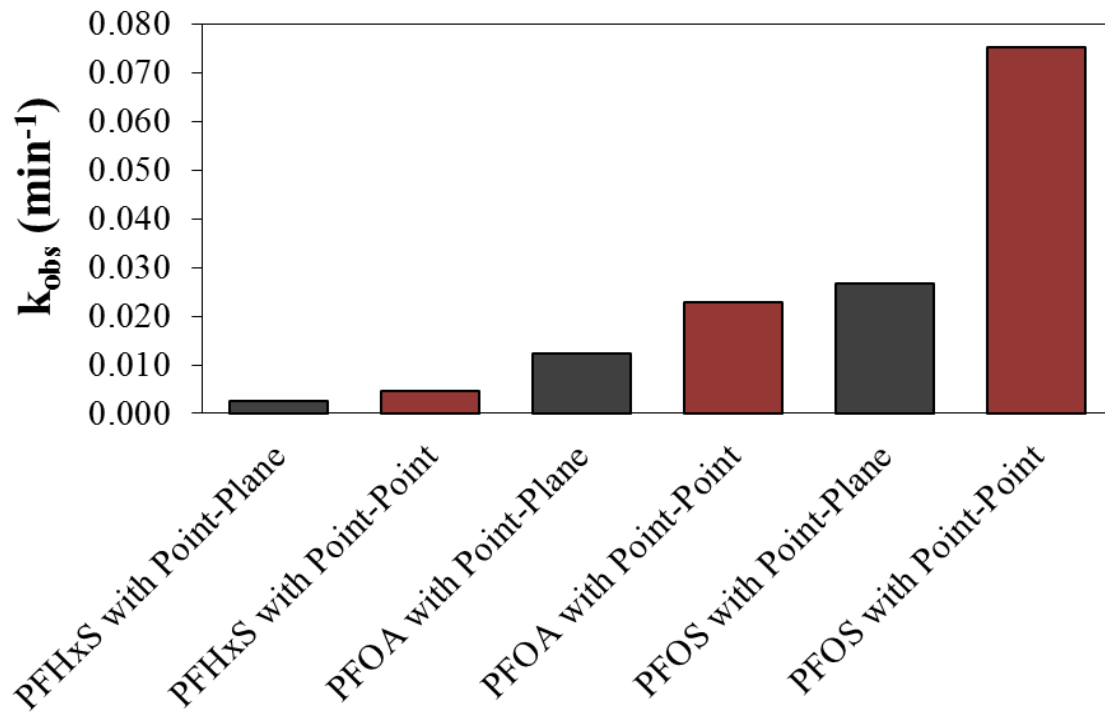
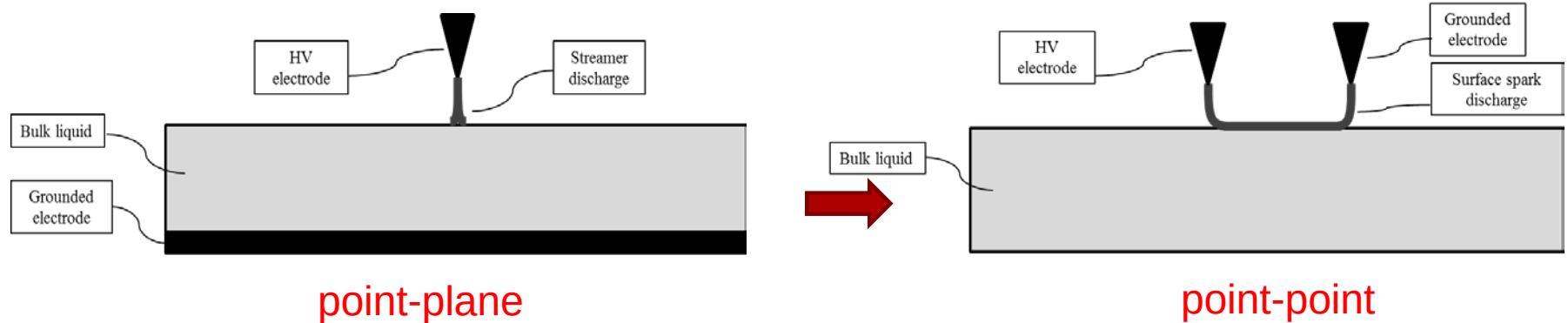
Plasma treatment results using PFAS IX regenerant brine from Pease AFB pilot IX system

- significant foaming
- small plasma area
- low treatment efficiency



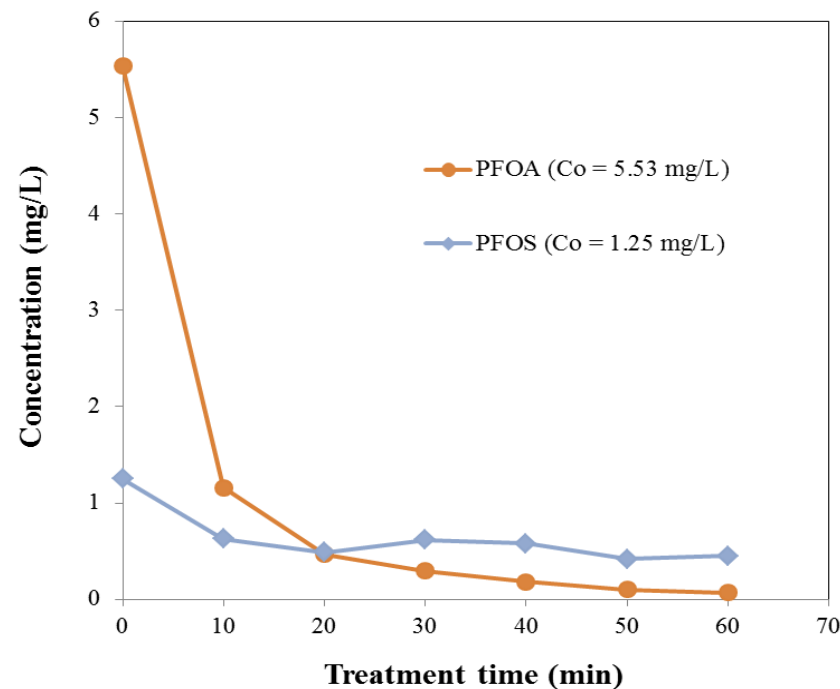
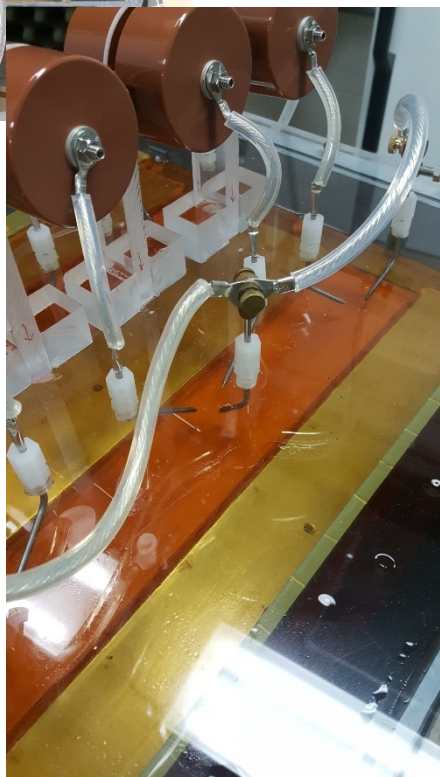
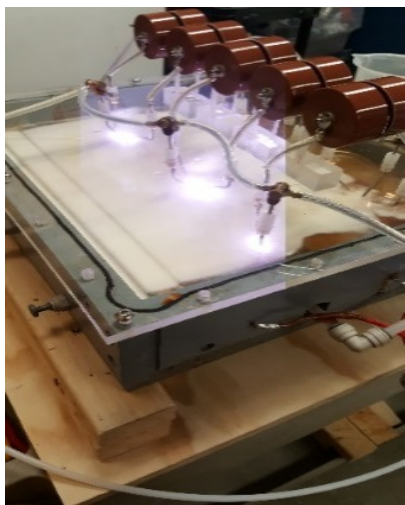
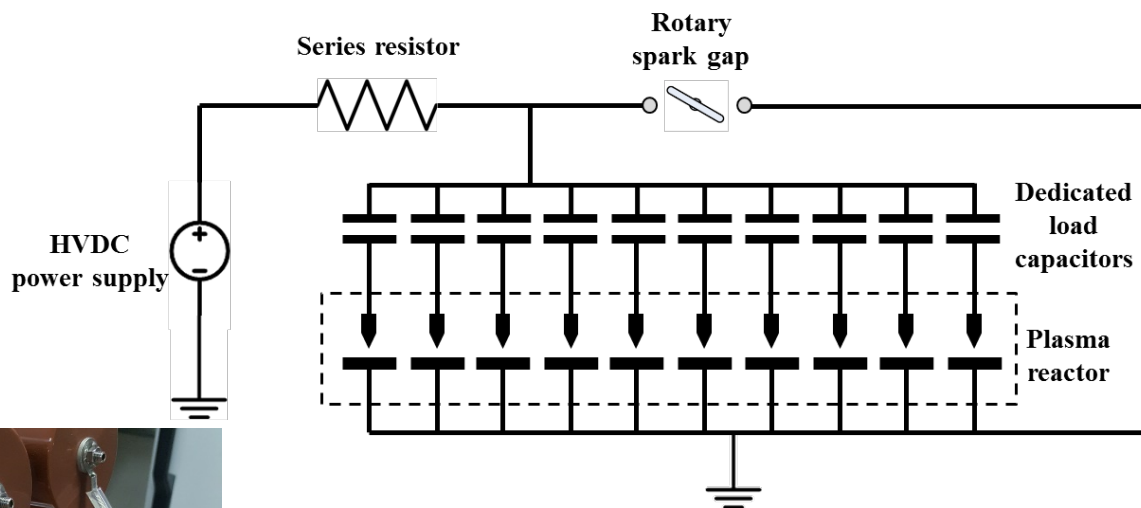
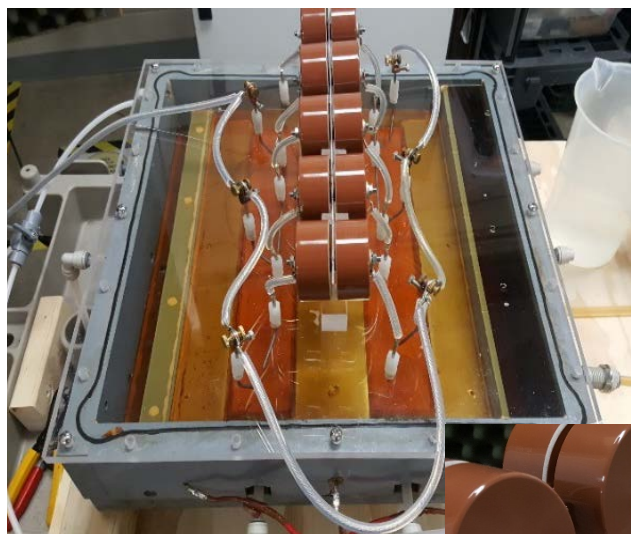
Plasma appearance as a function of solution conductivity (no bubbling for clarity)

Discharges Over Highly Conductive Water



Discharge shown without bubbling for clarity

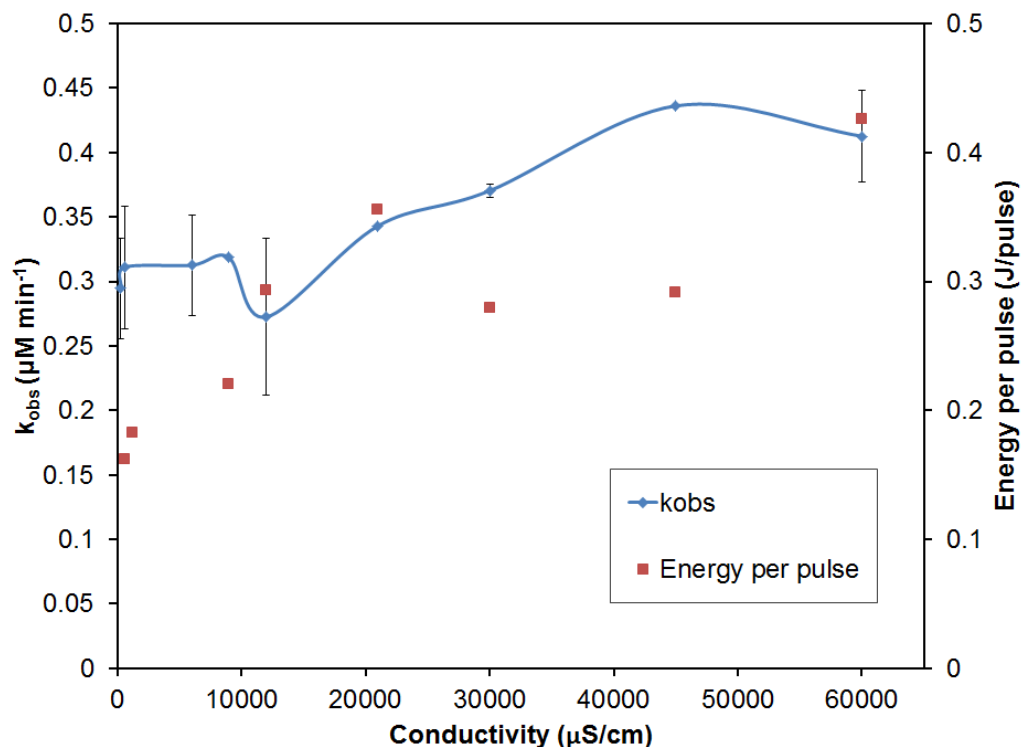
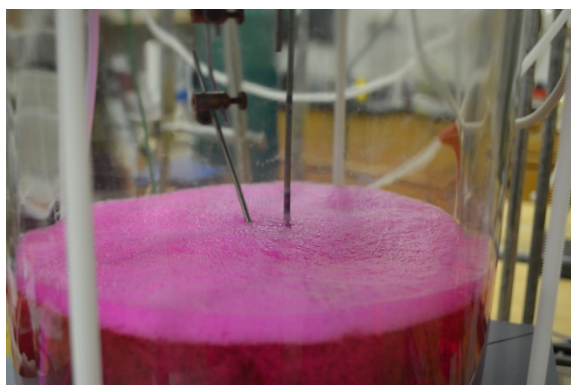
Point-Point Plasma Reactor Scaleup and Performance



Treatment of Highly Conductive Water: Physical and Chemical Mechanisms of Degradation

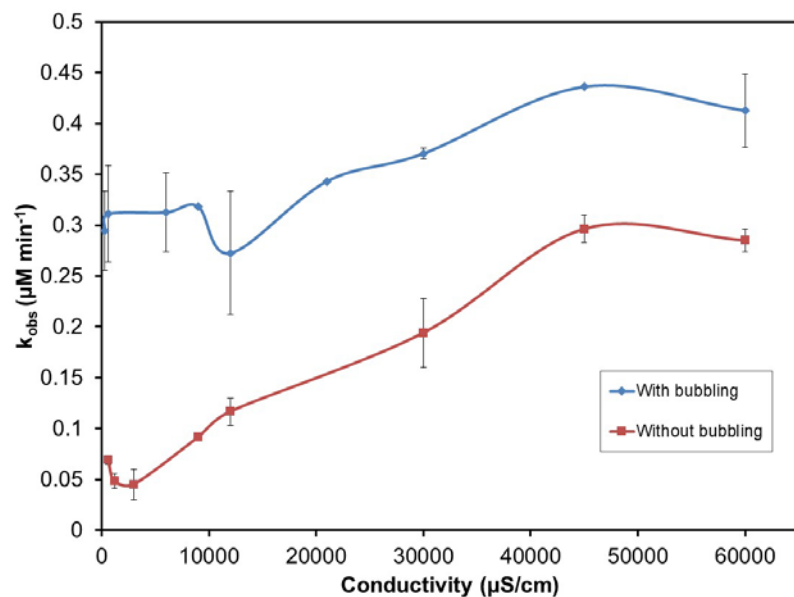
Removal of RhB dye as a function of solution conductivity

- Argon bubbled at 4.3 L/min, NaCl electrolyte
- Negative polarity at 25 kV
- Fixed electrode distance (2.2 cm) = constant plasma area

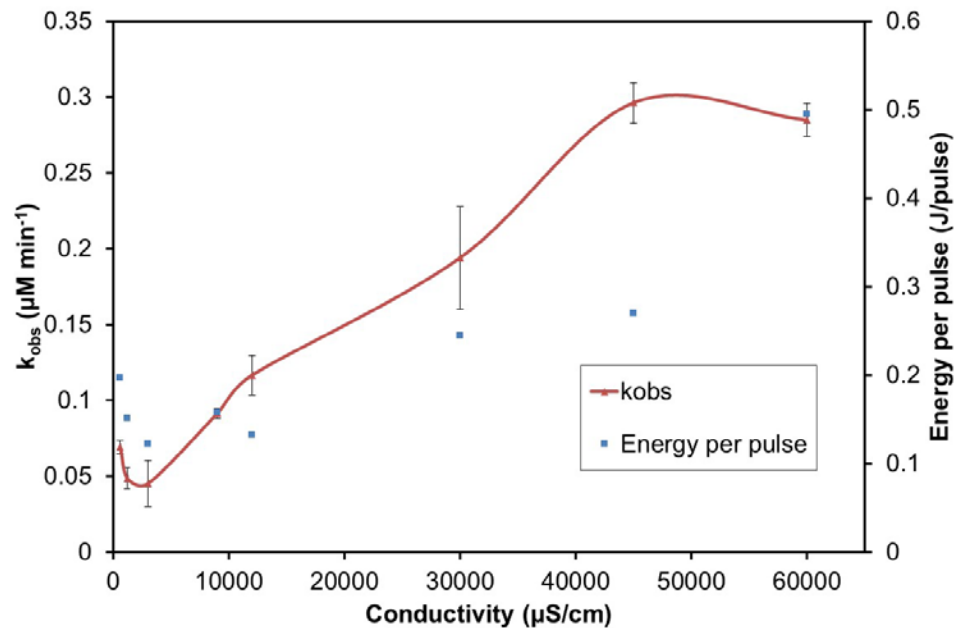


Treatment of Highly Conductive Water: Role of Argon Bubbling

Bubbles appear finer at high NaCl concentrations.

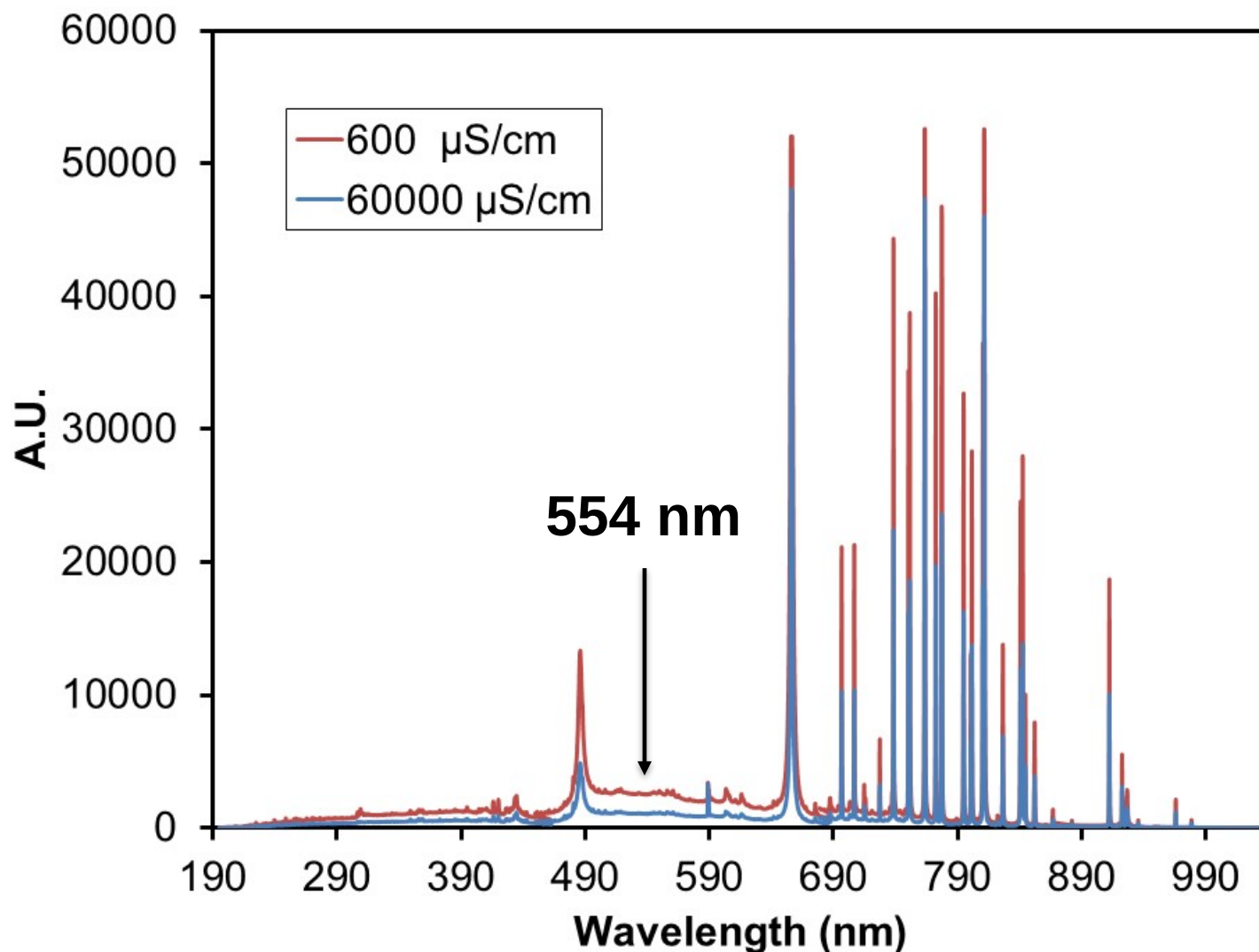


Bubbling vs. no bubbling
Negative polarity discharges
at 25 kV and fixed electrode
distance

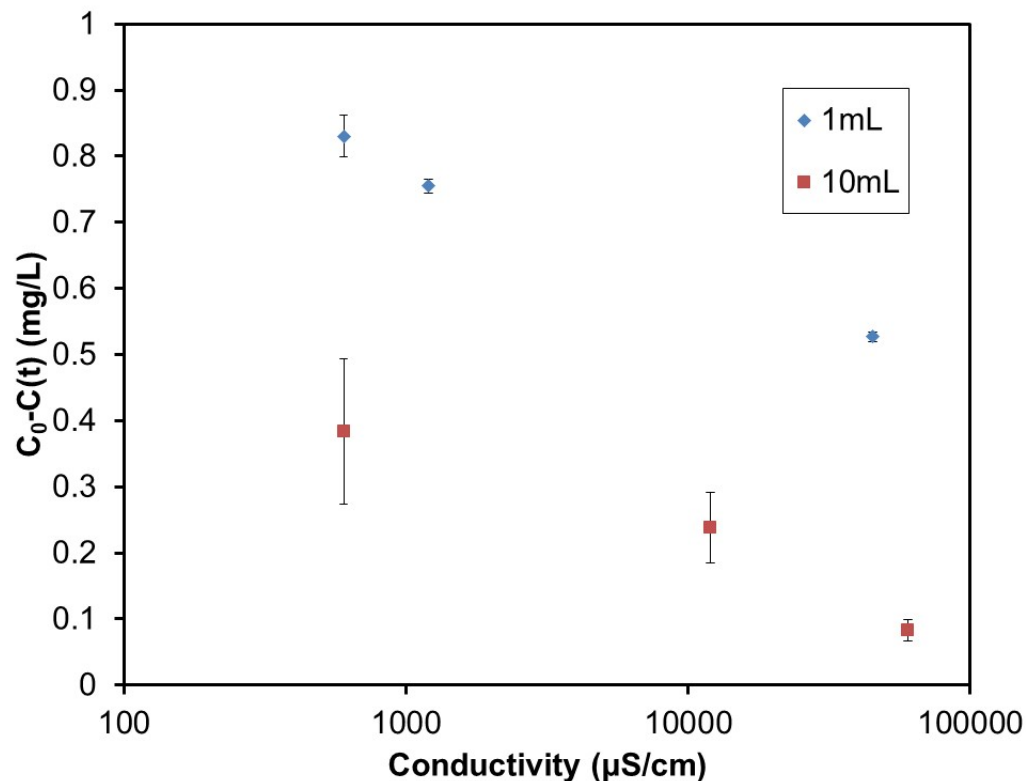
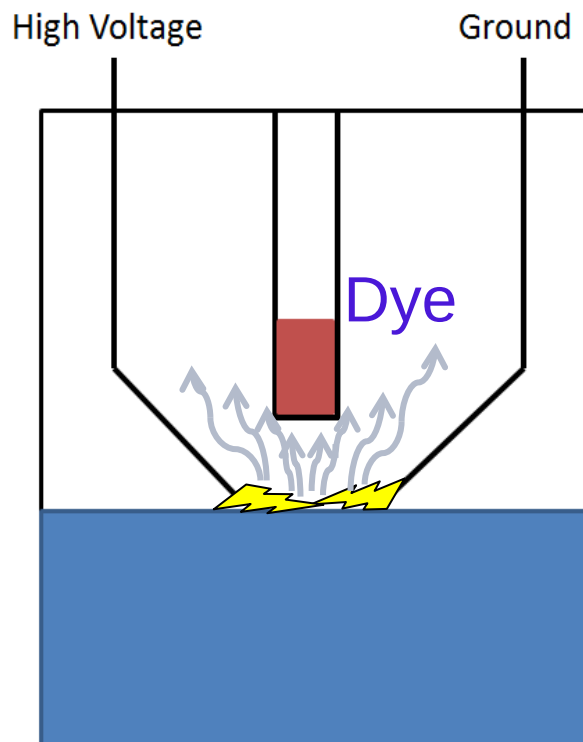


No bubbling
Negative polarity discharges
at 25 kV and fixed electrode
distance

Treatment of Highly Conductive Water: Role of Plasma-Generated Light in the Degradation of RhB

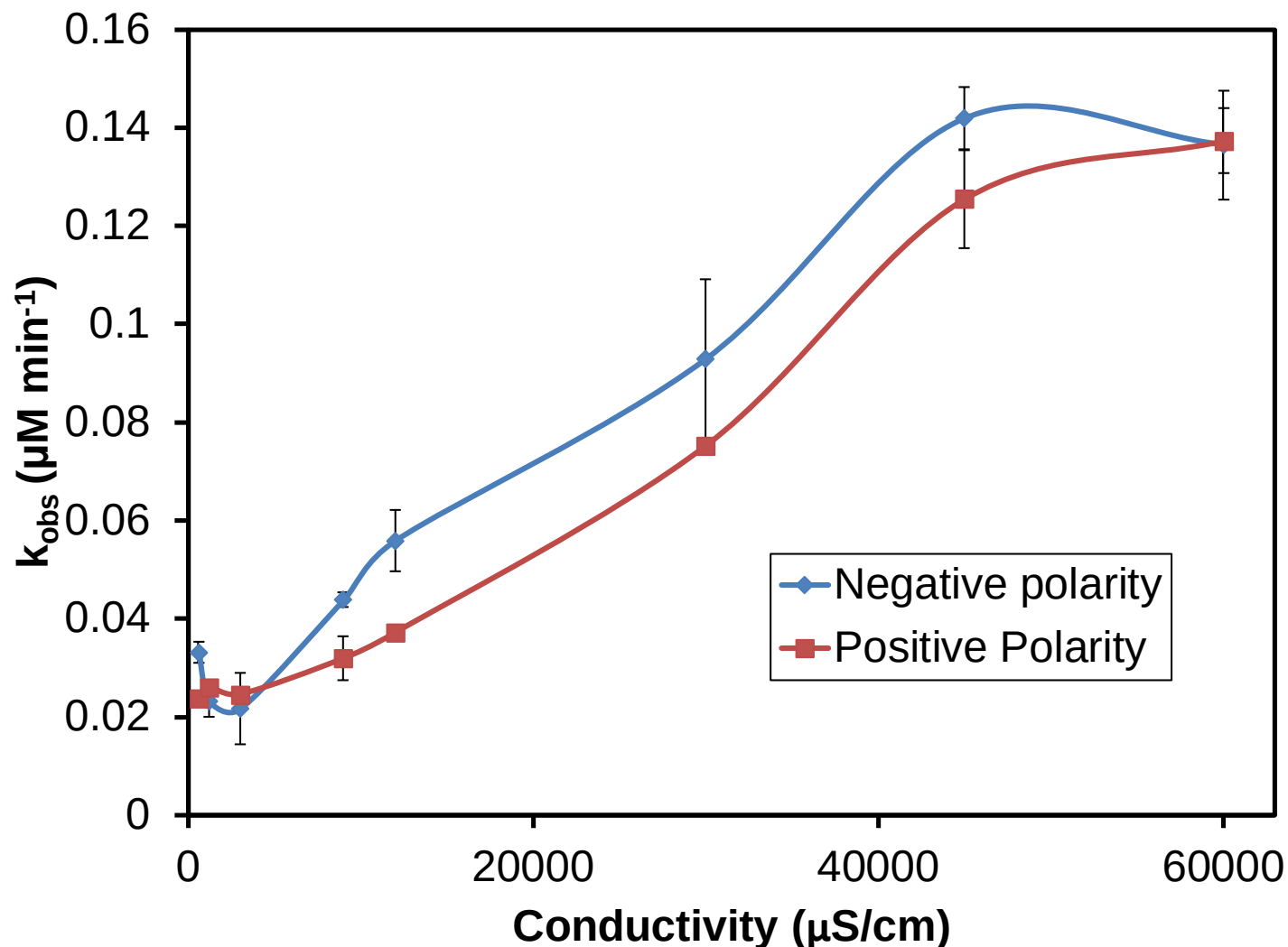


Treatment of Highly Conductive Water: Role of Plasma-Generated Light in the Degradation of RhB

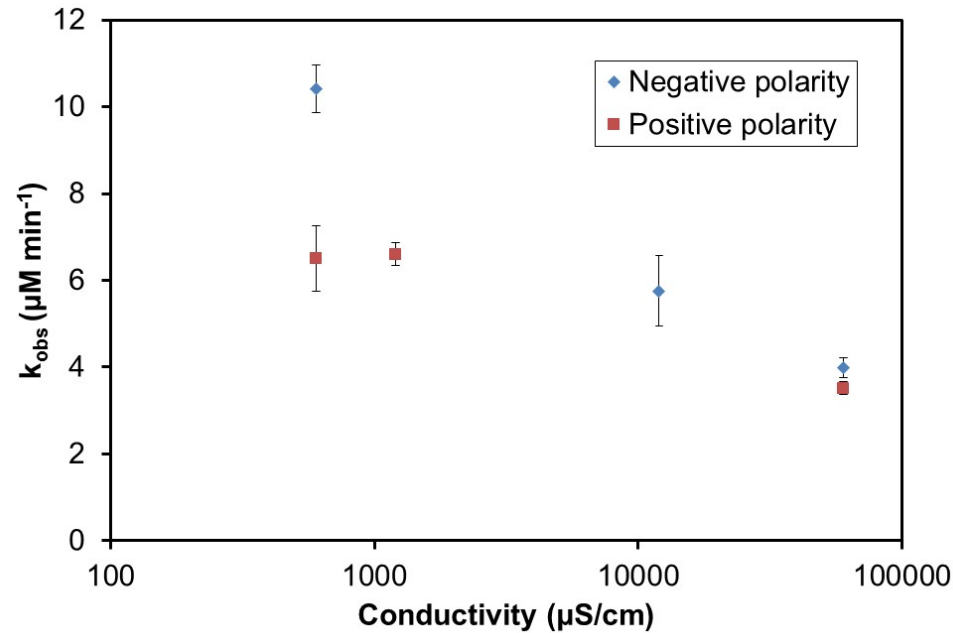


The light-induced degradation decreases at higher conductivities.

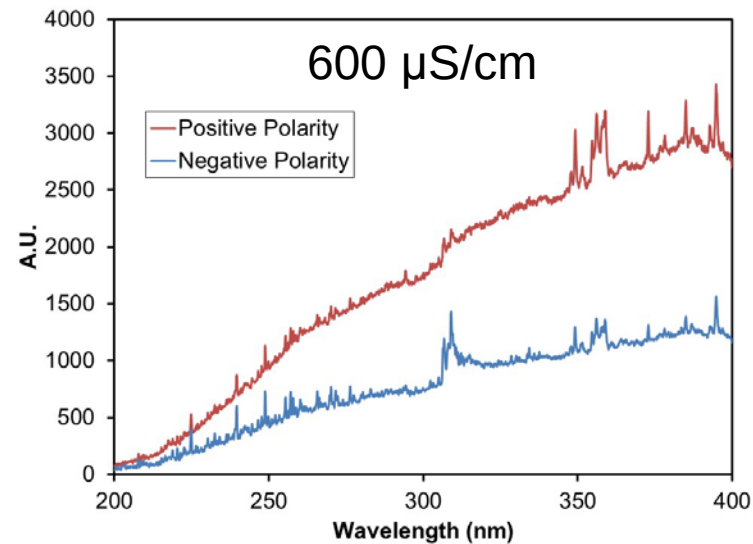
Treatment of Highly Conductive Water: Role of Electrode Polarity in the Degradation of RhB



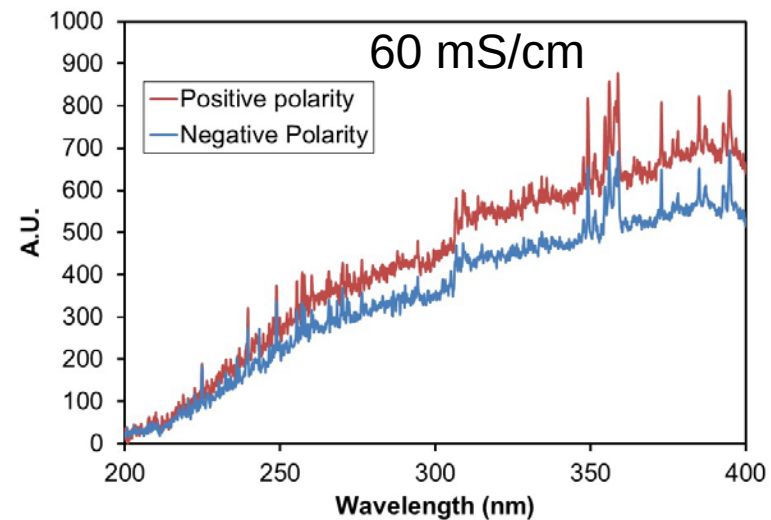
Treatment of Highly Conductive Water: H_2O_2 and OH Radicals



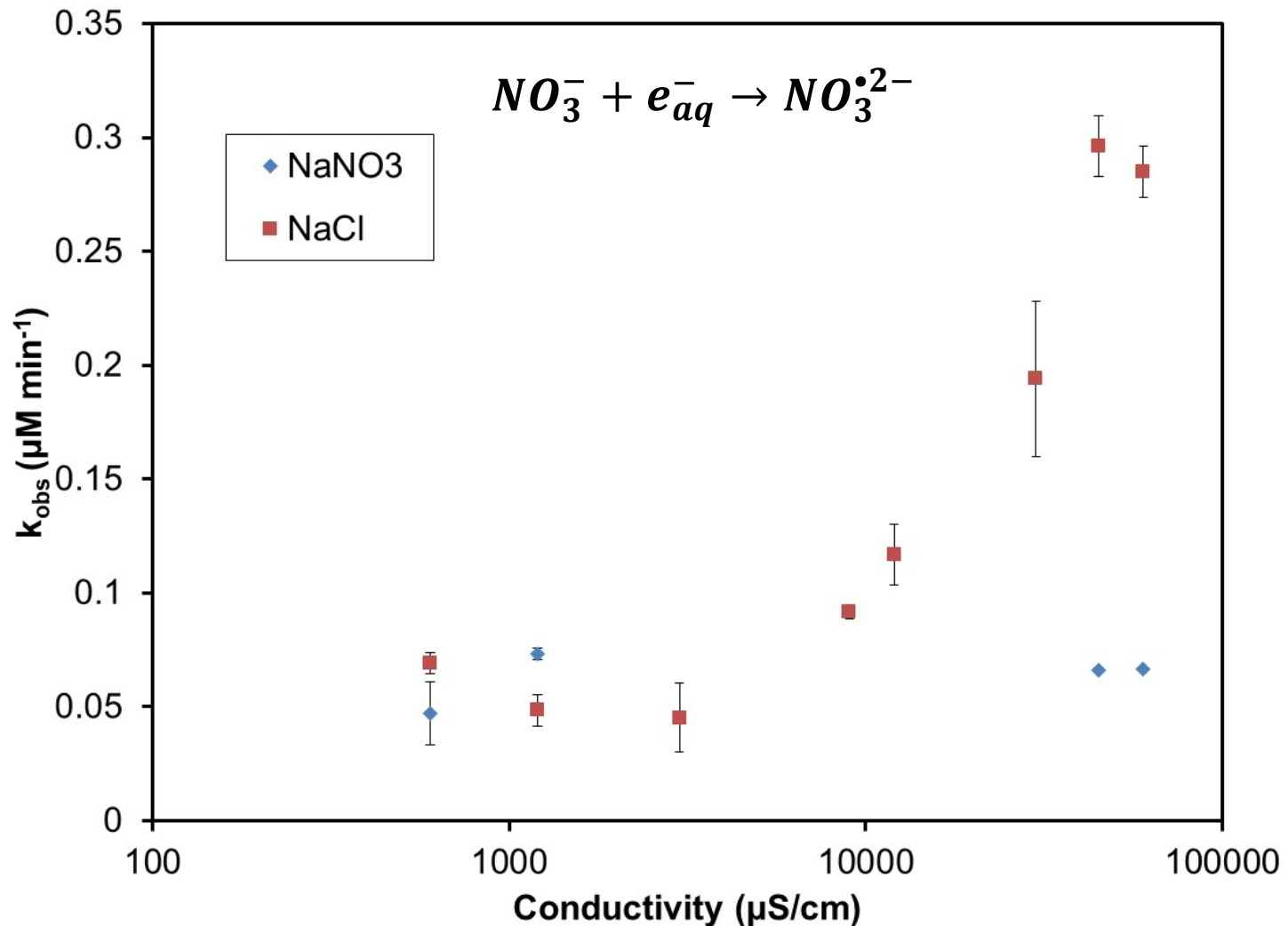
Production rate of H_2O_2 as a function of solution conductivity for positive and negative polarity discharges



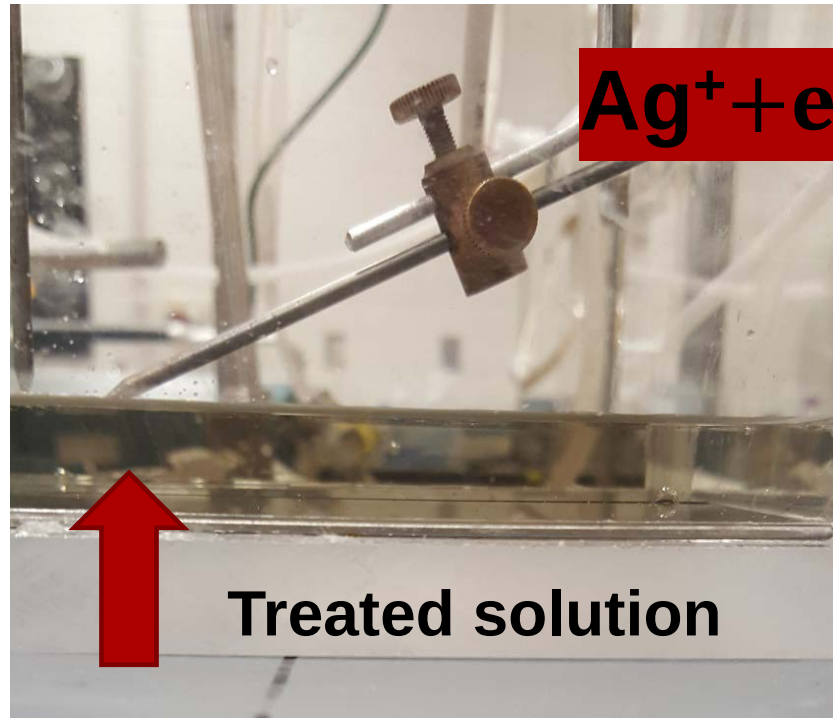
UV part of the OES spectra for positive and negative polarity discharges



Treatment of Highly Conductive Water: Scavenging of Aqueous Electrons (Negative Polarity)

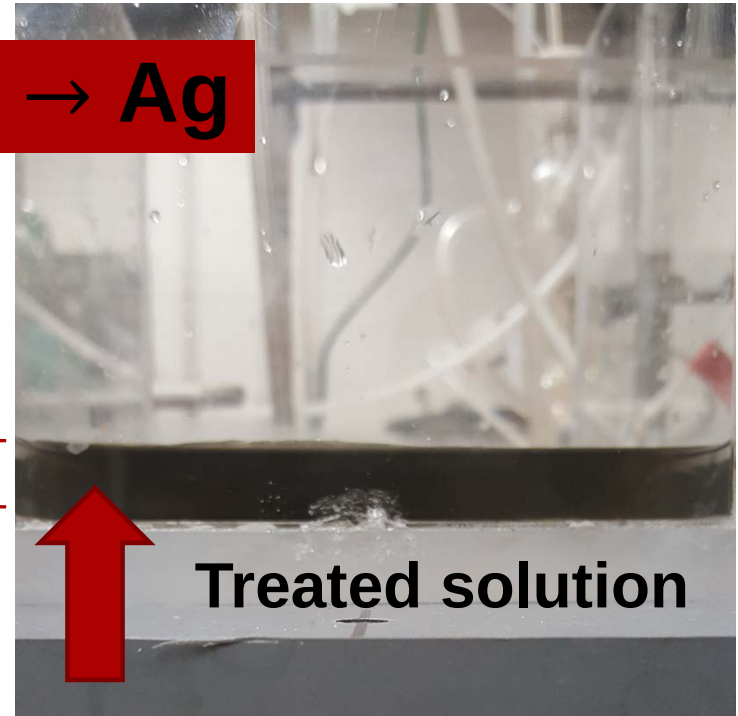


Treatment of Highly Conductive Water: Scavenging of Aqueous Electrons



Ag-salt (0.3 g)

Conductivity=1200 $\mu\text{S}/\text{cm}$



Ag-salt (0.3 g)

Conductivity=7.5 mS/cm

Summary

- Treatability is largely determined by compounds' surface activity, making treatment of surfactant-like contaminants the most promising application for PWT (Plasma Water Treatment).
- PWT is more efficient than leading alternative processes for treatment of PFAS-contaminated water, and is relatively unaffected by the presence of co-contaminants.
- Discharge frequency, compound's initial concentration and presence of bubbling all control the treatment effectiveness.
- Bulk liquid transport plays a significant role in the compound removal (plasma-induced mixing or bubbling).
- Treating surfactants at high solution conductivity required modification of the plasma reactor.
- Chemical mechanisms involving electrons become extremely important at high solution conductivities.

Contributors

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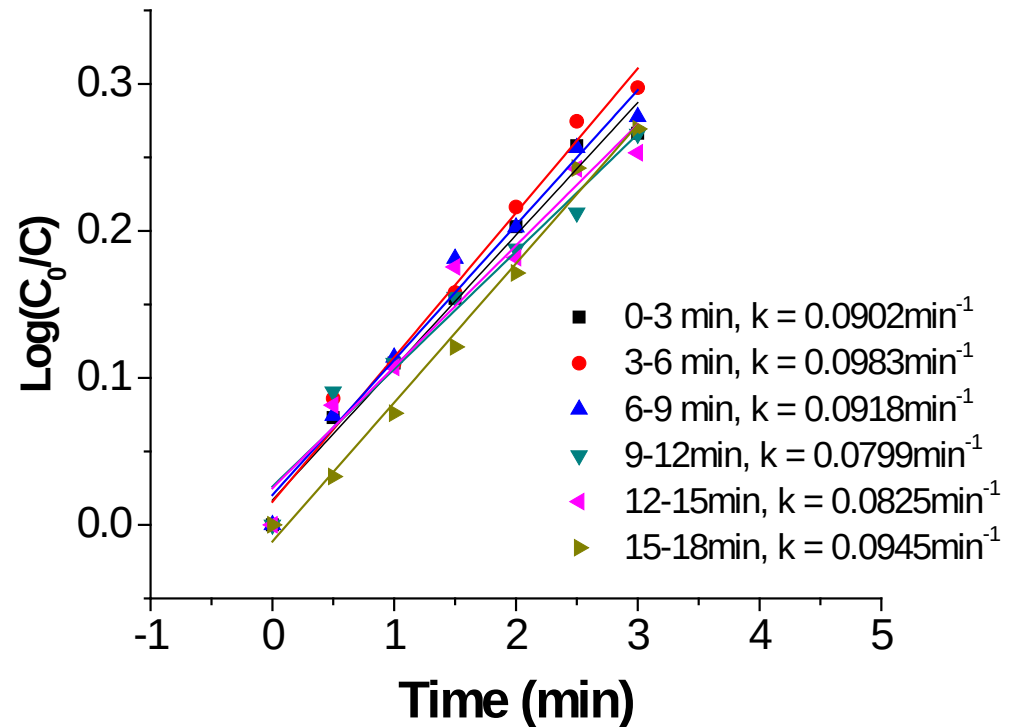
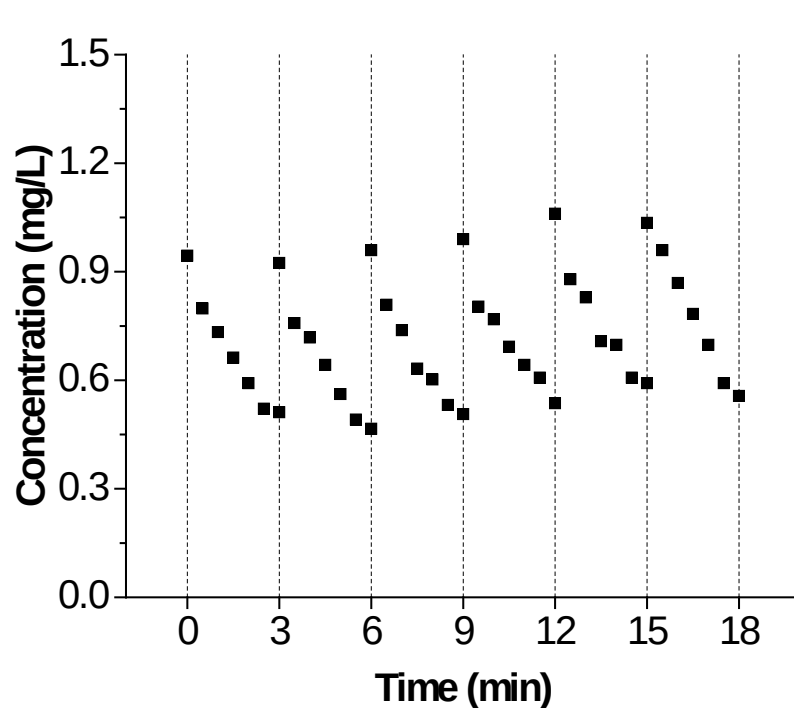
Acknowledgments



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Parent compound and byproducts competition for OH radicals: RhB byproducts accumulation experiments



Byproduct competition would change the kinetic behavior of RhB which for these experiments is constant. This behavior could be different for other compounds.

