The effect of bulk liquid mixing on the performance of gas-liquid plasma reactors

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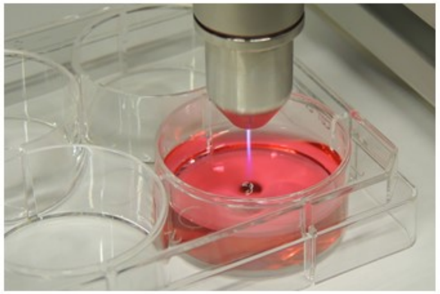
INTERNATIONAL ONLINE PLASMA SEMINAR
March 11th, 2021

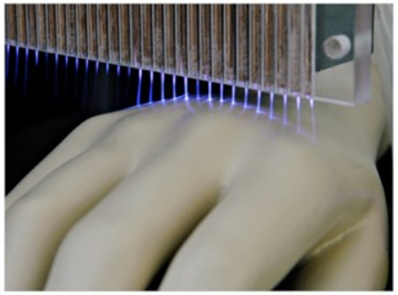
Gas-liquid plasma systems

Chemical analysis

Disinfection

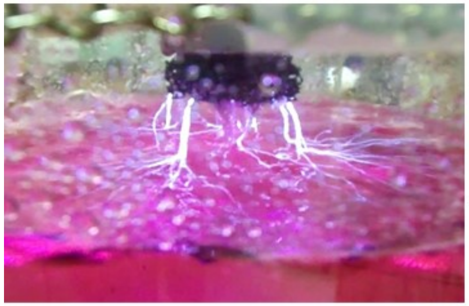


Surface sterilization

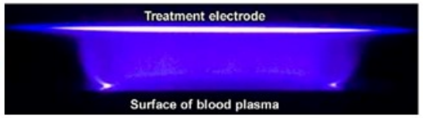


Food decontamination

Water treatment

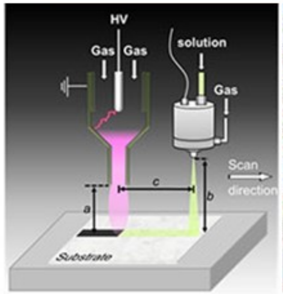


(Bio)medicine



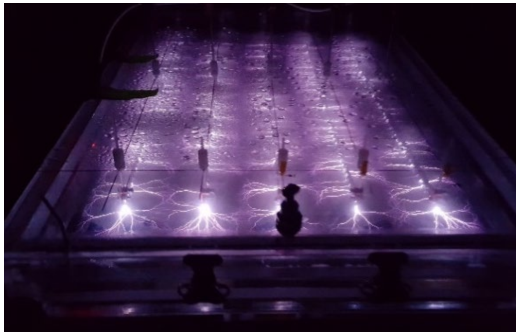
Plasma agriculture

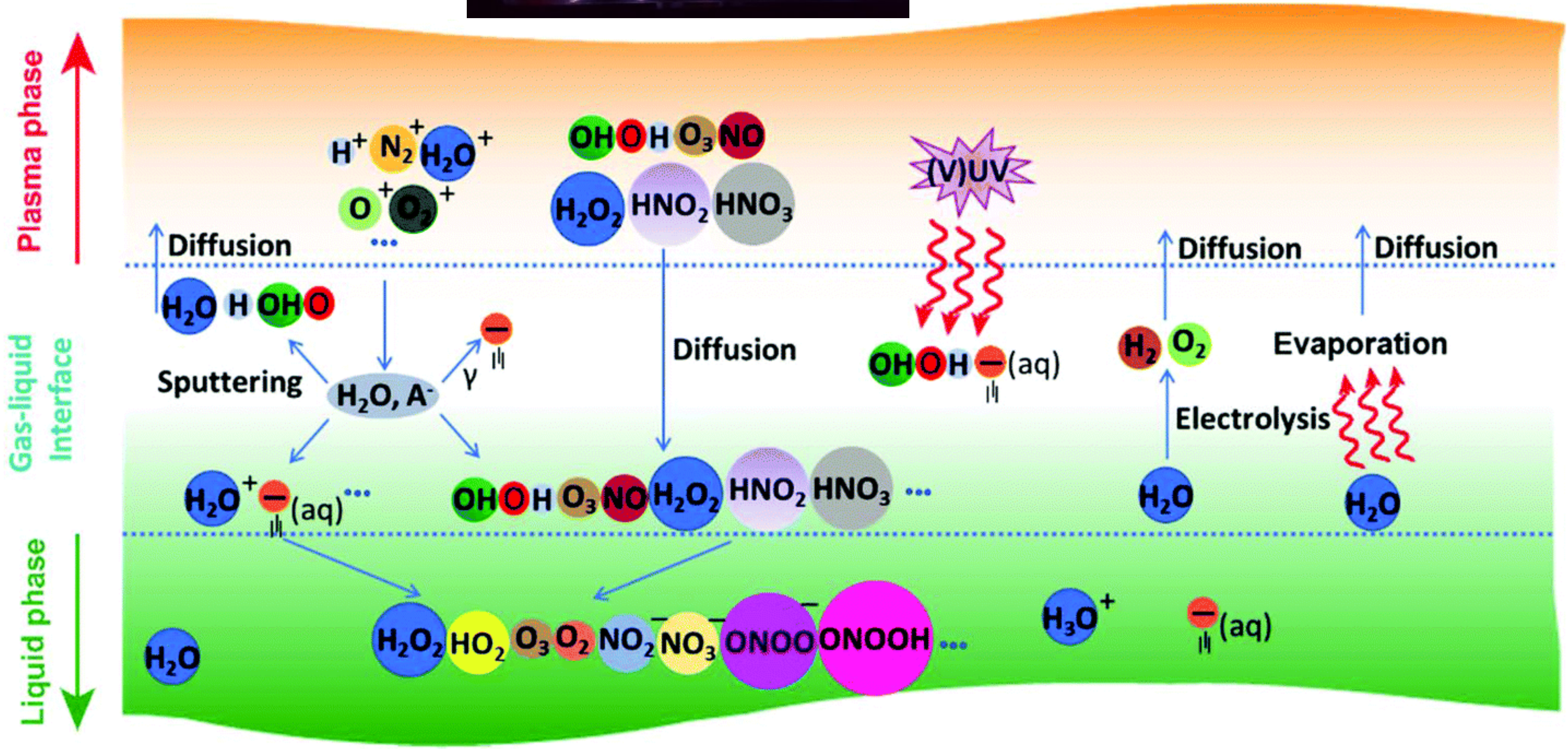
Material synthesis



Kuo, S. P., *et al.* *New Journal of Physics* 11.11 (2009): 115016.
E., Flora-Glad Chizoba *et al*., *Trends in Food Science & Technology* 69 (2017): 46-58.
www.nist.gov
www.sameerkalghatgi.com
Plasma Research Laboratory, Clarkson University

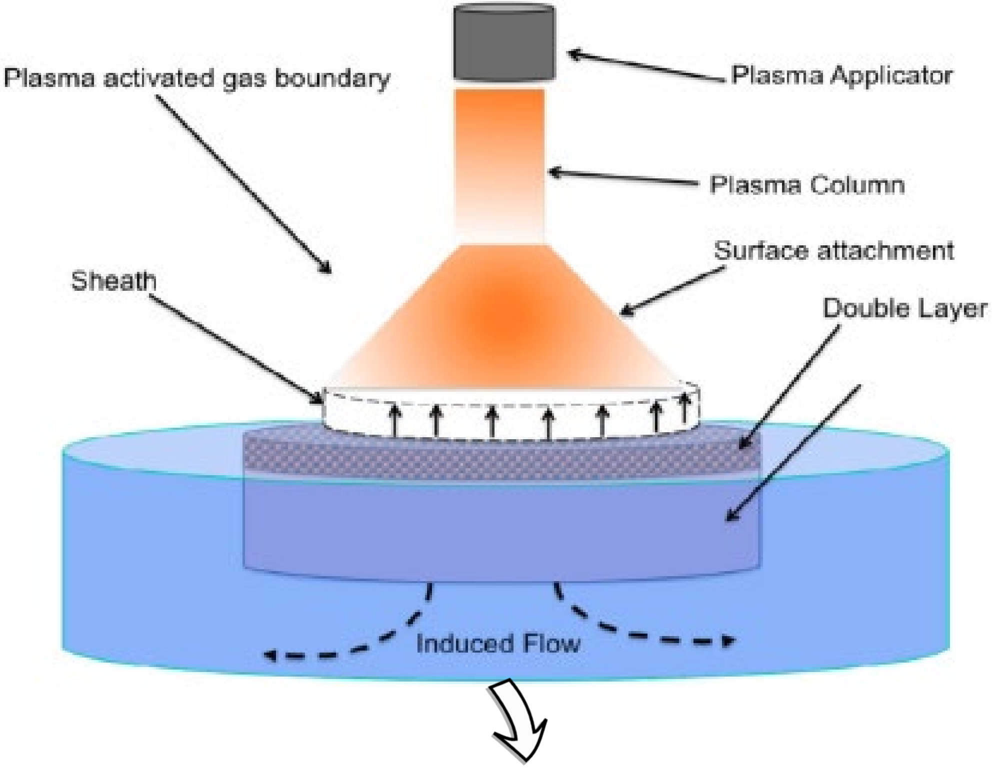
Plasma-liquid interface: the key driver of plasma-induced reactivity





Zhou, Renwu, *et al*. *Green Chemistry* 20.23 (2018): 5276-5284.

Bulk liquid transport processes also control interfacial reactivity

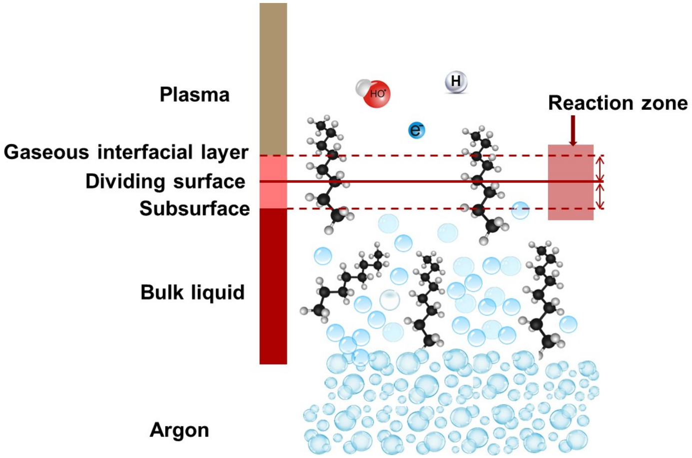


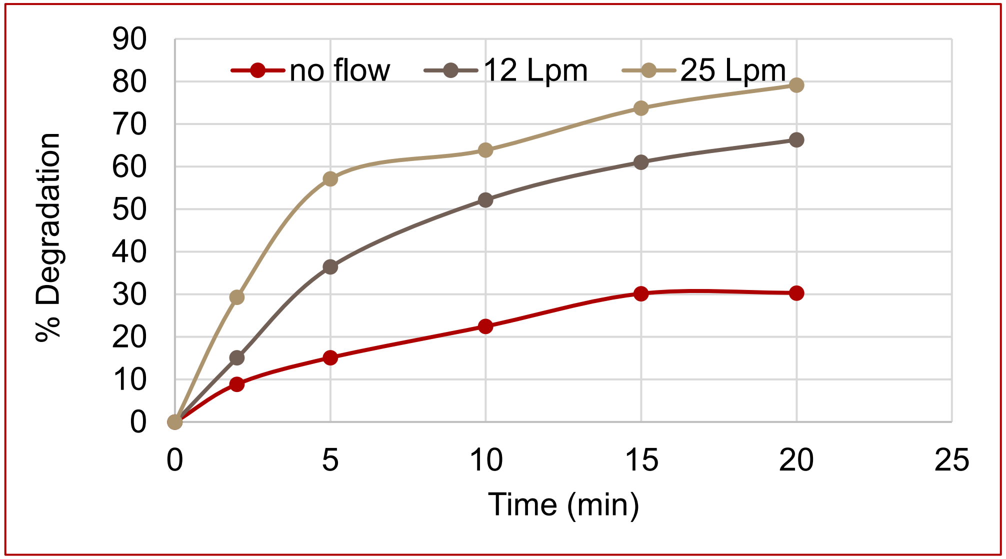
Plasma-induced flow and bulk liquid mixing strongly affect interfacial chemistry

Foster, J. E., *et al*. *Journal of Physics D: Applied Physics* 51.29 (2018): 293001.

Mixing affects the performance of gas-liquid plasma reactors for treatment of surfactant compounds

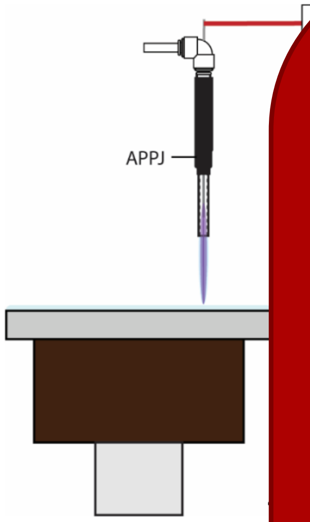
Minimized bulk liquid mass transport vs. enhanced liquid renewal rates and gas-liquid mass transport





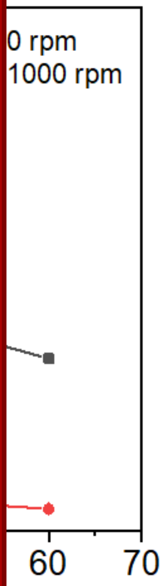
The effect of argon gas flowrate on the degradation of perfluorooctanoic acid (PFOA) in a 10 gpm enhanced contact plasma reactor.

"The means of contact" affects the plasma rector performance

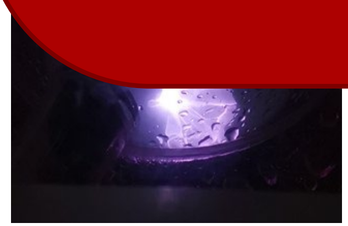


Is the plasma reactor performance ultimately determined by the "mode of mixing", that is, the way the liquid in the reactor contacts the plasma-liquid interface? Or are the magnitudes of fluxes of reactive species arriving at the interface more or equally important?

We have no clear understanding on the effect of mixing on the plasma reactor performance….



dye in the plasma spinning disc reactor

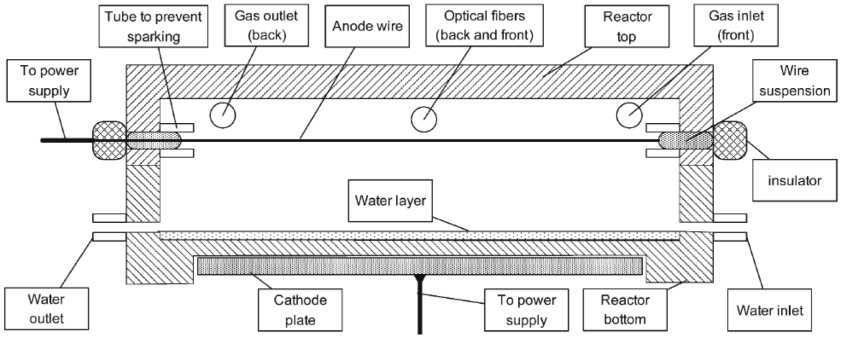


Treatment volume 500 mL

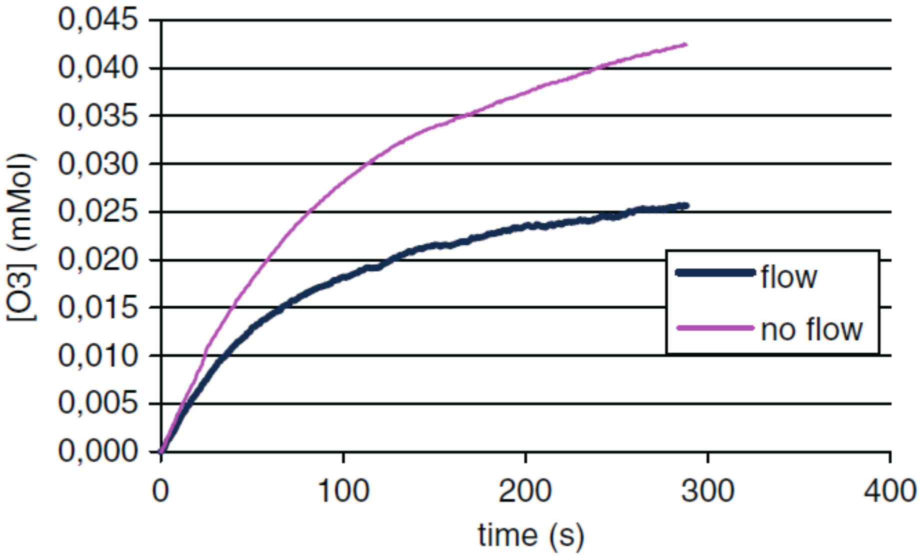
Minimized bulk liquid mass transport vs. enhanced liquid renewal rates and gas-liquid mass transport

Bulk liquid mixing enhances gas-liquid mass transport

Wire-to-plane corona



Recirculation flow rate = 0.3 LPM
Treatment volume = 0.15 L
Solution layer thickness = 3 mm

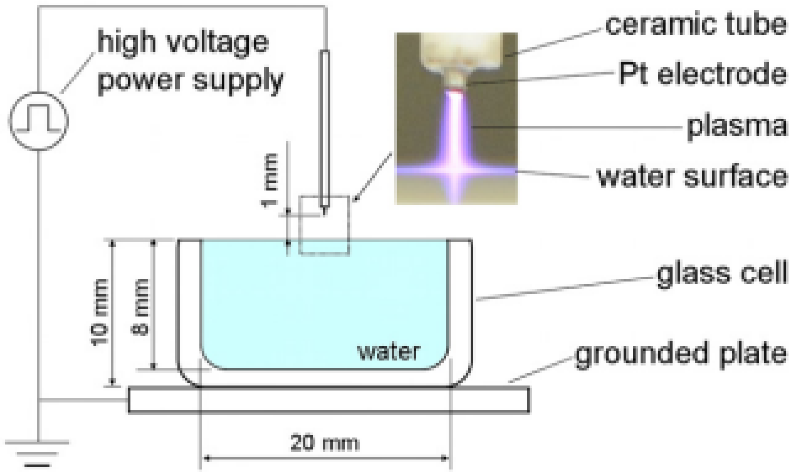


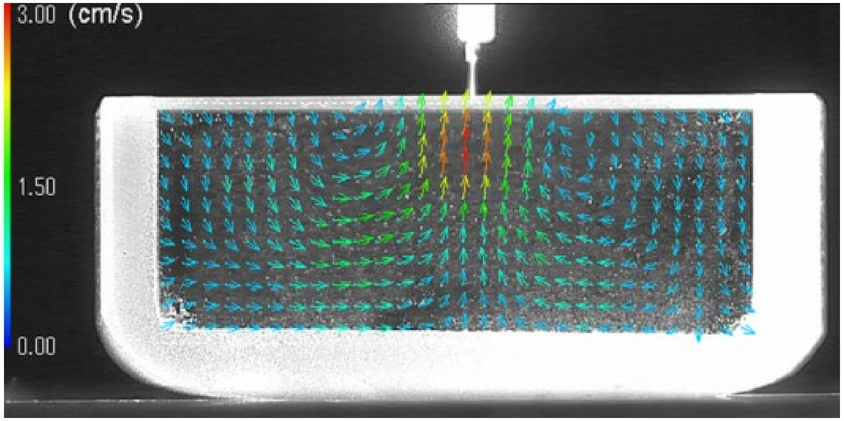
Effect of liquid flow on ozone penetration

The liquid flow increased the ozone uptake by 23% compared to the “no flow” case.

Grabowski, L. R., *et al. Plasma Chemistry and Plasma Processing* 26.1 (2006): 3-17.

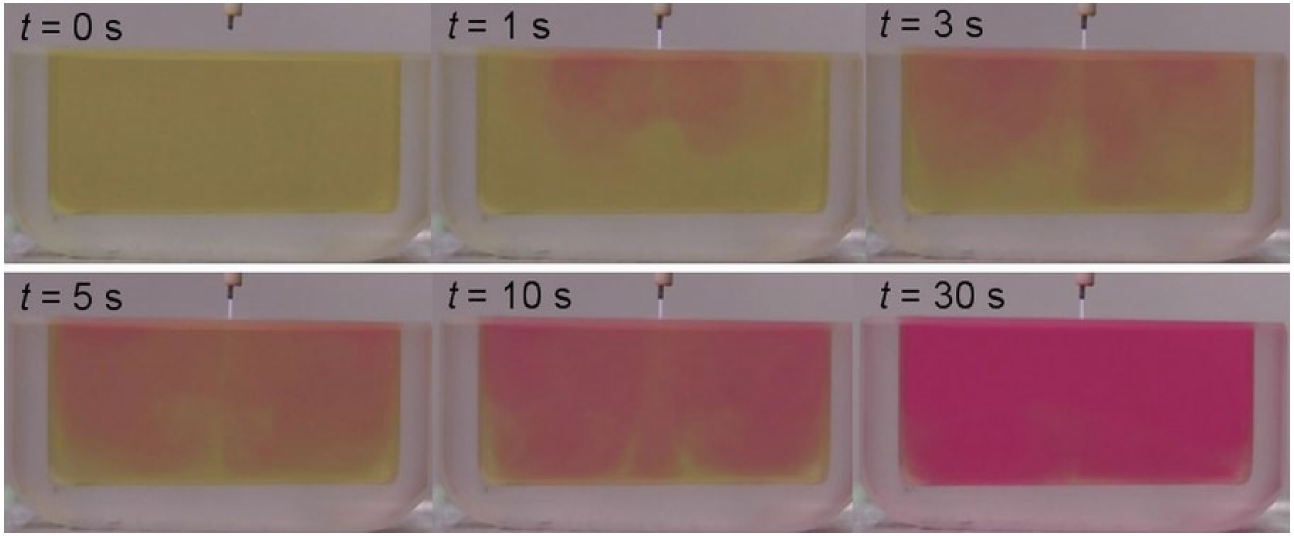
Plasma-induced bulk liquid effects





Typical velocity vector field in water measured by PIV.

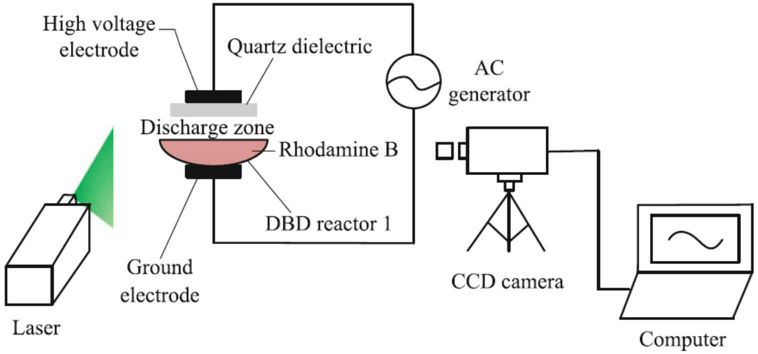
Yellow (pH=6.2)→Red (pH=4.2)



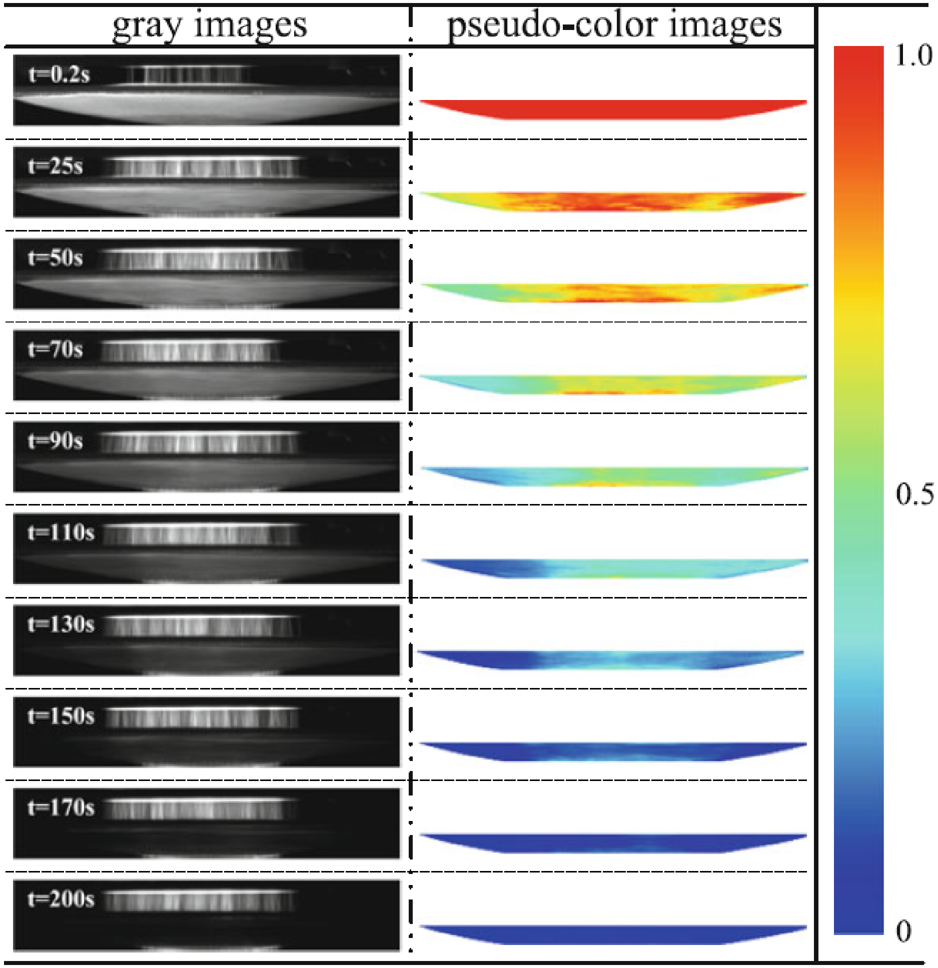
Temporal evolution of methyl red color change. Air is the process gas.

Shimizu, T., *et al. New Journal of Physics* 13.5 (2011): 053025.

Plasma-induced interfacial mixing: degradation of RhB dye



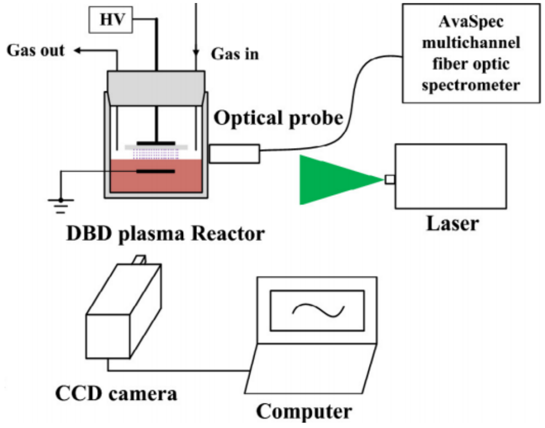
Random DBD current filaments induce fluctuations at the interface which accelerate the diffusion of the oxidants and assist in the degradation of Rhodamine B dye.



Temporal evolution of Rhodamine B concentration using oxygen as the process gas.

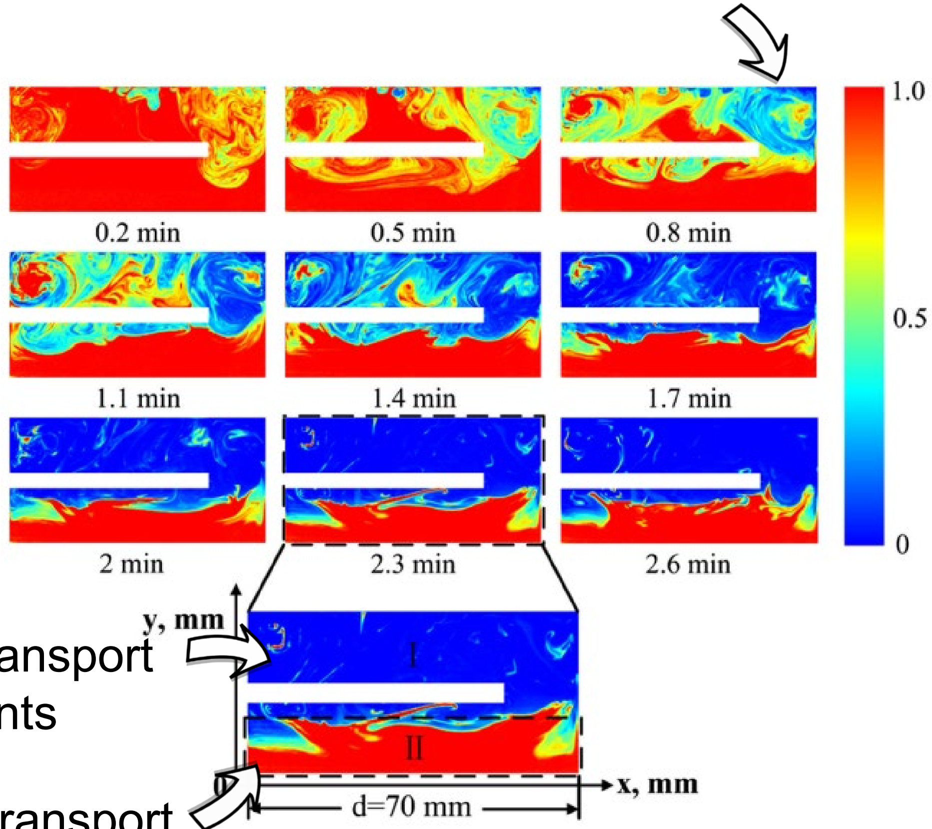
Feng, X., *et al. Plasma Chemistry and Plasma Processing* 32.6 (2012): 1127-1137.

Visualization of coupled mass transfer and reaction: degradation of RhB dye



Reactive-PLIF setup

Location of O_2 introduction



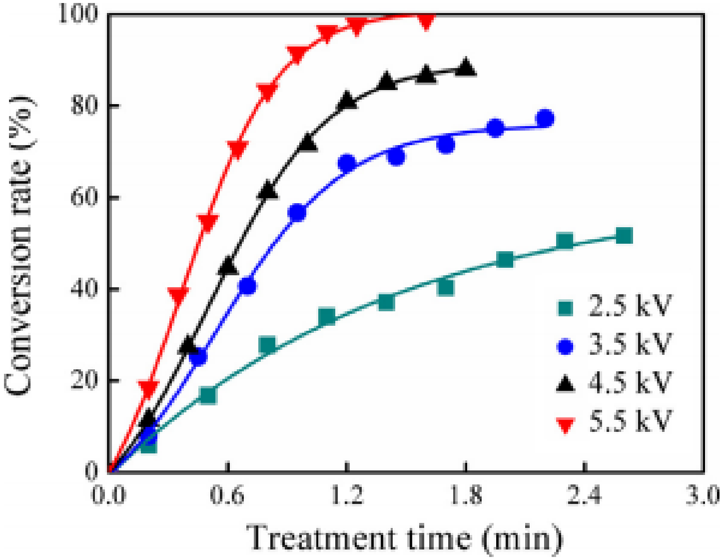
Region of convective transport induced by DBD filaments

Diffusional transport

Temporal evolution of Rhodamine B concentration fields at 2.5 kV. Oxygen is the process gas.

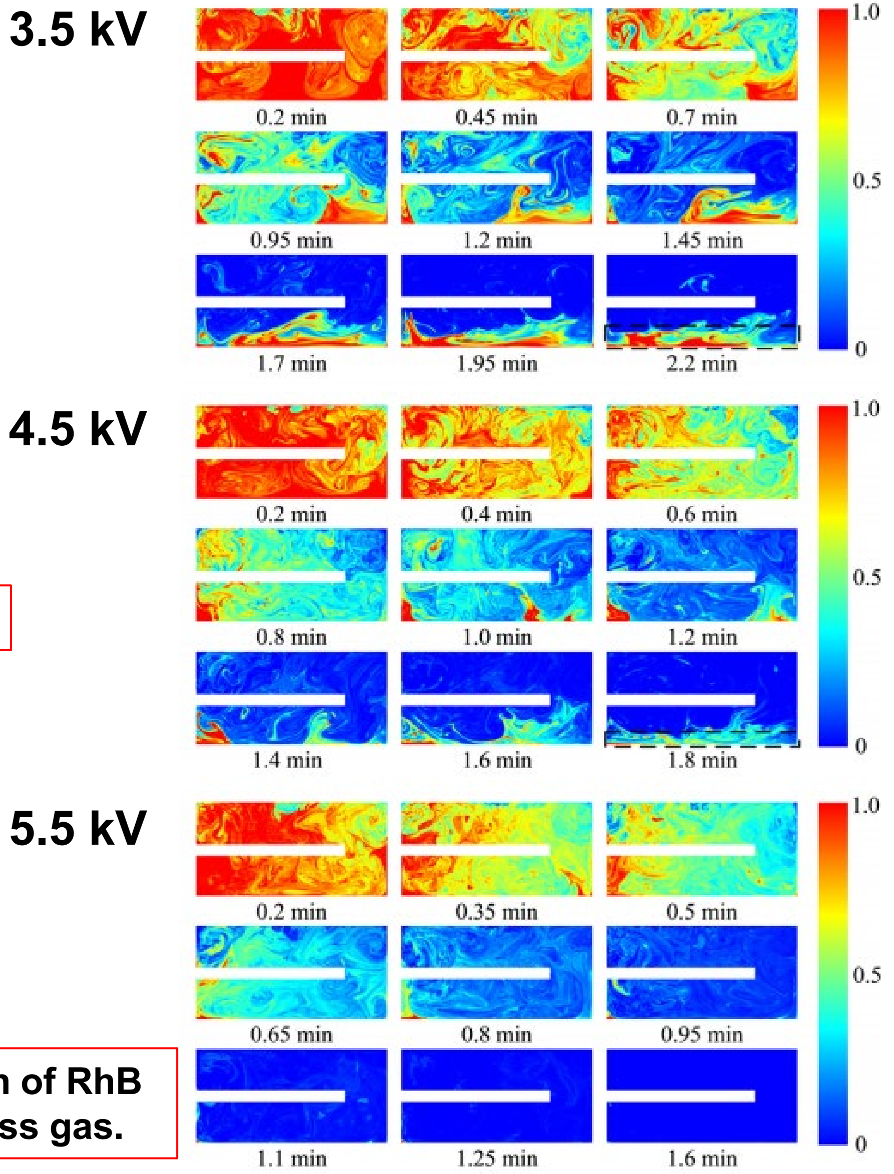
Feng, X., *et al*. *Chemical Engineering Journal* 245 (2014): 47-55.

Visualization of RhB degradation: the effect of applied voltage



The effect of voltage on the conversion of RhB

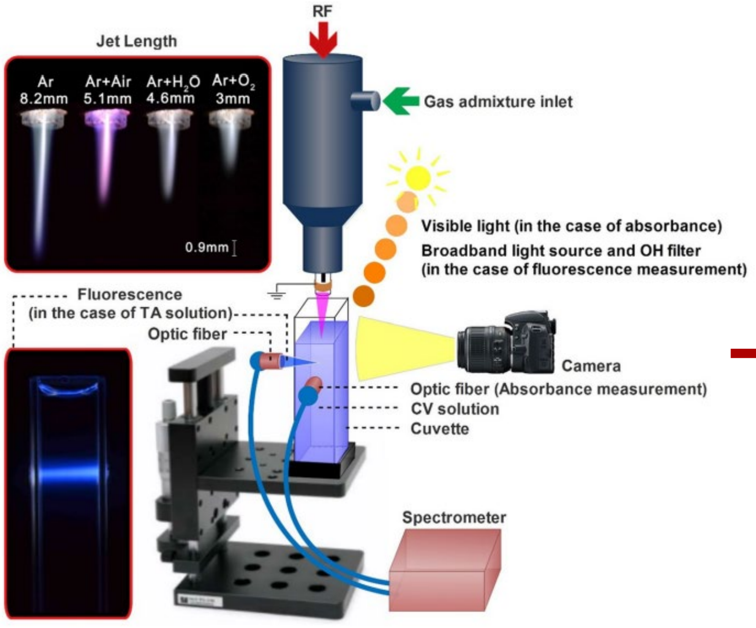
Species generation and the magnitude of the convective transport in the liquid increase with voltage.

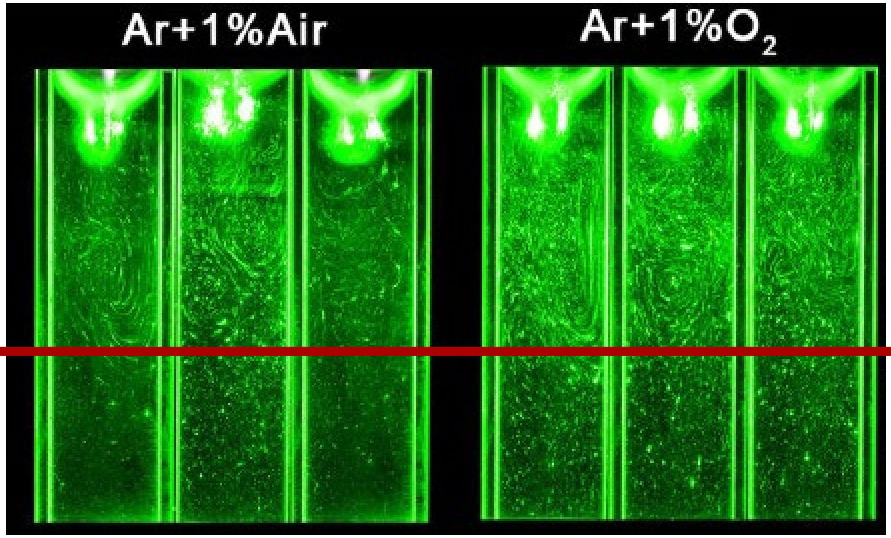


The effect of voltage on temporal evolution of RhB concentration fields. Oxygen is the process gas.

Feng, X., *et al*. *Chemical Engineering Journal* 245 (2014): 47-55.

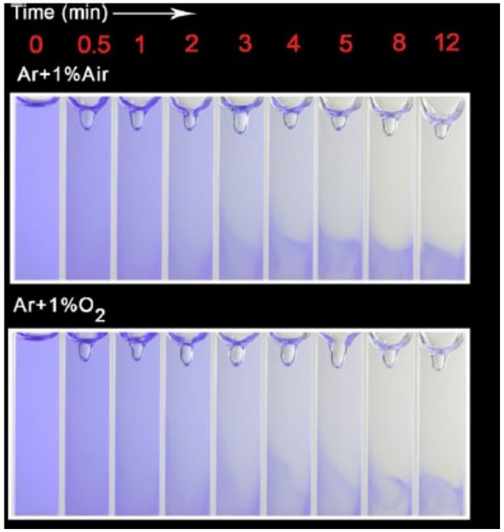
The role of convective transport in the decomposition of crystal violet (CV) dye





Visualization of the flow pattern by PIV for different plasma conditions.

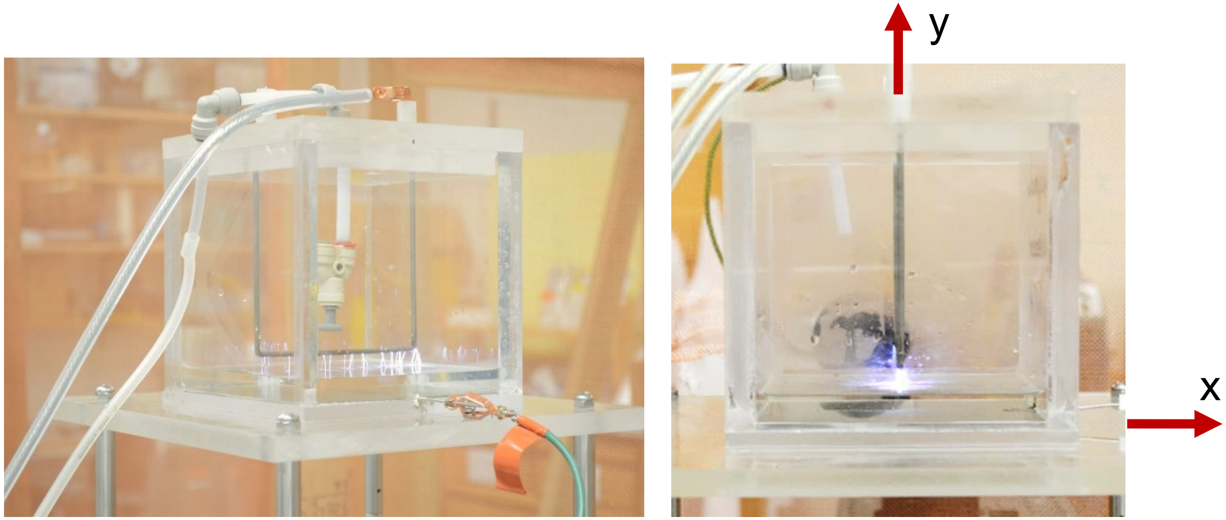
- CV is degraded at the interface most likely by OH
- Decolorization rate is limited by the CV transport to the near-boundary region



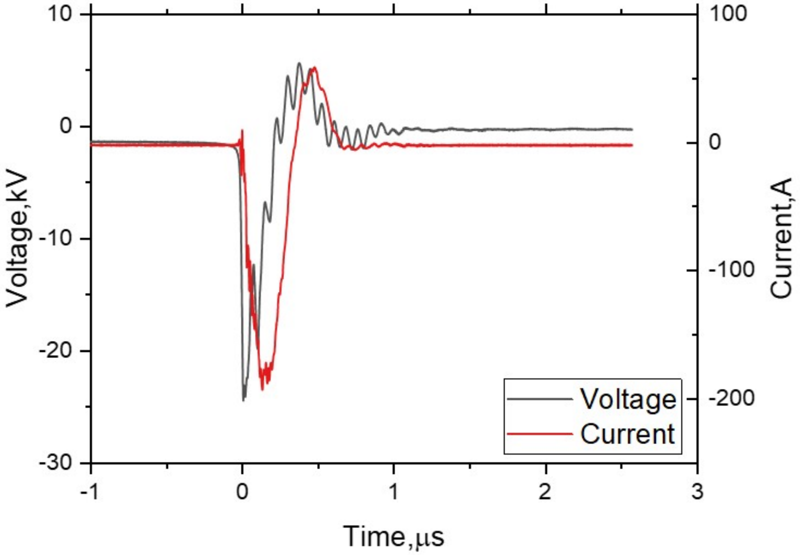
Visualization of the spatially and time resolved CV decolorization plasma treatments using Ar + 1% O$_2$ and Ar + 1% air plasma jet.

Taghvaei, H., *et al. Plasma Chemistry and Plasma Processing* 39.4 (2019): 729-749.

Can the type of the compound in the liquid also affect the convective transport in the liquid?



Rail-plane batch reactor



- Plane of symmetry allows to treat the reactor as a 2-D system
- Liquid volume: 0.2 L (depth = 1 cm)
- Conductivity: 300 μS/cm (NaCl)
- Headspace gas: argon
- **No external mixing**
- PIV performed by D. Bohl's group at CU

Time evolution of the flow field for the base case (no chemicals added)

- Aqueous NaCl solution at 300 μS/cm, f=40 Hz, V=(+) 25 kV
- Argon in the reactor headspace (no flow)

Discharge location

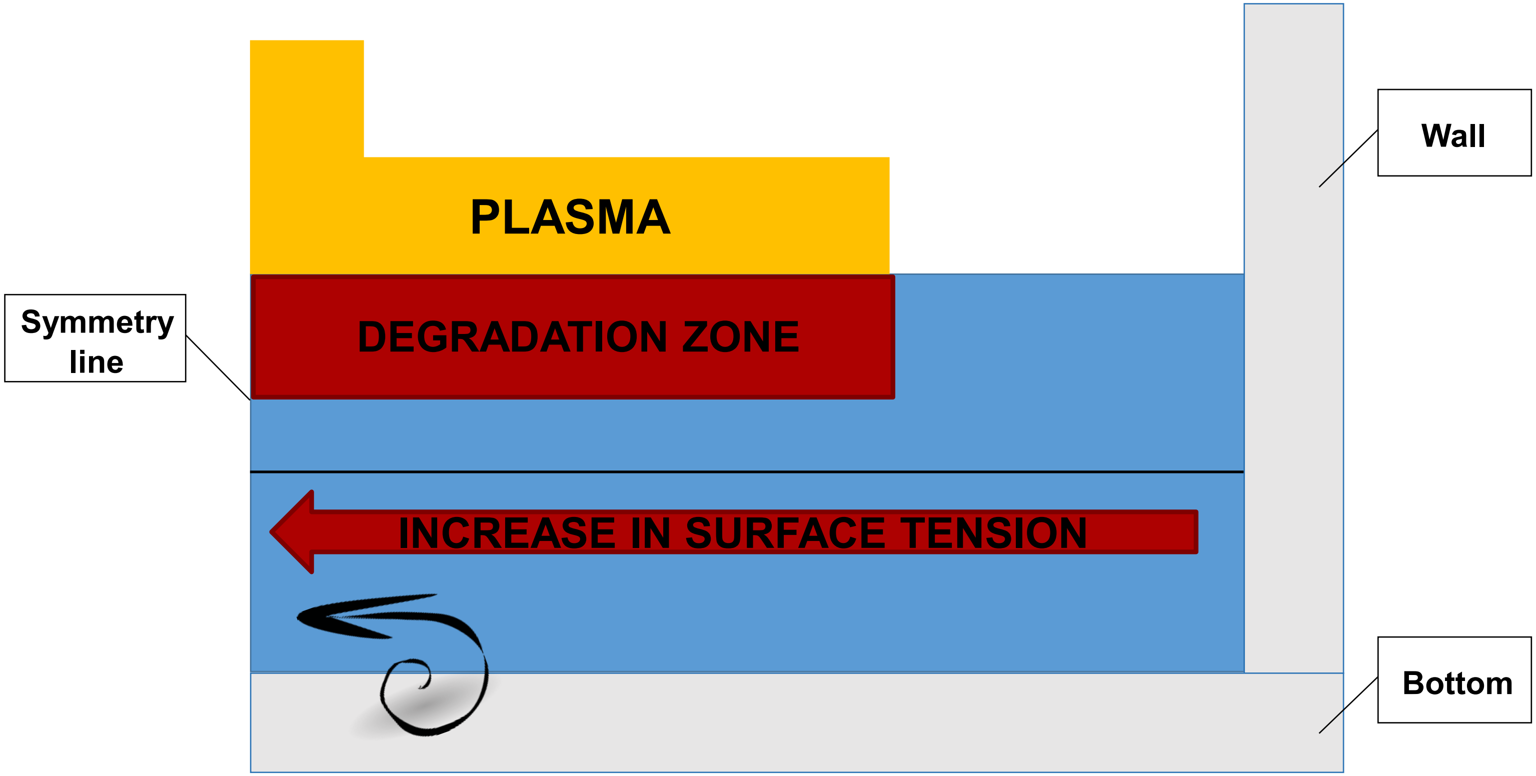
Time evolution of the flow field for Rhodamine B

- Aqueous NaCl solution + 1 mg/L RhB at 300 μS/cm, f=40 Hz, V=(+) 25 kV
- Argon in the reactor headspace (no flow)

Discharge location

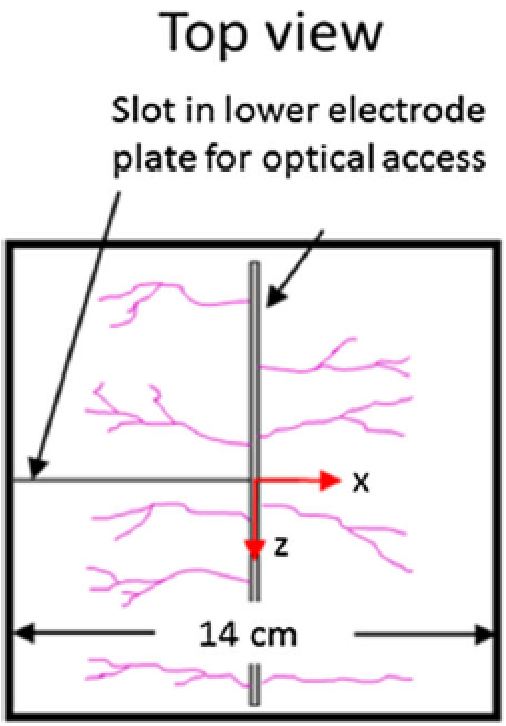
The flow reversal and the concentration gradient driven Marangoni flow

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



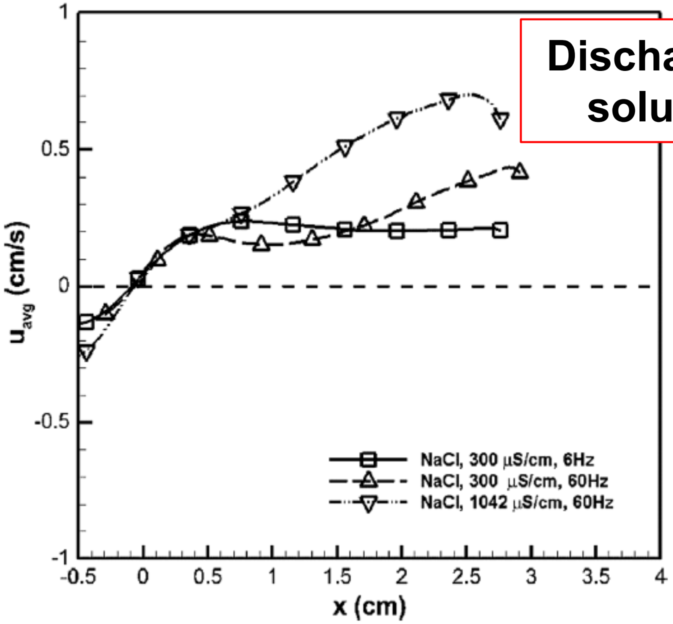
Mededovic Thagard, S., *et al*. *Plasma Chemistry and Plasma Processing* 38.4 (2018): 719-741.

Mean surface speed depends on multiple parameters

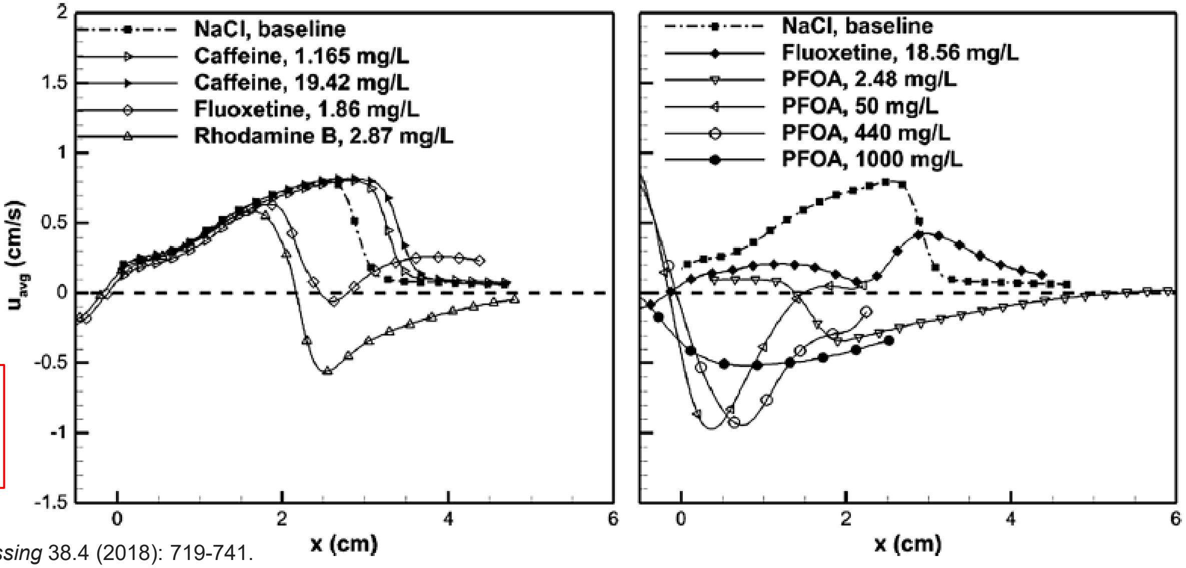


Experimental reactor

Type and compound concentration



Discharge frequency and solution conductivity



Mededovic Thagard, S., *et al*. *Plasma Chemistry and Plasma Processing* 38.4 (2018): 719-741.

Discharge frequency and bulk liquid chemistry

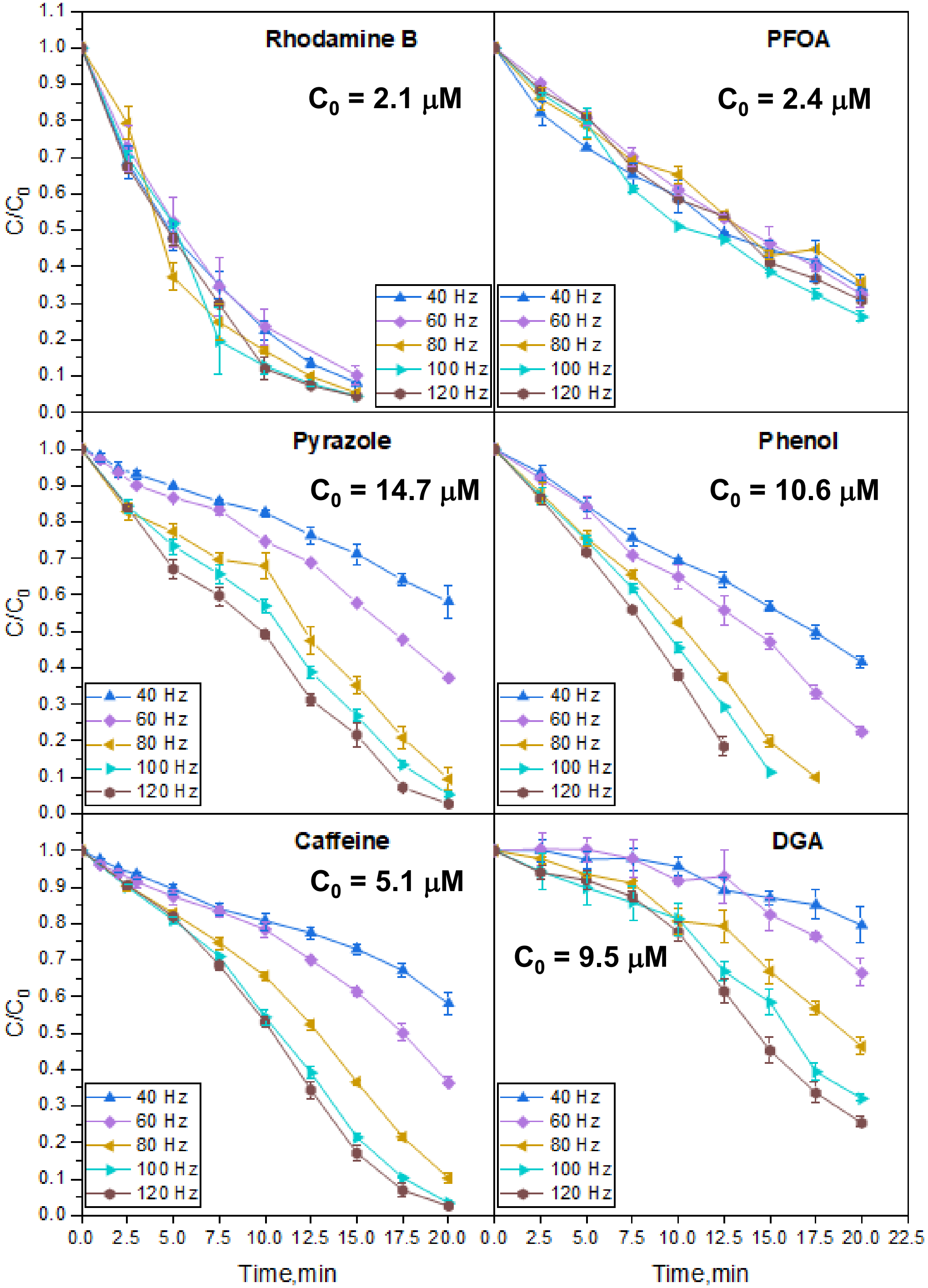
- Does the discharge frequency control the rates of chemical reactions in a gas-liquid electrical discharge plasma reactor in the absence of external (forced) mixing?

  The effect of frequency on overall reactor performance is not well understood due to conflicting literature findings

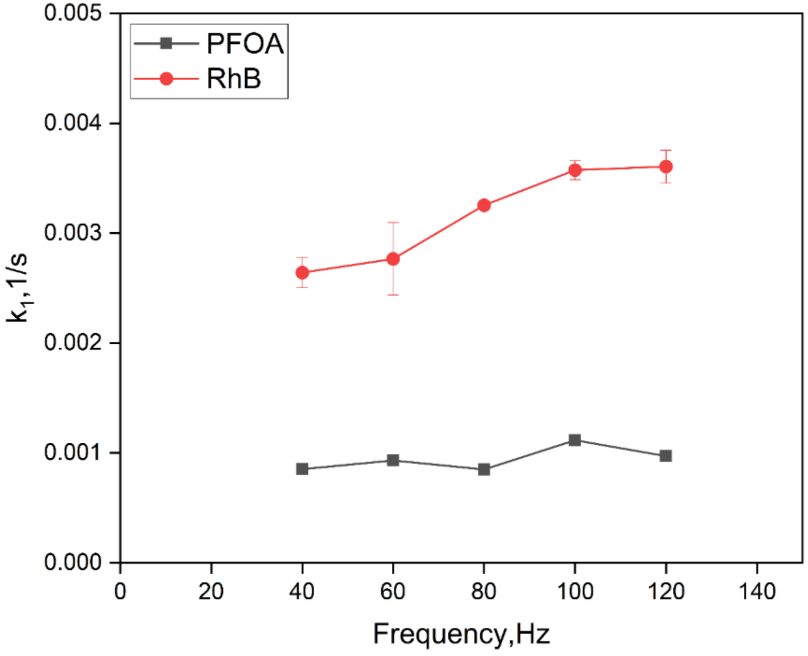
- This work investigates the effect of frequency on the degradation of six solutes: phenol, pyrazole, rhodamine B, perfluorooctanoic acid (PFOA), 2-(2-Aminoethoxy) ethanol (DGA), and caffeine between 40 Hz and 120 Hz.

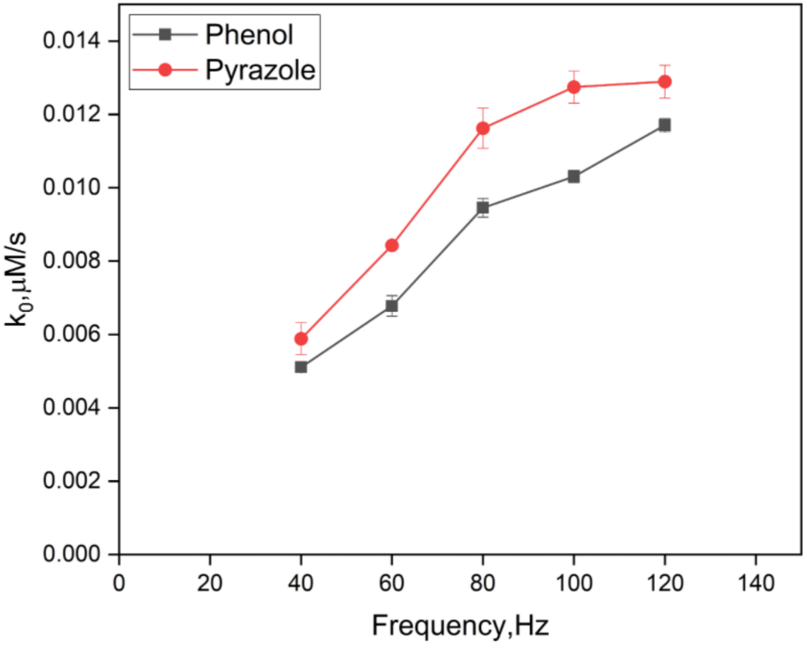
  The central approach focuses on coupling bulk liquid convective transport with the chemical kinetics.

Degradation profiles of six solutes vs. discharge frequency



Dependence of the rate constant on frequency for the investigated compounds

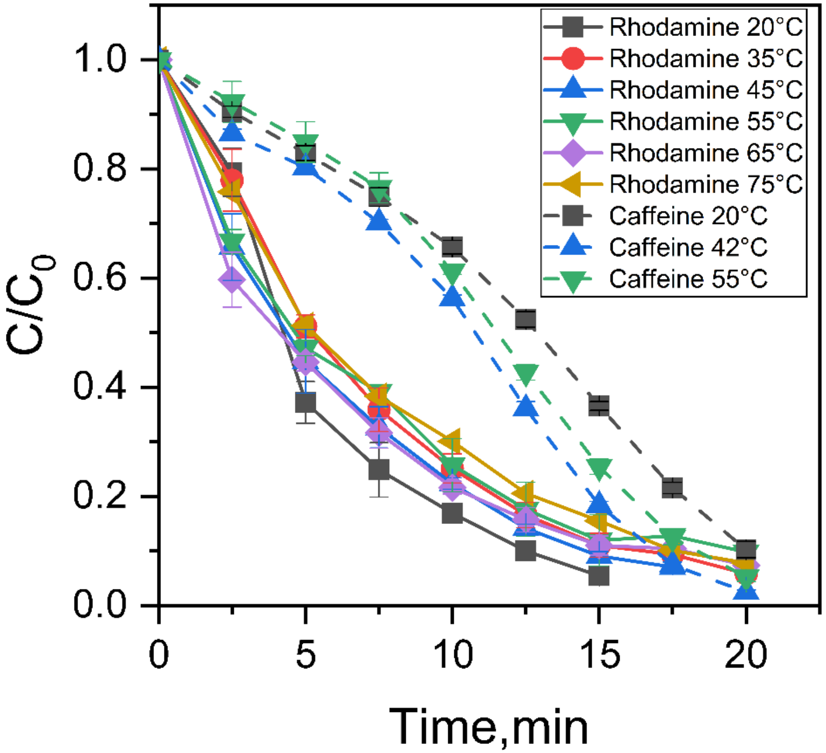




Caffeine and DGA exhibited complex concentration profiles that did not allow for kinetic analysis.

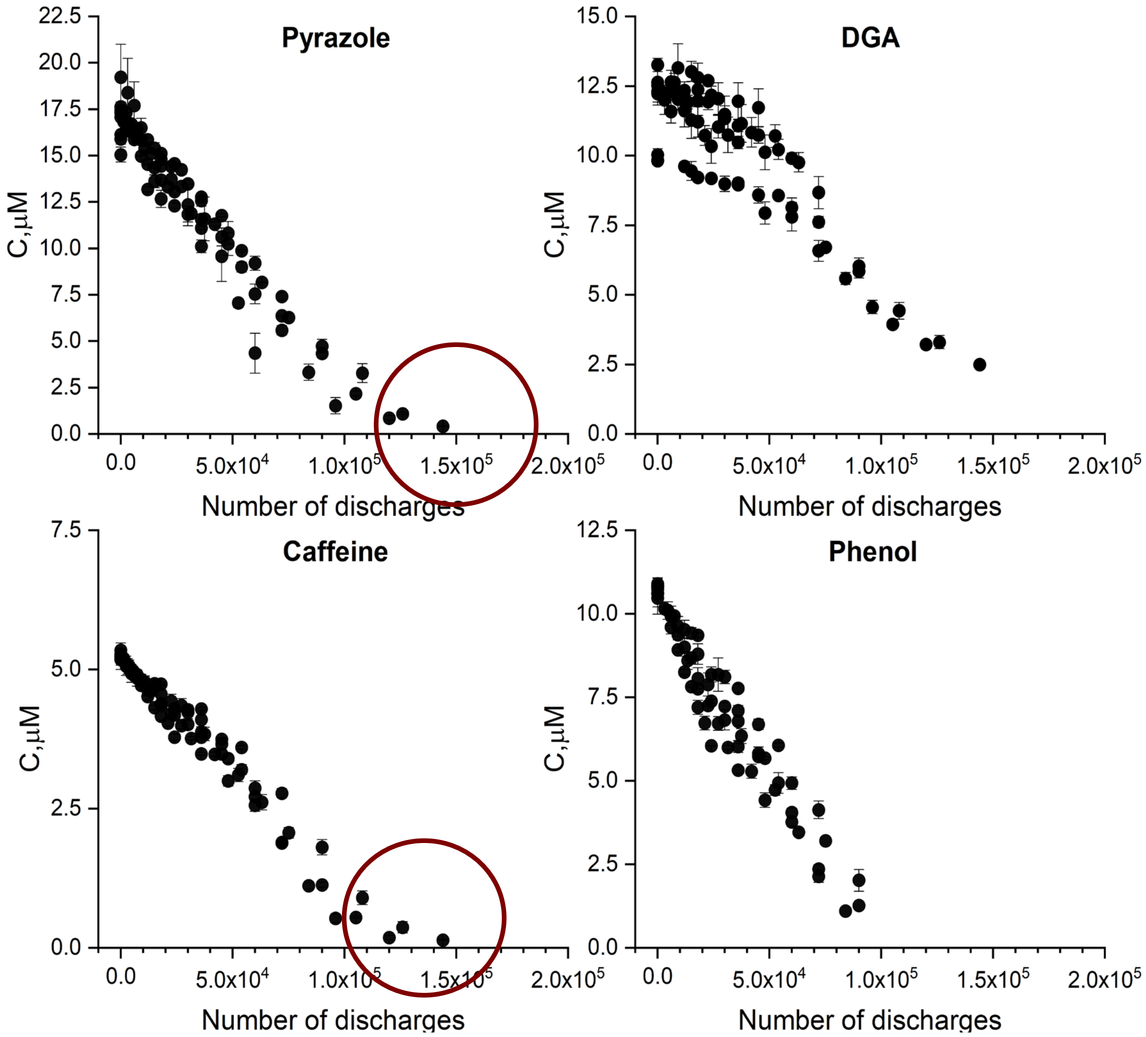
Temperature effect on degradation

- At f > 60 Hz, experiments were accompanied by a significant increase in the bulk liquid temperature (20°C in 20 minutes at 120 Hz).



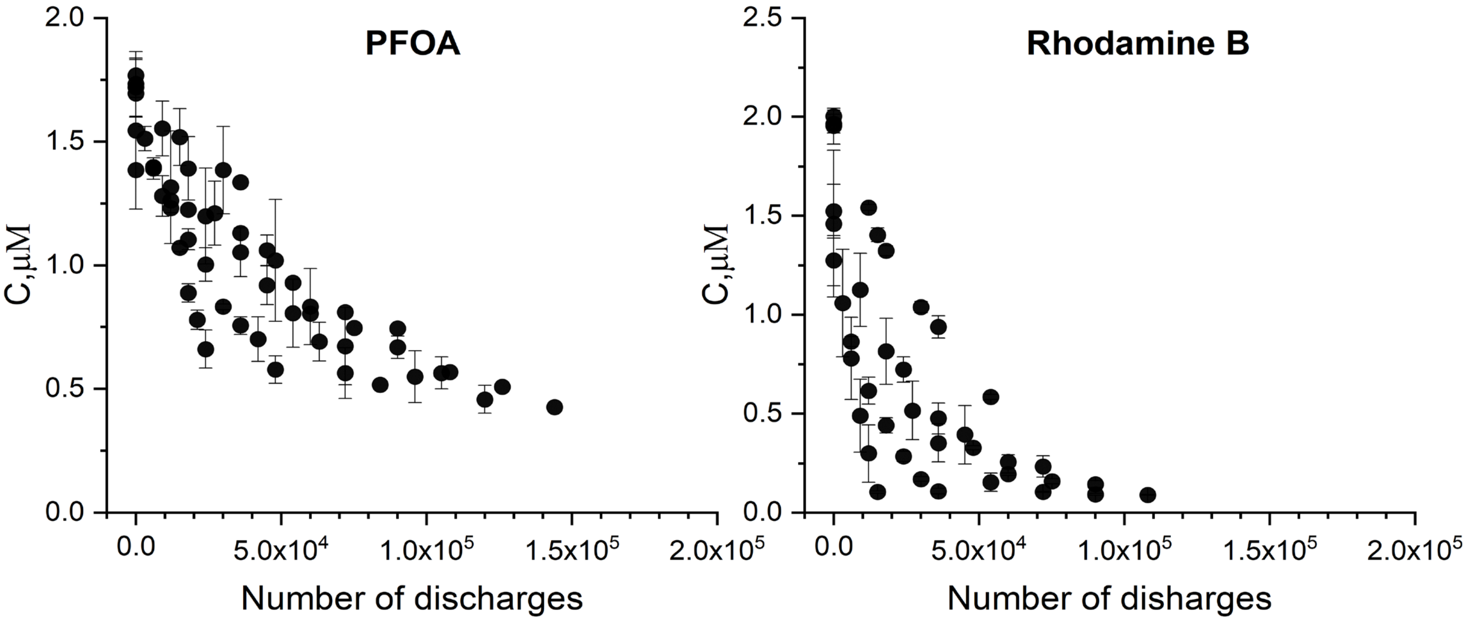
Rhodamine B and caffeine degradation profiles as a function of starting solution temperature acquired at 80 Hz

Linear dependence of the bulk liquid concentration on the number of discharges up to ~ 2 μM



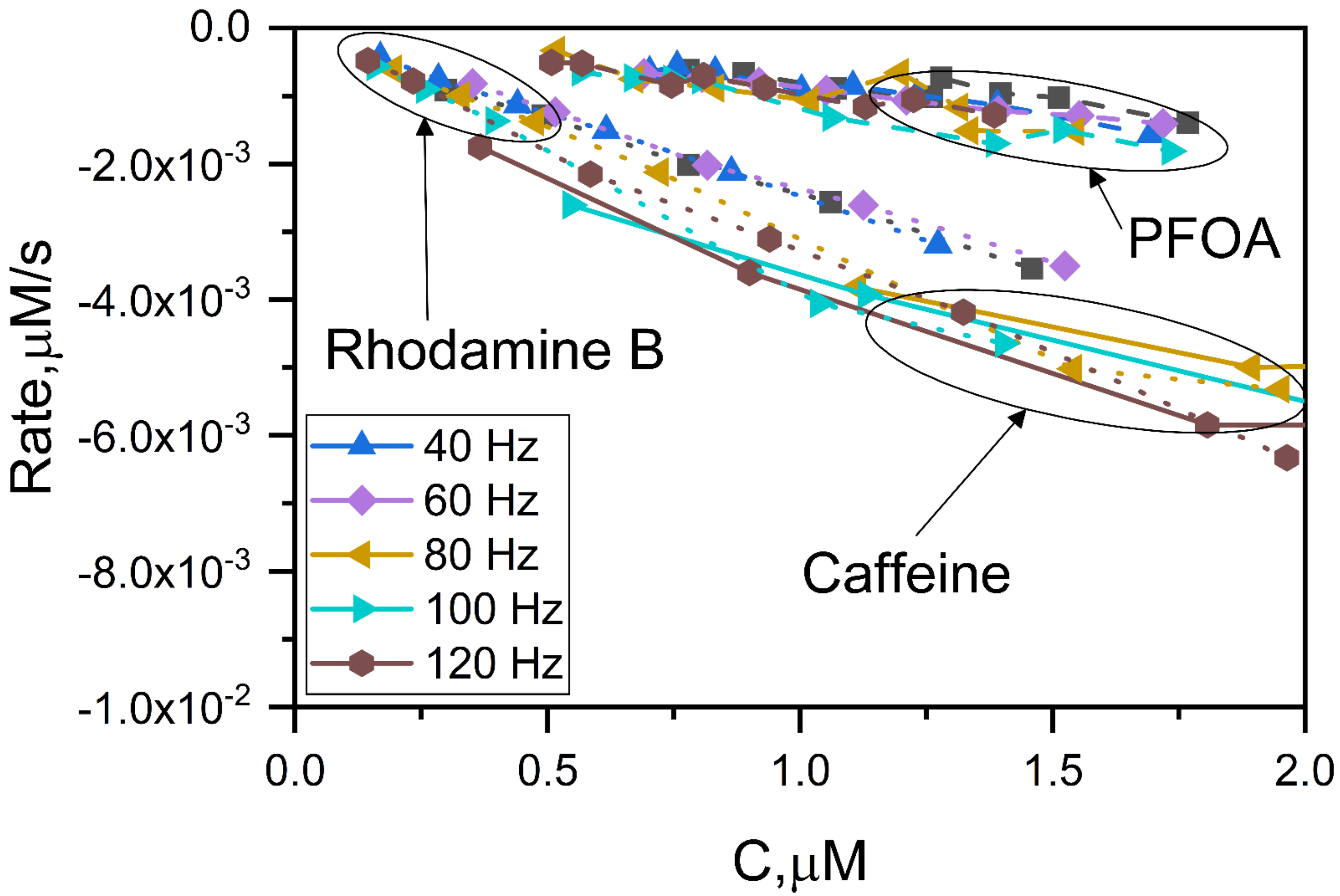
Removal rates depend on the discharge frequency.

Non-linear dependence of the bulk liquid concentration on the number of discharges below ~ 2 μM



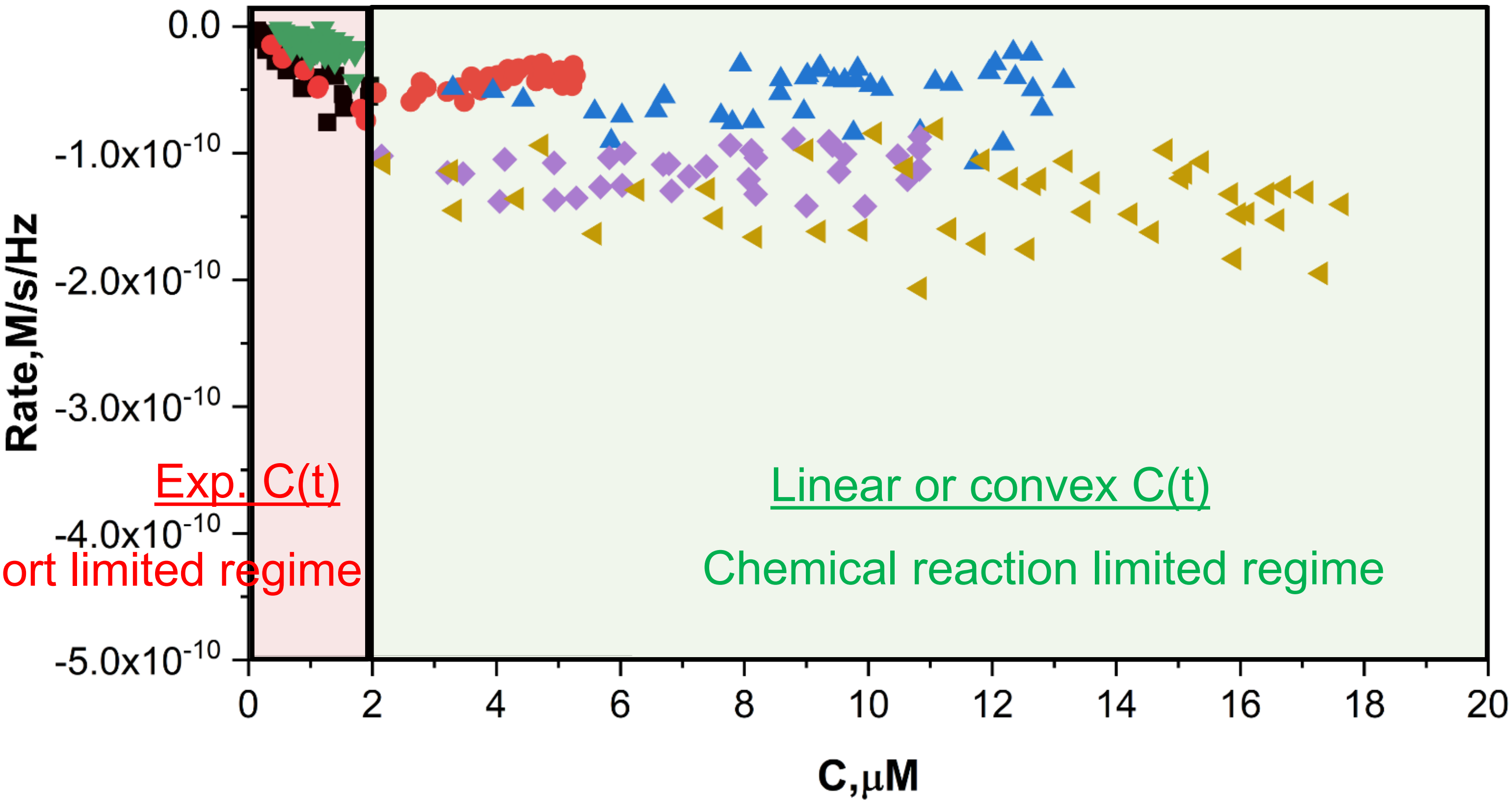
Removal rates may be independent of the discharge frequency.

Dependence of the removal rates on the concentration below ~ 2 μM



Removal rates are independent of the discharge frequency.

Transport and chemical reaction limited regimes



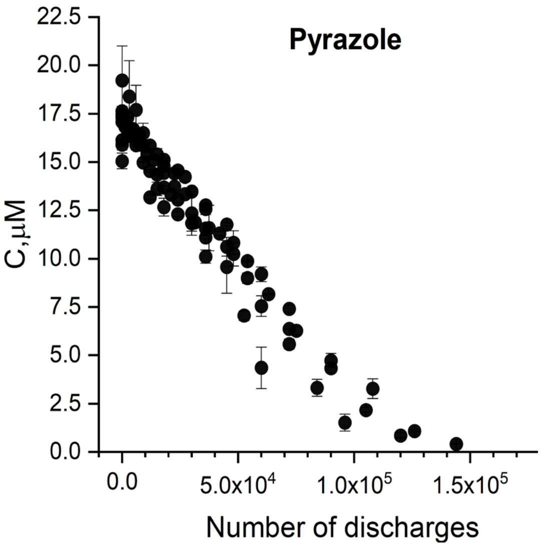
Exp. C(t)

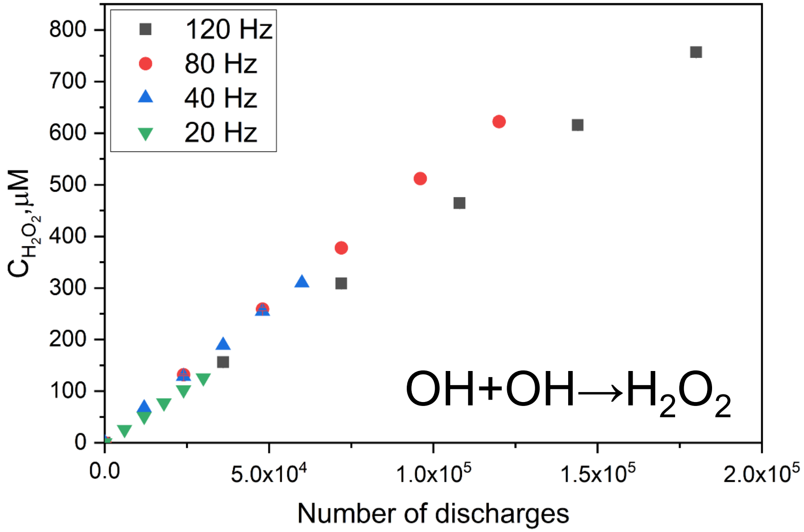
Transport limited regime

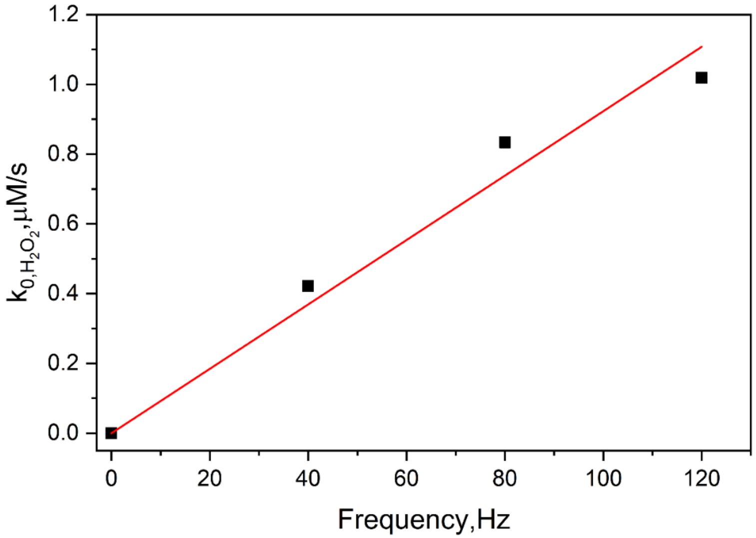
Linear or convex C(t)

Chemical reaction limited regime

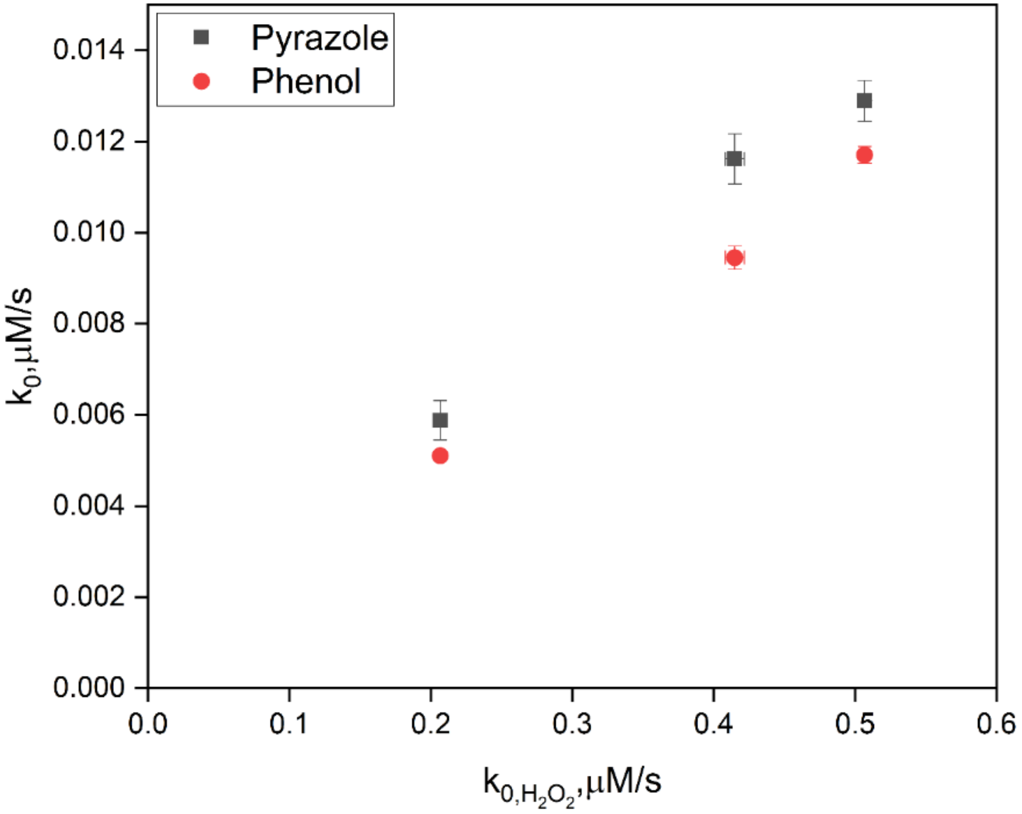
The chemical reaction limited regime





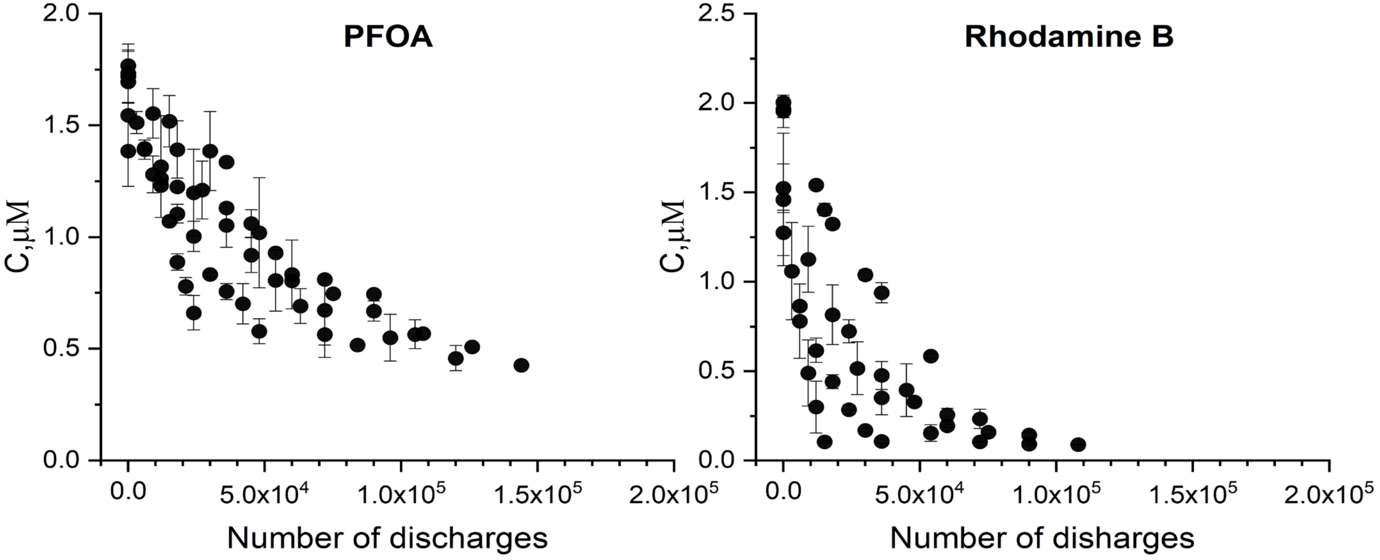


Verification of the chemical reaction limited regime



Degradation rates of compounds at concentrations > 2 μM depend on the flux of the reactive species.

The mass transport limited regime



- < 2 μM a solute degradation rate is proportional to its bulk liquid concentration and is independent of frequency.

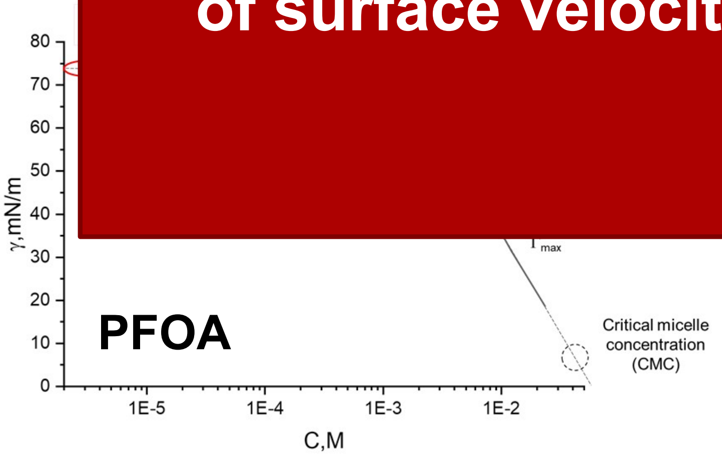
- The observed kinetic behavior is hypothesized to be a result of bulk liquid mass transport limitations, in particular convection in the liquid phase (Pe > 10^5)….BUT….

could a compound's tendency to accumulate at a gas-liquid interface be also controlling reaction rates? Both PFOA and RhB are surfactants.

Interfacial vs. bulk liquid compound concentrations

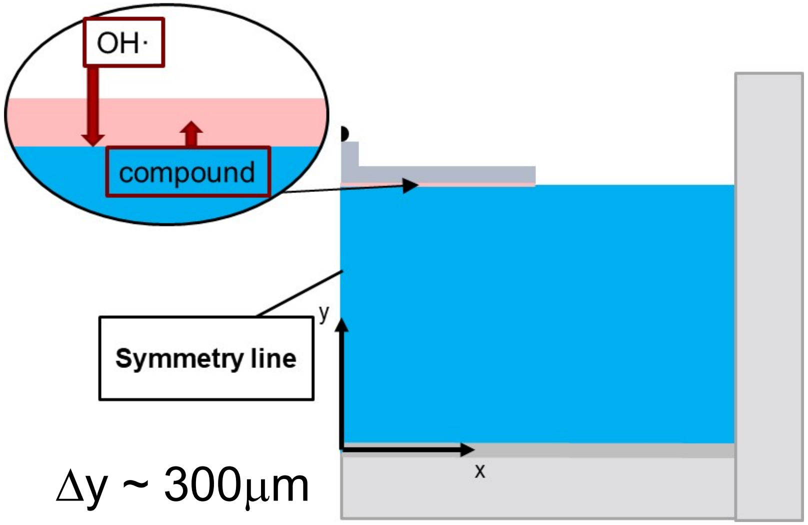
1. **UNIMPORTANT: solutes' interfacial excess concentrations**

2. **IMPORTANT: spatial gradients in the solutes' interfacial concentrations that are created in the x-direction as they affect the magnitudes of surface velocities.**



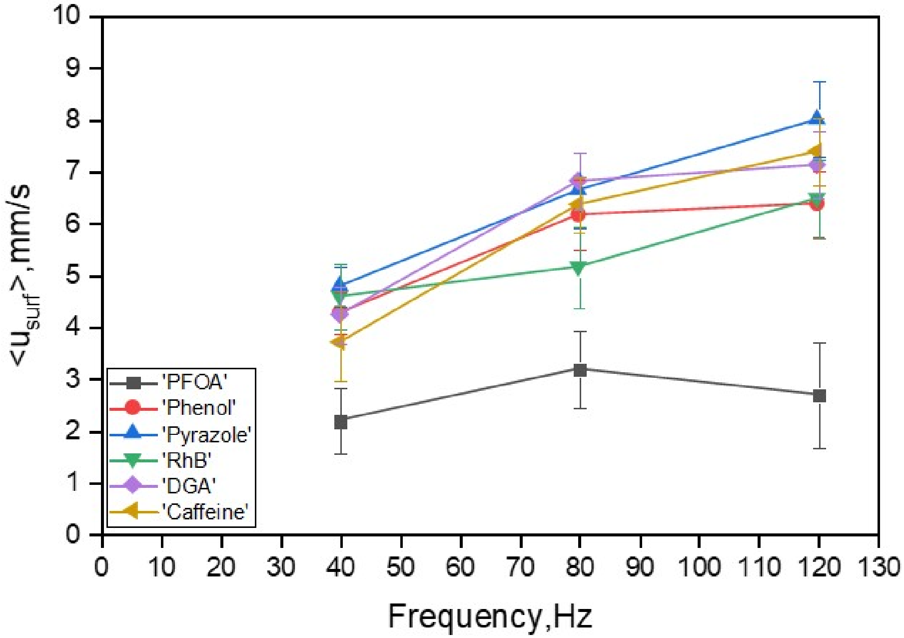
The concentration of any solute in the interfacial region can be assumed to be equal to its bulk liquid concentration.

The role of convective transport in overall removal: mean surface speeds



Δy ~ 300μm

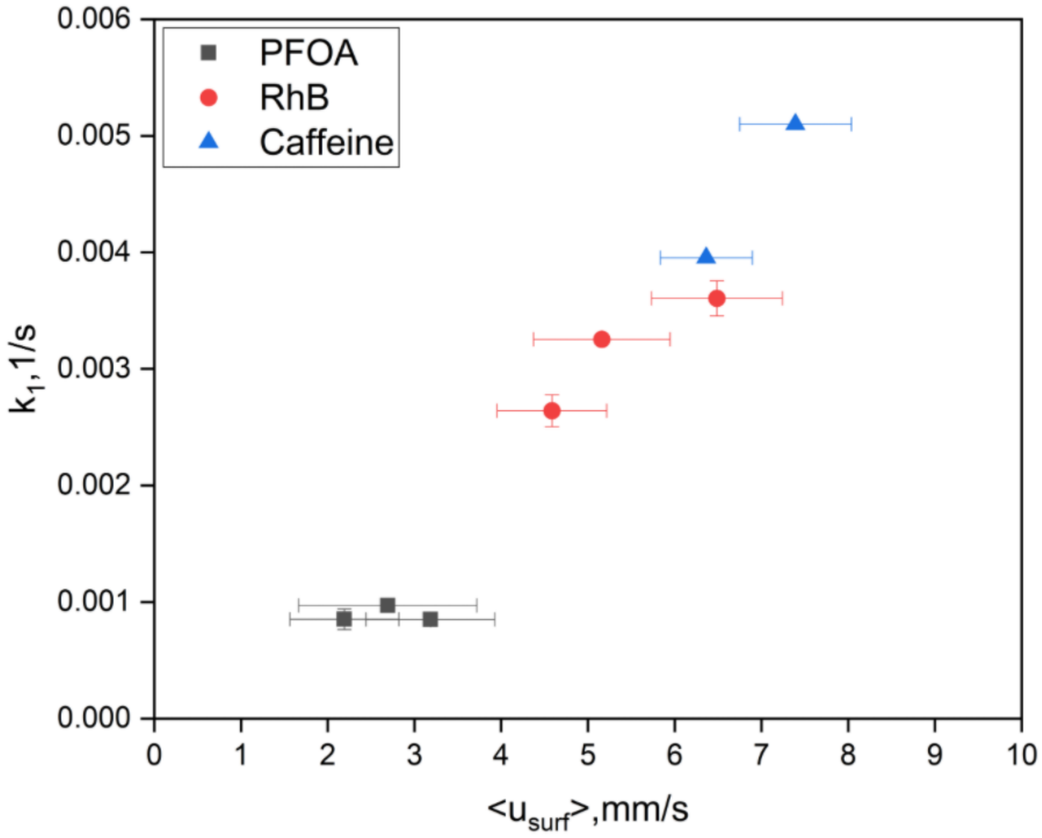
x-component of transient velocities for t >250 s was averaged in the region *x* = 0-30 mm



Mean surface velocities for the six non-surfactant compounds at their respective concentrations as a function of frequency as calculated from PIV data.

- The mean surface speeds for non-surface active compounds increase linearly with frequency (the highest range of velocities), consistent with the ionic wind mechanism.
- For surfactants, Marangoni stresses (2-3 orders of magnitude higher than for non-surfactants) counteract the ionic wind mechanism and reduce the effect of frequency on surface speed as well as the magnitude of the surface speed.

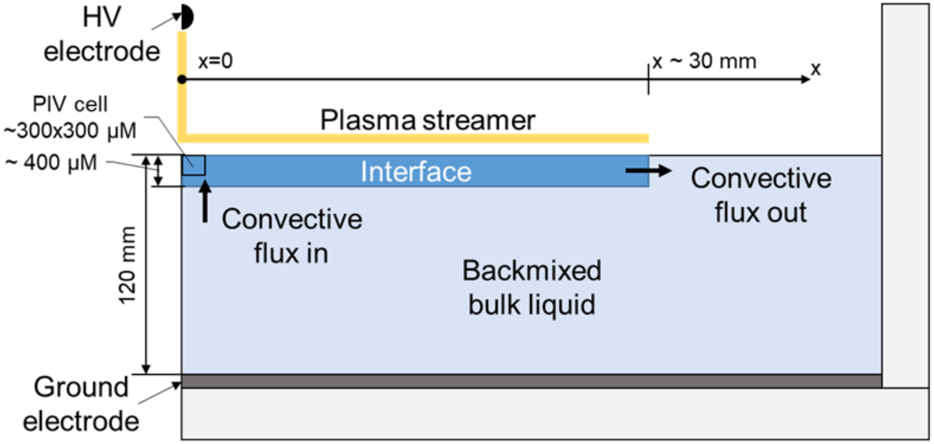
Verification of the mass transport limited regime

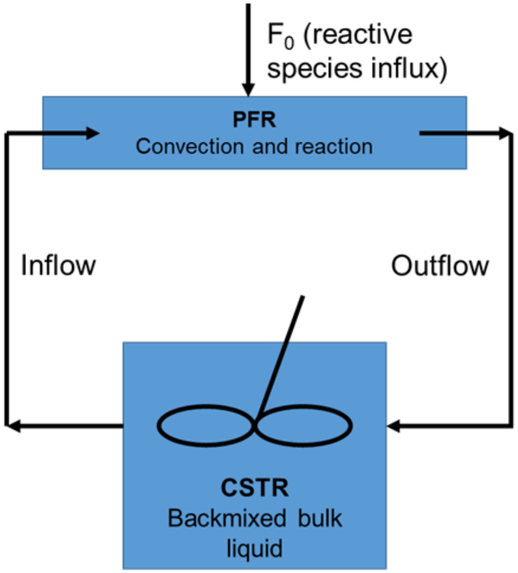


Degradation rates of compounds at concentrations < 2 μM depend on solute concentration and surface speeds.

Mathematical modeling of the system

- A numerical model that combines bulk liquid transport and chemical kinetics was developed to predict the three shapes of the degradation profiles: linear, exponential and complex nonlinear.





Coupling reaction zone and convective transport: caffeine

Caffeine mass balance in the PFR:

$$\boxed{\frac{\partial C}{\partial t} = -\left\langle u_{surf} \right\rangle \frac{\partial C}{\partial x} - k \cdot C \cdot C_{RS}}$$

$<u_{surf}>$ [m/s] = surface speed of the flow

k [$m^3/(mol \cdot s)$] = homogeneous reaction rate constant for the reaction of the compound with a reactive species (RS)

C_{RS} [mol/m^3] = concentration of the reactive species

Reactive species mass balance in the PFR:

$$\boxed{\frac{\partial C_{RS}}{\partial t} = -k \cdot C \cdot C_{RS} - k_r \cdot C_{RS}^{\ 2} + F_0(f)}$$

$R + OH \rightarrow$ products ….k

$OH + OH \rightarrow H_2O_2$ ….k_r

F_0 [$mol/m^3/s$] = time-averaged generation of the reactive species that is assumed to be constant along the length of the streamer

Model parameters

Caffeine macroscopic balance in the CSTR:

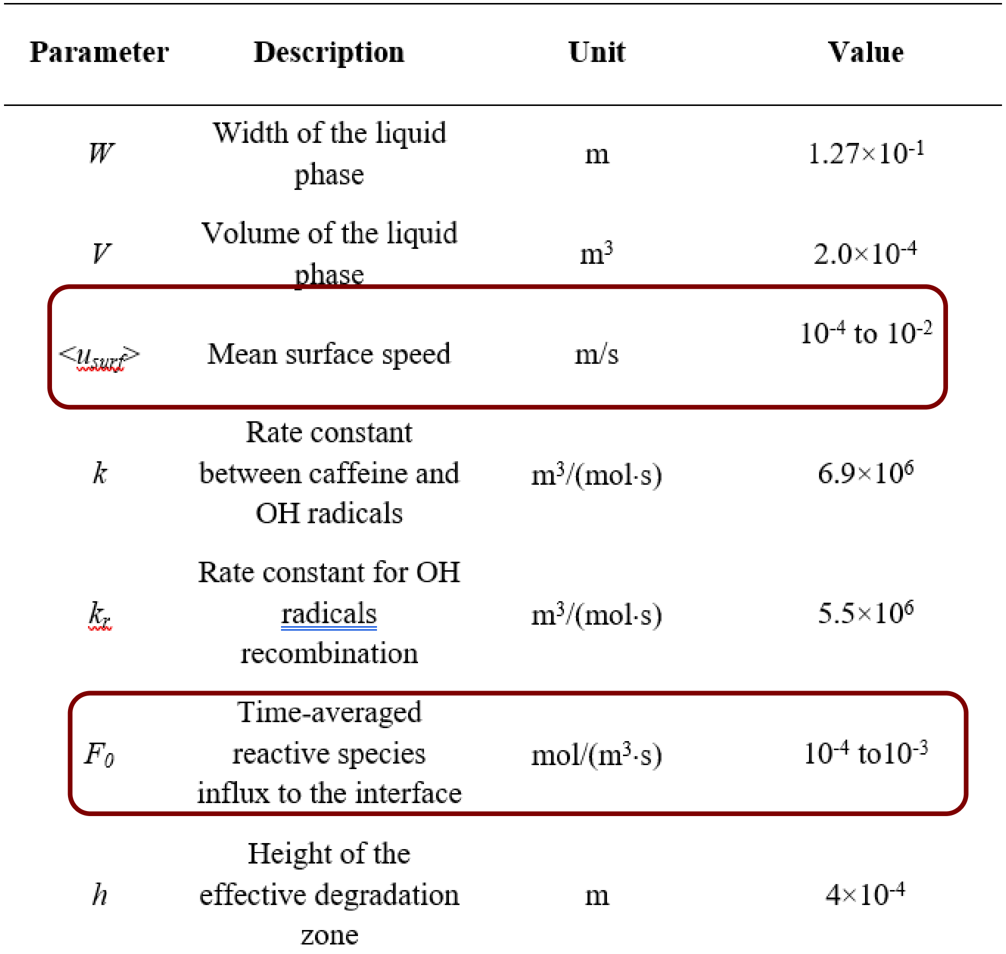
$$\boxed{\frac{dC_b}{dt} = 2\frac{\langle u_{surf} \rangle \cdot h \cdot W}{V} \cdot \left[C(x=L) - C(x=0)\right]}$$

h [m] = effective height of the interfacial region

W [m] = width of the reactor

V [m^3] = bulk liquid volume

C (x=L) and *C* (x=0) = concentrations of the solute at the exit and the inlet of the PFR, respectively



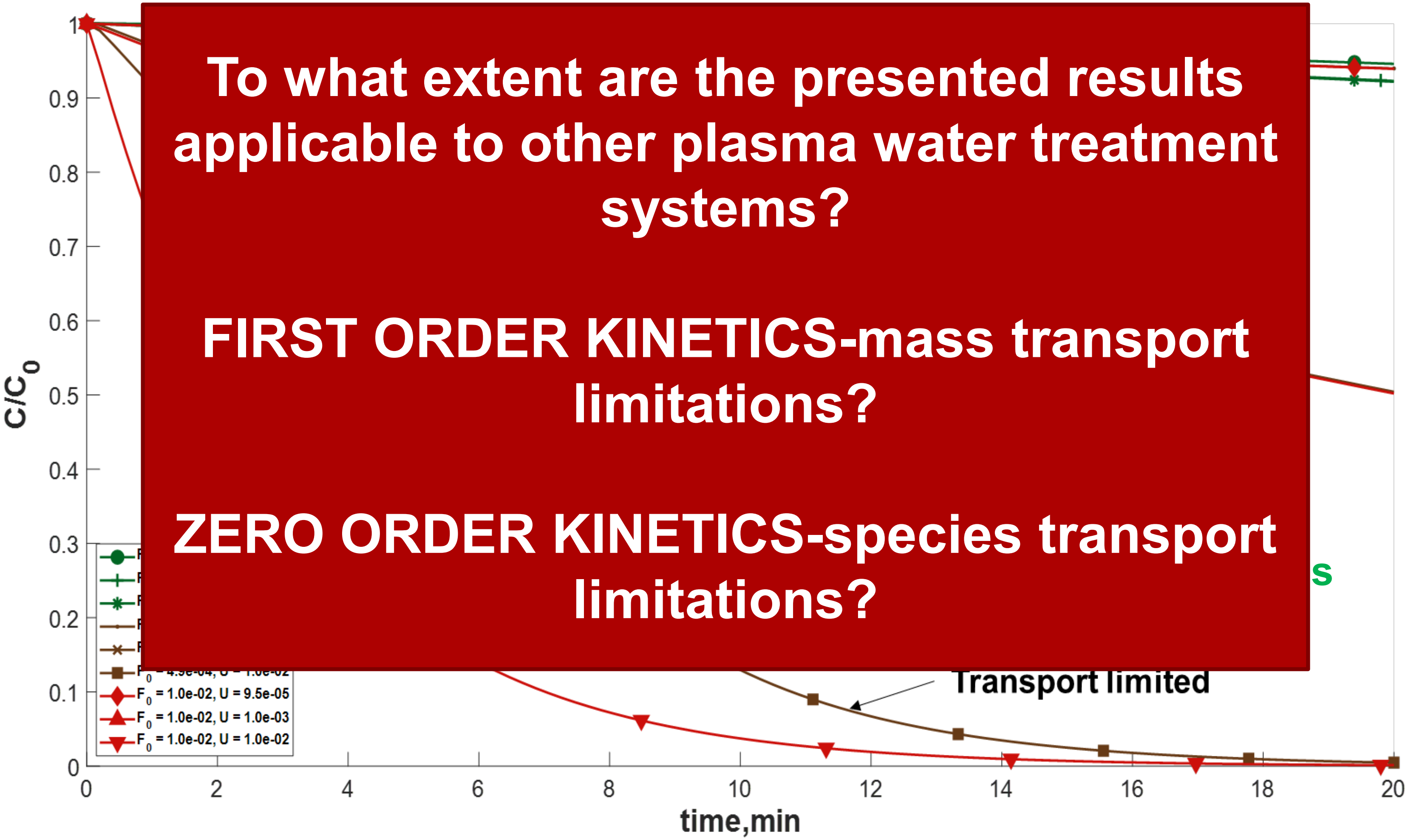
Parameter	**Description**	**Unit**	**Value**
W	Width of the liquid phase	m	1.27×10^{-1}
V	Volume of the liquid phase	m^3	2.0×10^{-4}
$<u_{surf}>$	Mean surface speed	m/s	10^{-4} to 10^{-2}
k	Rate constant between caffeine and OH radicals	m^3/(mol·s)	6.9×10^{6}
k_r	Rate constant for OH radicals recombination	m^3/(mol·s)	5.5×10^{6}
F_0	Time-averaged reactive species influx to the interface	mol/(m^3·s)	10^{-4} to10^{-3}
h	Height of the effective degradation zone	m	4×10^{-4}

Parametric study: variables F_0 and $<u_{surf}>$

F_0: influx of reactive species
$<u_{surf}>$: average surface speed

Degradation in the reaction limited regime:

$$F_0 < 2\frac{\langle u_{surf} \rangle \cdot h \cdot W}{V} C_b$$



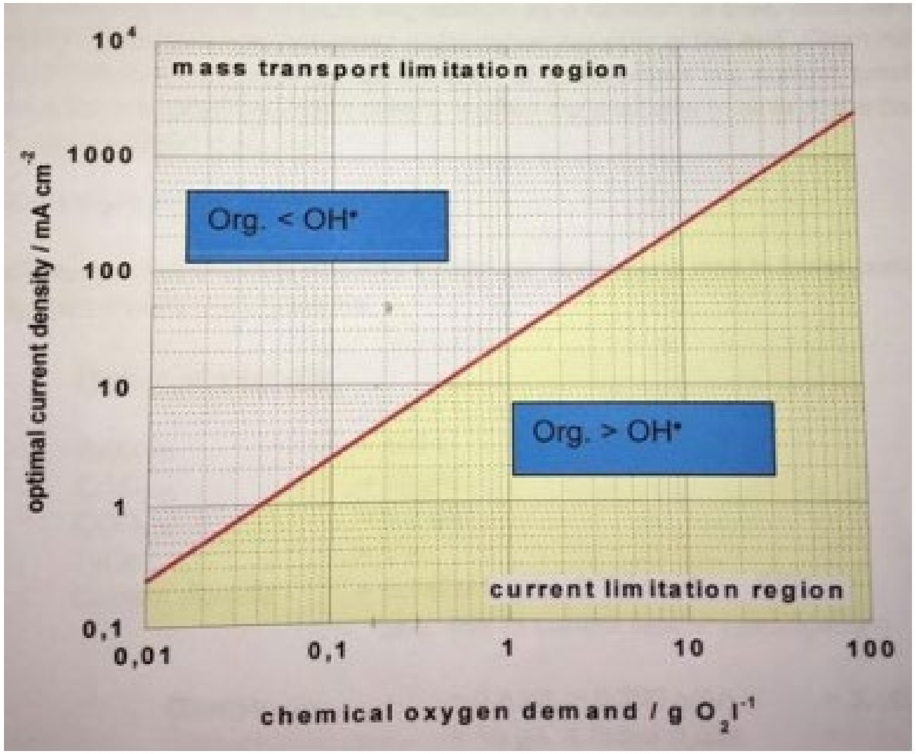
To what extent are the presented results applicable to other plasma water treatment systems?

FIRST ORDER KINETICS-mass transport limitations?

ZERO ORDER KINETICS-species transport limitations?

Model result implications: lessons from electrochemistry

Current Limited vs. Mass Transport Limited Regimes



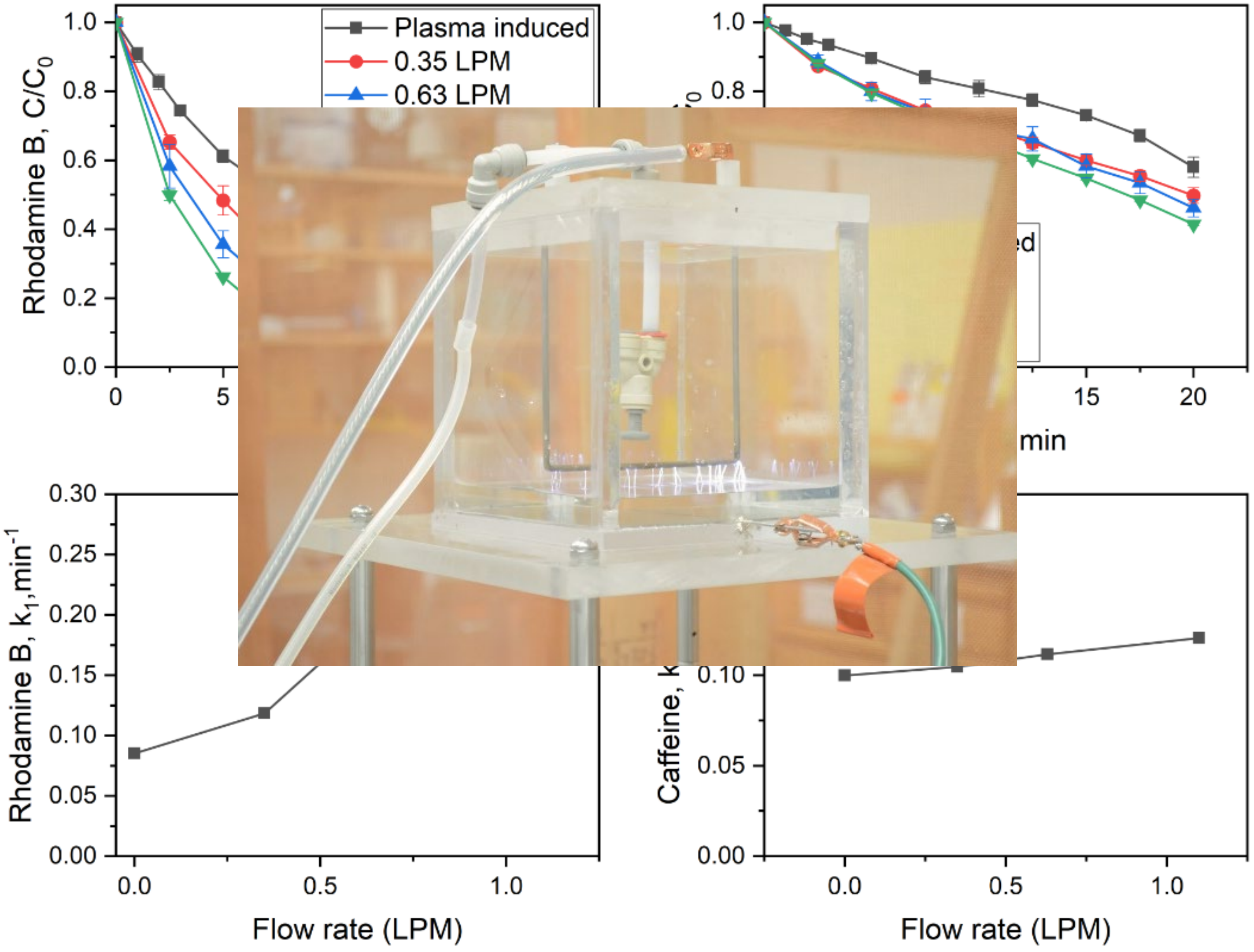
- Yellow area: degradation of 100% current efficiency
- White area: too many OH• are produced relative to COD concentration
- Higher degradation rate with increasing current: current limited.
- No increase in degradation rate with increasing current: mass transport limited.

https://www.ideals.illinois.edu/bitstream/handle/2142/106646/20190418%20-%20Rusinek.pdf?sequence=2&isAllowed=y

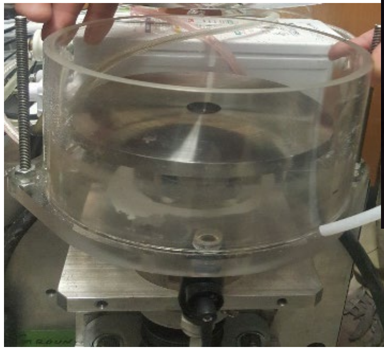
The effect of the recirculation on the degradation of rhodamine B and caffeine

Mass transport limited regime

Reactive species limited regime

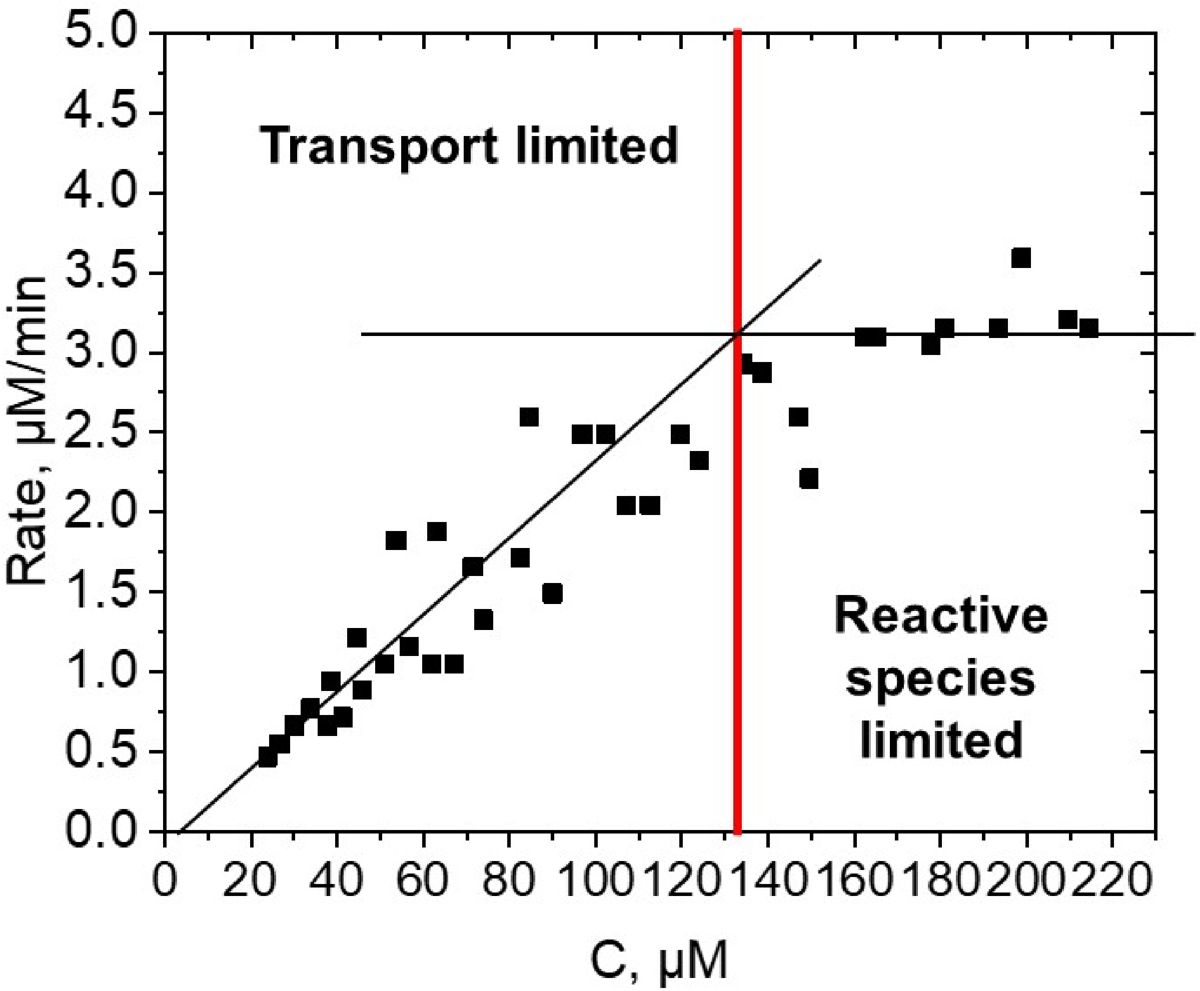


Regime control in the plasma spinning disc reactor

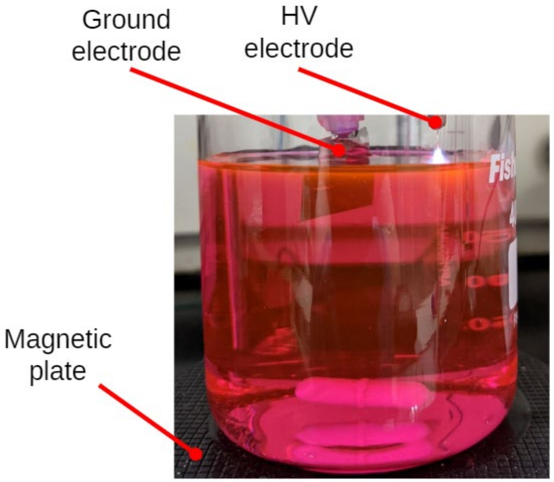


- Treatment vol
- Rotational spe
- Argon gas flo

Rhodamine B d
disc reactor

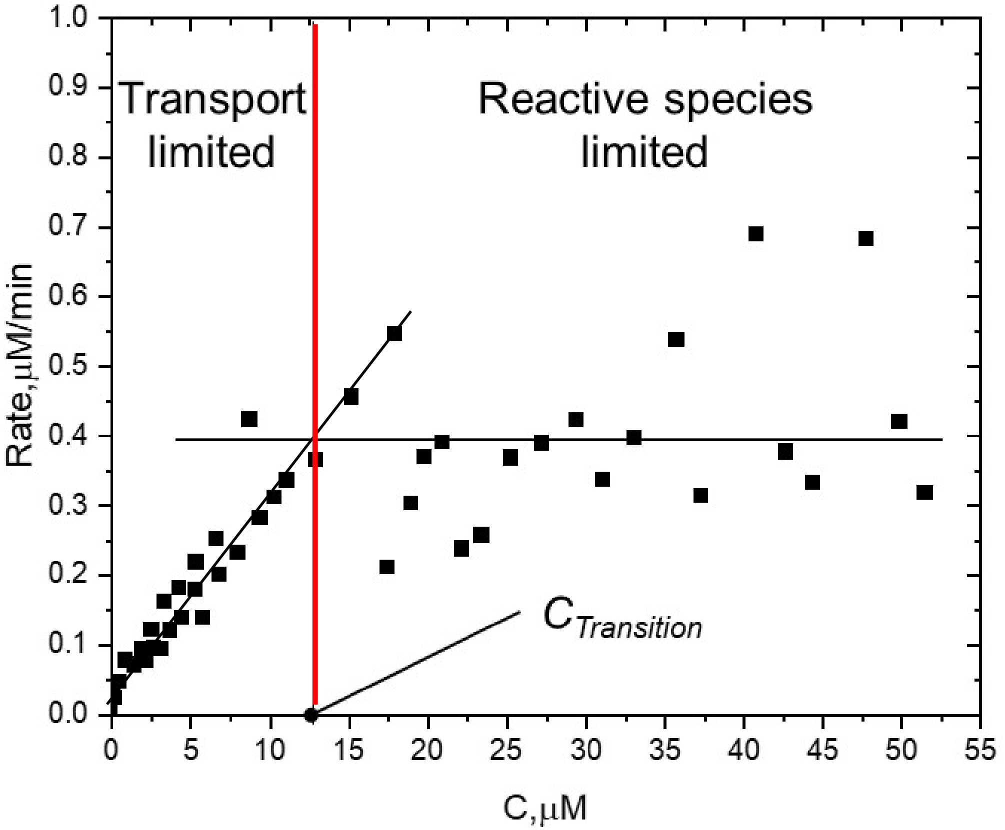


Regime transition in a DC plasma system



- Volume: 250 mL
- Voltage: 9 kV
- Mixing: magnetic stirrer
- Cathode: platinum wire
- Anode: platinum-plated plate
- Headspace: argon

$$\left.\frac{dC}{dt}\right|_{C_{Transition}} = -k_1 C_{Transition} = -k_0$$



Rate of rhodamine B degradation vs. instantaneous concentration showing the regime transition

Summary

- Bulk liquid composition and mixing strongly influence the effectiveness of plasma reactors for water treatment applications.
- Compound concentration (among other parameters) in the liquid may control the reactor's operating regime; below a certain concentration the system operates in the mass transport limited regime. Above that critical concentration, the process is limited by the production of reactive species.
- The concentration at which the regime transition occurs will be different for different plasma treatment systems. Kinetic analysis of the concentration-time profiles may assist in determining the current operating regime for the system in question.
- Knowledge of the operational regime may assist in the plasma reactor design through manipulation of the relative magnitudes of the governing fluxes.

Acknowledgments

- Dr. Thomas Holsen
- Chase Nau-Hix, PhD student
- Mikhail Vasilev, PhD student
- Xudong Su, PhD student
- Dr. Raj Kamal Singh
- Dr. Rui Li
- Osakpolo Isowamwen, PhD student

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