Efficient Treatment of 2,3,3,3-Tetrafluoro-2-(Heptafluoropropoxy) Propanoic Acid (GenX) by Electrochemical Degradation on a Boron-Doped Diamond Electrode

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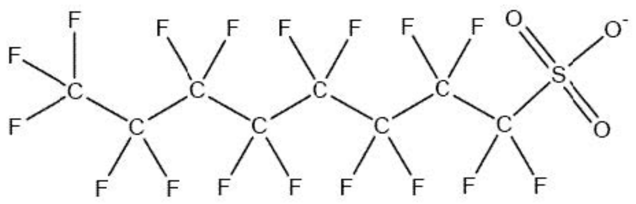
Introduction

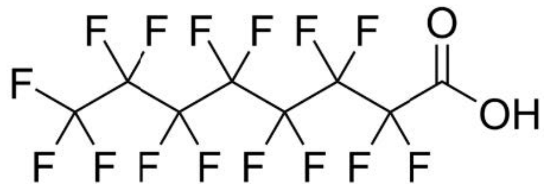
PFOS

C8HF17O3S



PFOA

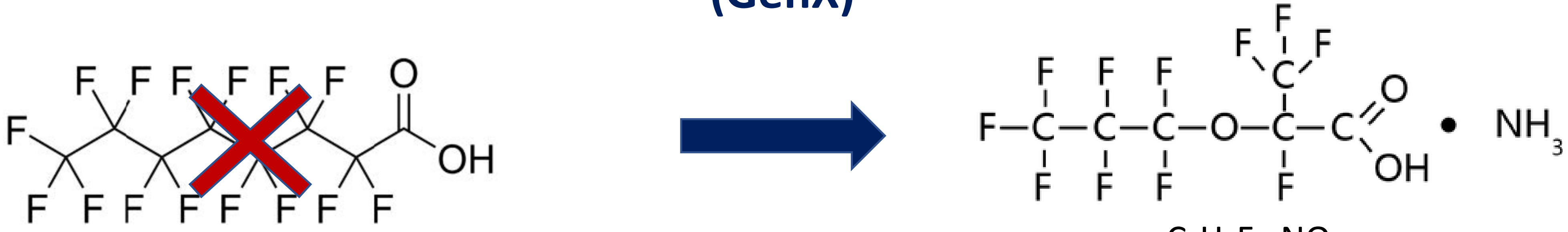
C8HF15O2



- manufacturing
- food packaging
- lubricants
- water-resistant coating
- fire-fighting foams

https://ntp.niehs.nih.gov/pubhealth/hat/noms/pfoa/index.html

2,3,3,3-Tetrafluoro-2-(Heptafluoropropoxy) Propanoic Acid (GenX)

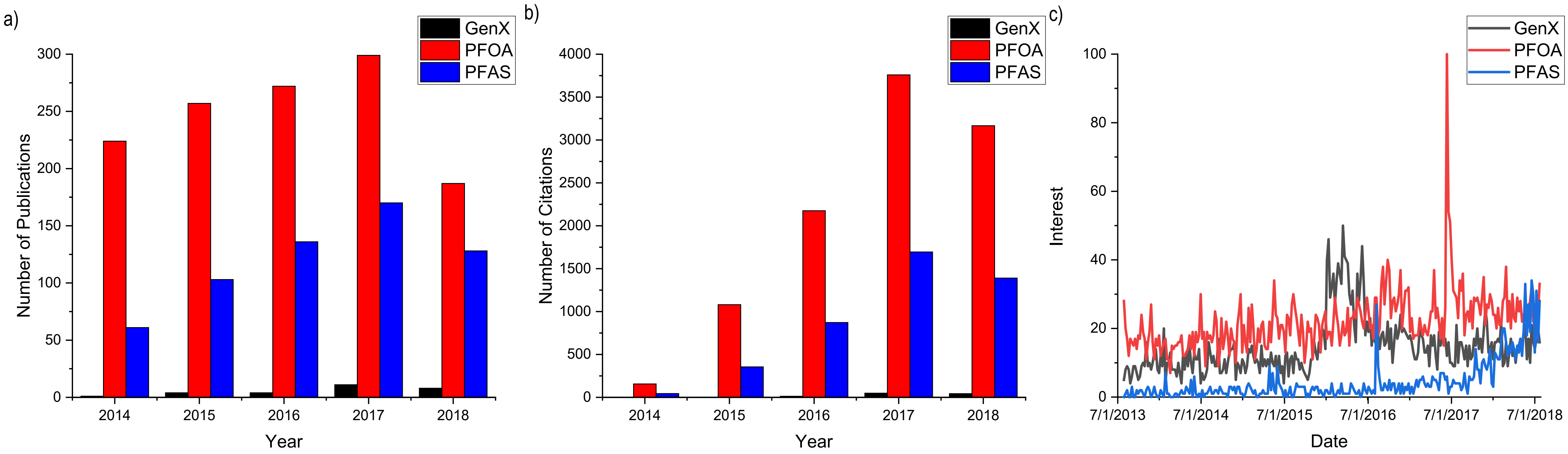


$C_6H_4F_{11}NO_3$

- Bioaccumulation > Detected in ~ 6 millions Americans drinking water
- Long half-life in water human body
- Replace long chain with short chain

http://chemistryfes.blogspot.com/2013/03/cookware-chemical-linked-to-thyroid.html

GenX Popularity



Different Methods for PFAS Removal

Treatment	PFEAs (e.g., GenX)
Coagulation/ sedimentation/ filtration	Not effective
Chlorination/ chloramination	Not effective
Ozonation	Not effective
UV/H_2O_2	Not evaluated, but not expected to be effective
PAC adsorption	Moderately effective (e.g., PFO4DA) to not effective (e.g., PFMOAA)
GAC adsorption	Moderately effective (e.g., Nafion byproduct 2) to somewhat effective (e.g., GenX, PFO2HxA); additional data needed, bench- and pilot-testing is ongoing
Anion exchange	Under evaluation, very effective for Nafion byproduct 2, moderately effective for GenX; removal of short-chain PFEAs such as PFMOAA needs further study
High-pressure membranes (nanofiltration, reverse osmosis)	Not evaluated, but likely effective based on results obtained with short-chain PFASs and household reverse osmosis systems

(Z. R. Hopkins, 2018)

TABLE 1. FILTRATION OF PERFLUOROALKYL SUBSTANCES

Compound	*Material*	*Conditions*	*NaCl rejection (%)*	*[PFAS]$_0$ (mg/L)*	*Time (h)*	*PFAS rejection (%)*	*References*
Nanofiltration							
PFOA, PFBA, PFPeA, PFHxA, PFNA, PFDA	NF270	200 L, 18°C, pH 6.7, 0.17–0.97 MPa, feed flow = 1 L/min	>50%	0.001	24	93–99	Appleman *et al.* (2013)
PFOS, PFBS, PFHxS	NF270	200 L, 18°C, pH 6.7, 0.17–0.97 MPa, feed flow = 1 L/min	>50%	0.001	24	95–99	Appleman *et al.* (2013)
PFOS	DK	25°C, pH 4, 1.38 MPa, feed flow = 1.37 L/min	66.4	10	96	90–99	Tang *et al.* (2007)
	NF270	25°C, pH 4, 1.38 MPa, feed flow = 1.37 L/min	56.9	10	96	90–99	Tang *et al.* (2007)
	NF90	25°C, pH 4, 1.38 MPa, feed flow = 1.37 L/min	94.4	10	96	90–99	Tang *et al.* (2007)
Reverse osmosis							
PFOS	SG	25°C, pH 4, 1.38 MPa, feed flow = 1.37 L/min	95.2	10	96	>99	Tang *et al.* (2006, 2007)
	LFC1	25°C, pH 4, 1.38 MPa, feed flow = 1.37 L/min	97.3	10	96	>99	Tang *et al.* (2007)
	LFC3	25°C, pH 4, 1.38 MPa, feed flow = 1.37 L/min	98.5	10	96	>99	Tang *et al.* (2006, 2007)
	BW30	25°C, pH 4, 1.38 MPa, feed flow = 1.37 L/min	97.9	10	96	>99	Tang *et al.* (2006, 2007)
	ESPA3	25°C, pH 4, 1.38 MPa, feed flow = 1.37 L/min	94.9	10	96	>99	Tang *et al.* (2006, 2007)

(N. Merino, 2016)

Electrochemical Degradation on BDD Electrodes

Electrochemical degradation efficiency

- Electron transfer capacity
- Hydroxyl radical generation ability

❖ High oxygen potential

❖ Long life span

❖ With superior chemical stability

❖ Mechanical strength result in applying

❖ BDD electrodes to oxidize dyes

❖ Acetic acid

❖ Maleic acid

❖ Perfluorinated compounds

https://www.exportersindia.com/nb__enterprises/boron-doped-diamond-electrode-1264652.htm

Electrochemical Degradation on BDD Electrodes

a) HO$^{\bullet}$ with –SO_3 group
- HSO_4
- Perfluorooctyl radical

b) HO$^{\bullet}$ attack fluorine atom
- O replaces a fluorine atom > HF

C) HO$^{\bullet}$ attack C-C bond
- Perfluorobutyl radical
- 1-hydroxyperfluorobutane sulfonate

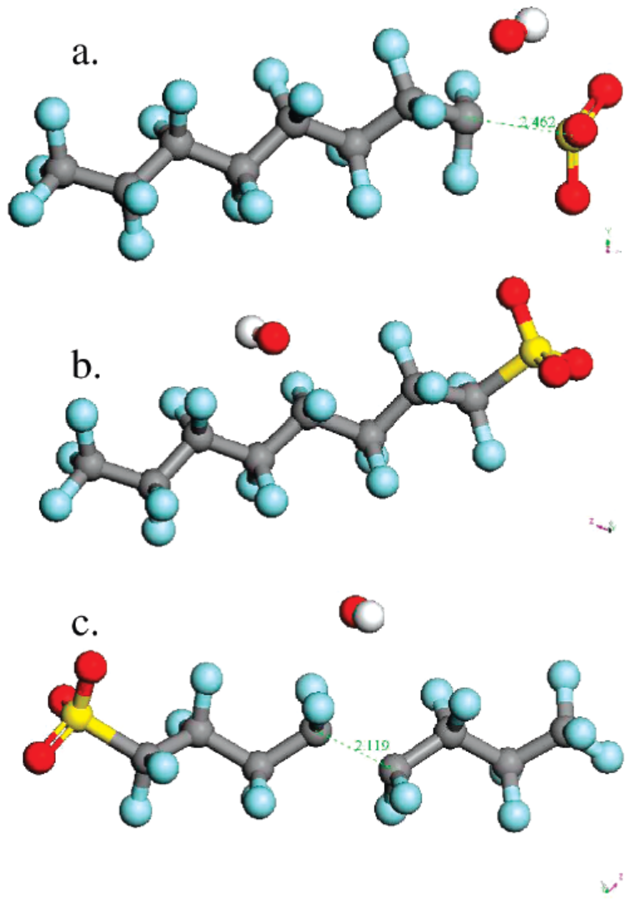
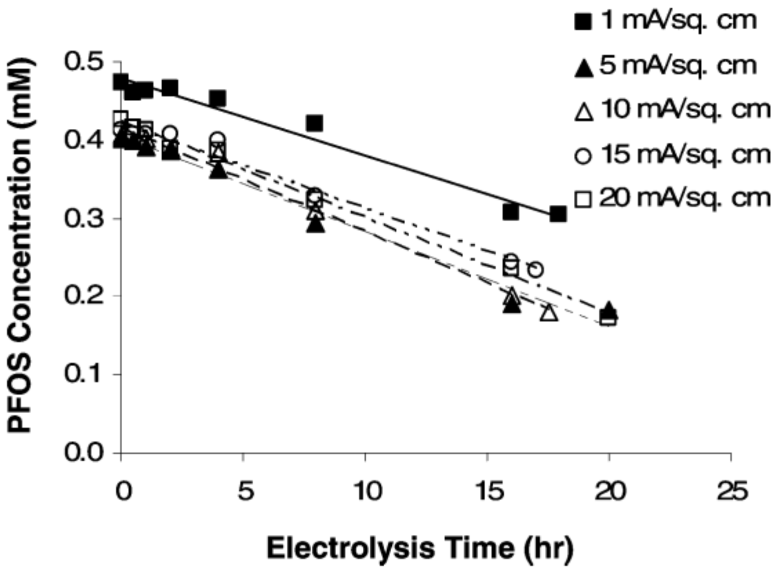


FIGURE 3. Transition state for hydroxyl radical attack at (a) the –SO_3 site, (b) an –F site, and (c) a C–C bond. Atom key: C, gray; F, blue; S, yellow; H, white; and O, red.



(K. E. Carter, 2008)

Electrochemical Degradation on BDD Electrodes

1) Electron transfer from functional group to anode
- PFAS radical
- Perfluorooctyl radical

2) Decarboxylate or desulfonate of PFAS radical
- Perfluoroalkyl radical

3) Defluorination reaction between hydroxyl radical and Perfluoroalkyl radical

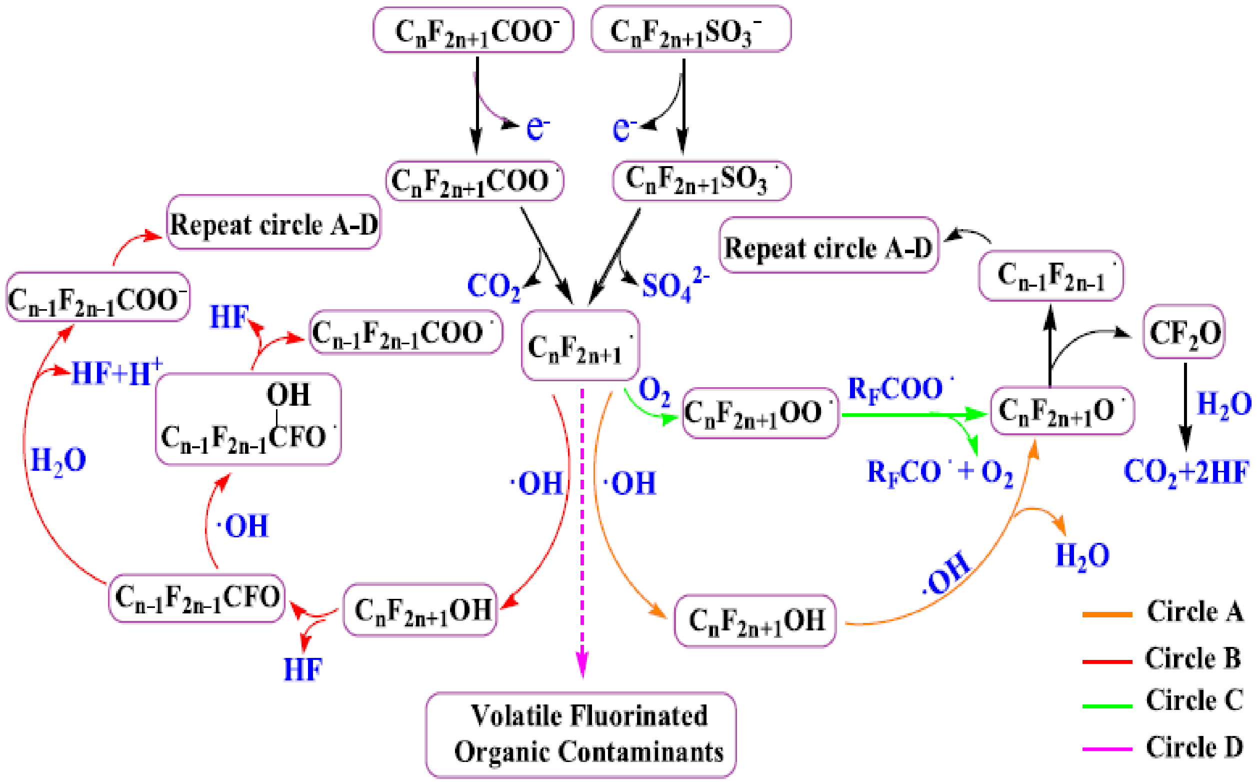
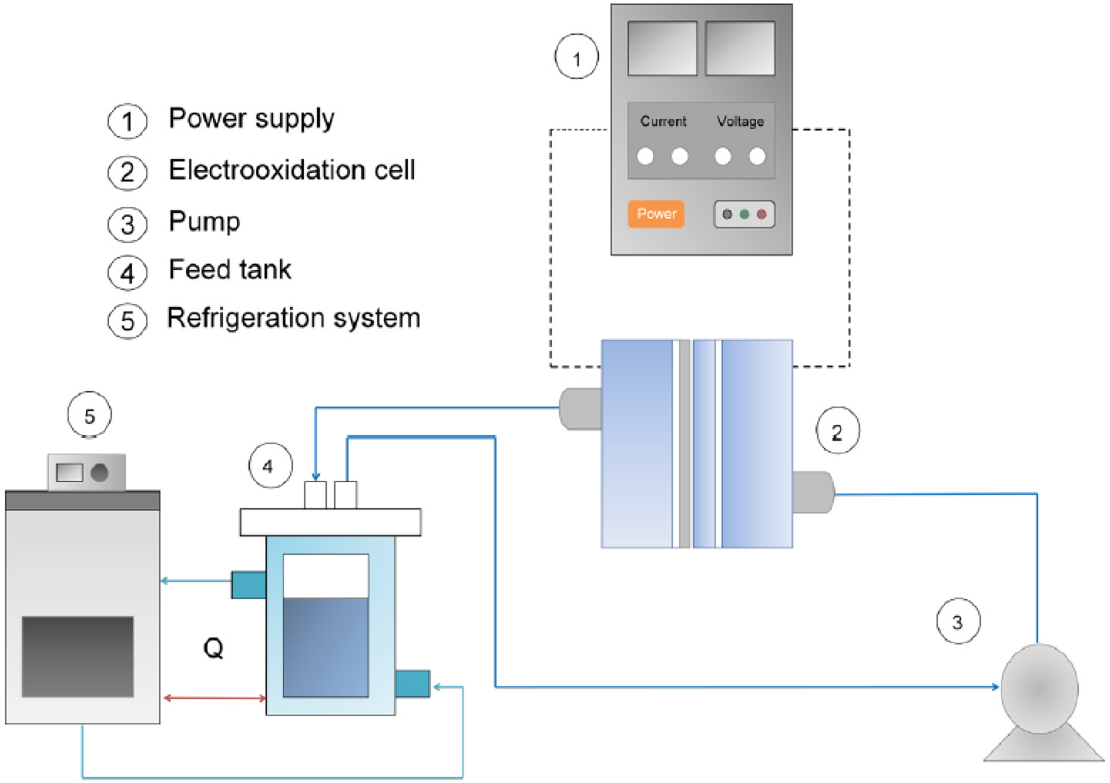


Fig. 1. Proposed pathways for electrochemical oxidation of PFCs in water.

(J. Niu, 2016)

BDD Electrodes Set-up



(A. Urtiaga, 2015)

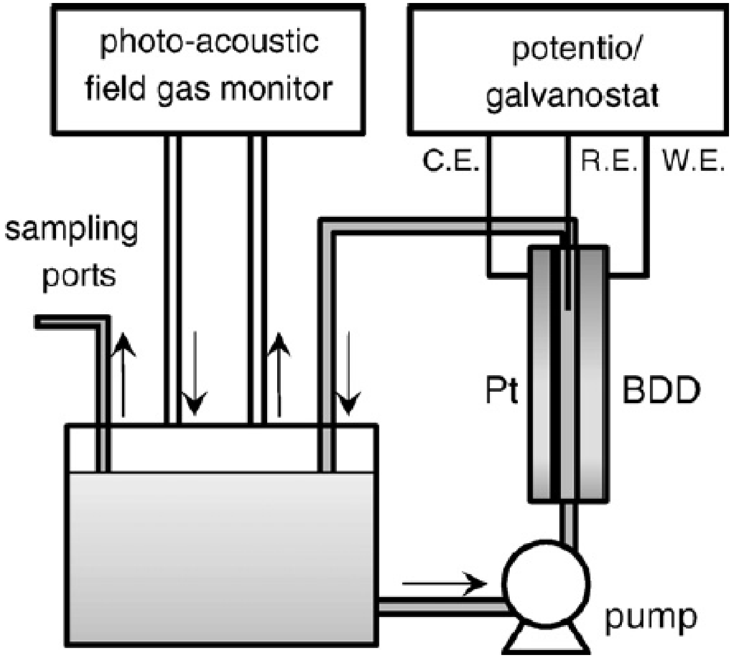


Fig. 1. Schematic illustration of the system.

(T. Ochiai, 2011)

BDD Experiment set-up in Dr. Greenlee's Lab

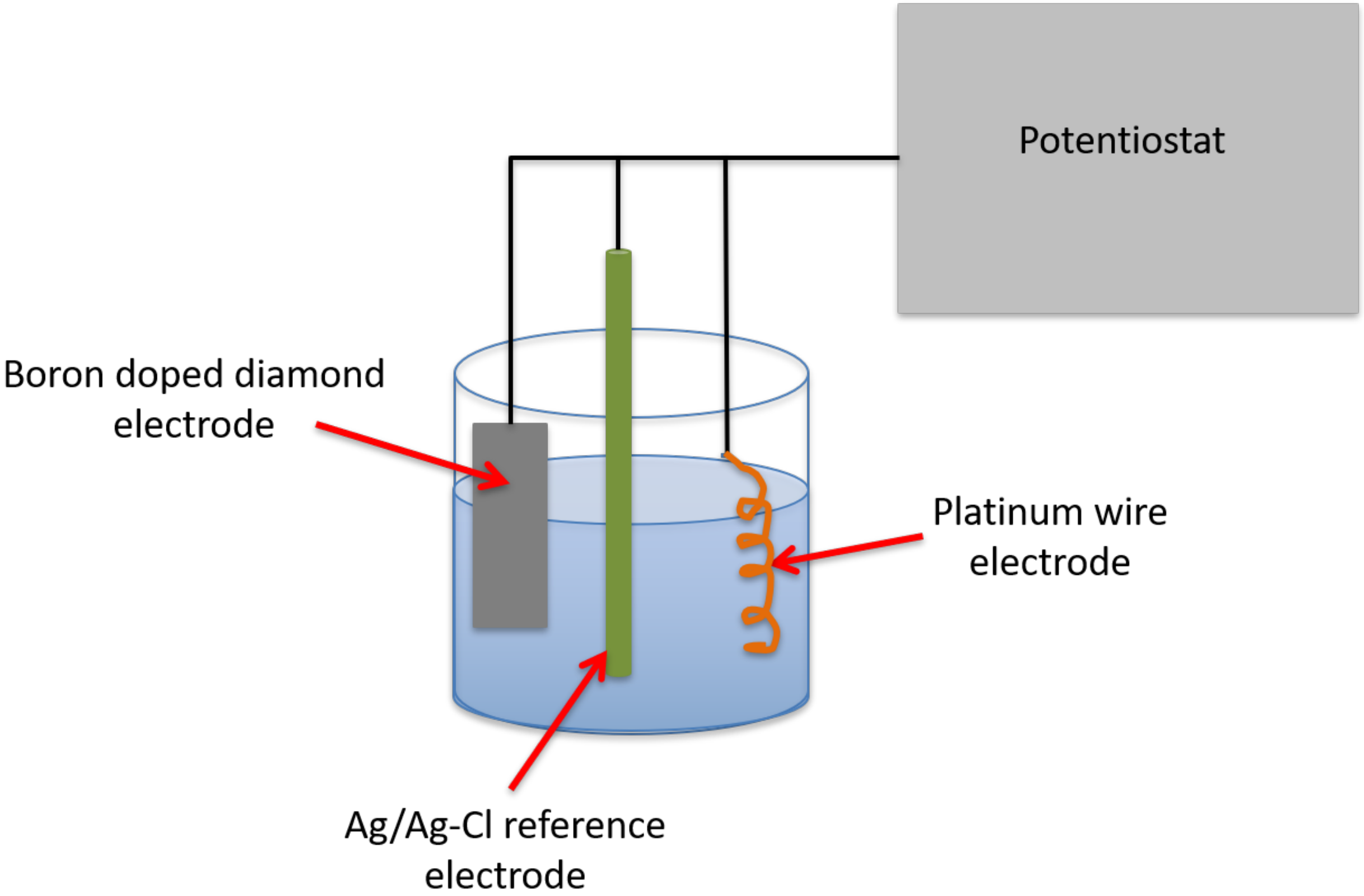
- GenX concentration:
10, 100 and 1,000 ppb

- Salt solution concentration:
2000 mg/L sodium sulfate

- Working electrode:
10,000 ppm boron doped diamond (BDD) electrode (NeoCoat) cut into a 5 cm X 2.5 cm

- Sampling:
1-hour intervals

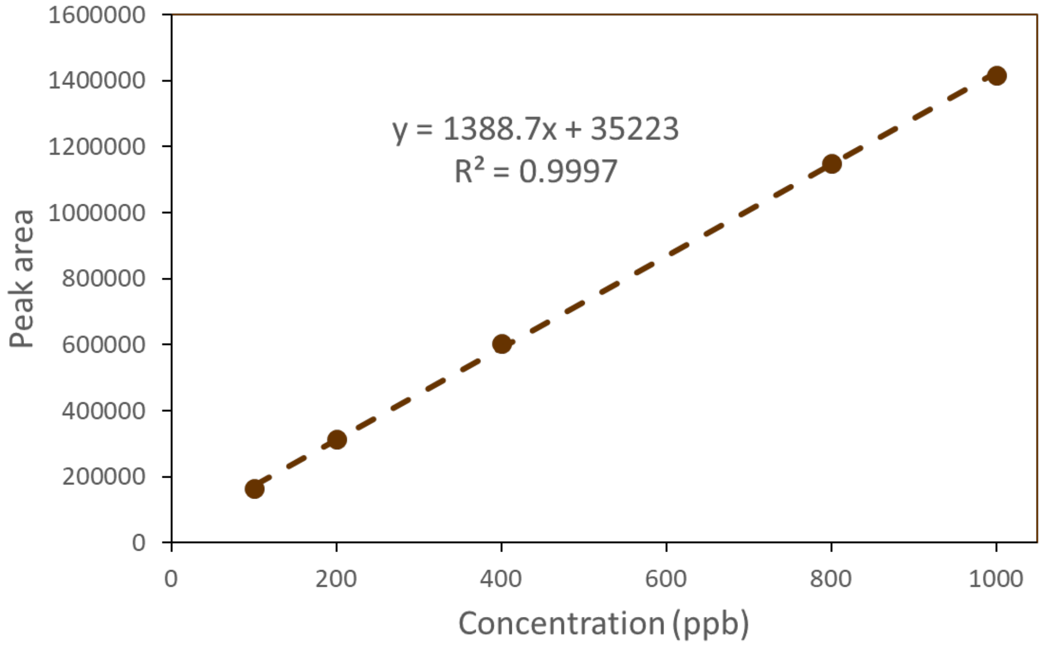
- Chronopotentiometry was used to apply a constant current



UPLCMSMS

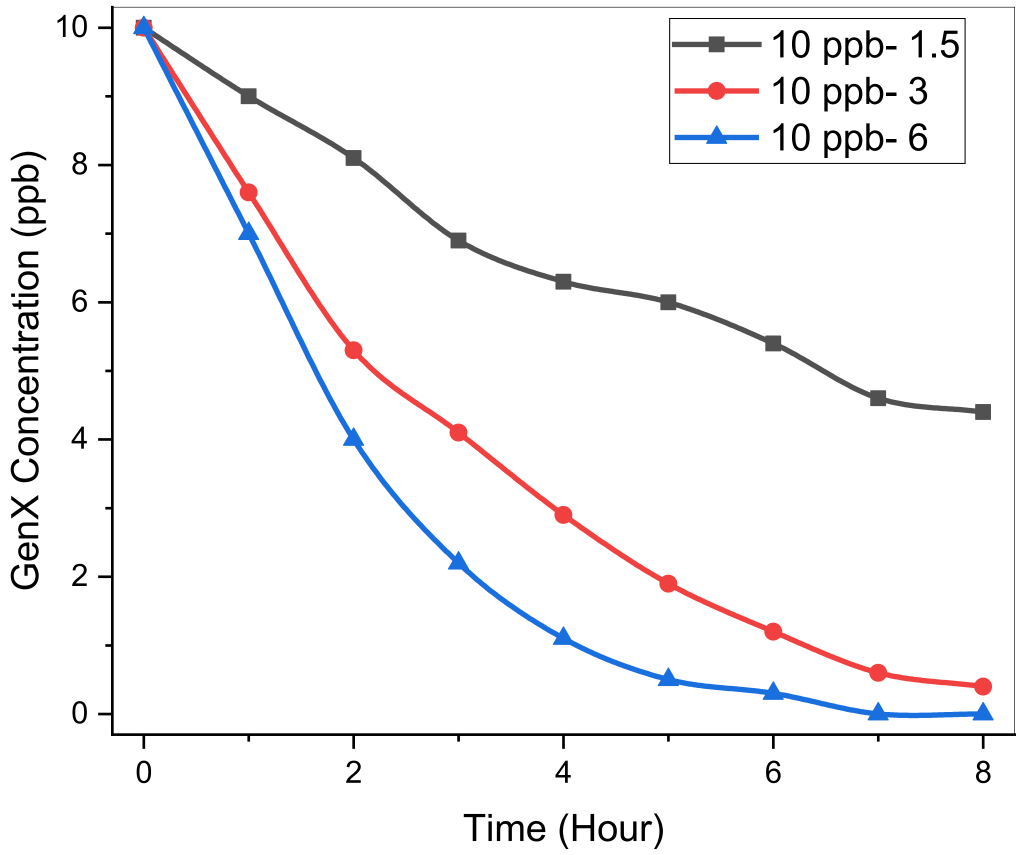
Shimadzu 8040 triple quadrupole mass spectrometer with an ESI source
Connected to a Shimadzu Nexera UPLC
C18 column, 2.1 x 50mm, with a 1.9 um particle size

Three mass analyzers in the instrument: Q1, Q2, and Q3
In Q1, isolate the intact ion of interest, so that it is the only thing that makes it through.
In Q2, fragment the ion into smaller pieces by colliding it with an inert gas; in this case, argon.
In Q3, isolate one of the resulting fragment ions, so that it is the only thing that makes it through.



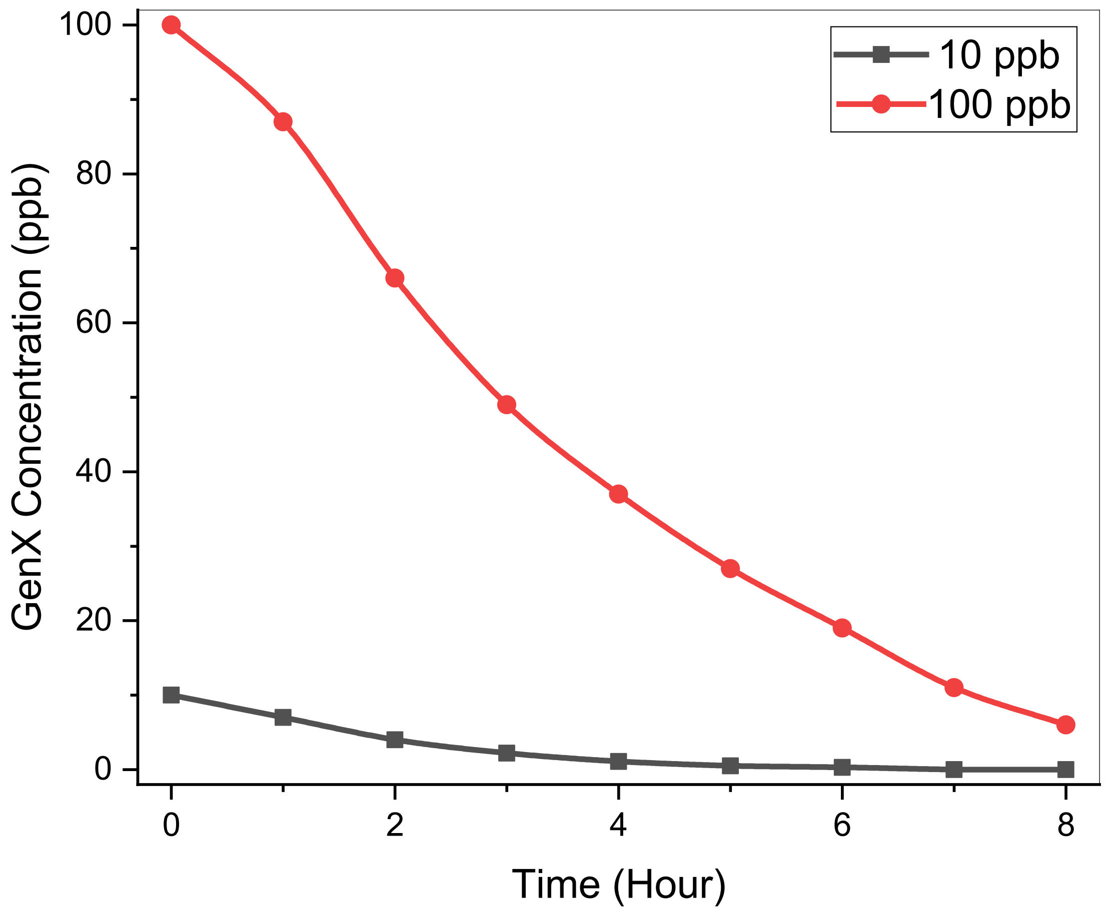
The Effect of Current Density on GenX Removal

- ➢ Initial GenX concentration 10 ppb
- ➢ Different current density: 1.5, 3, and 6 mA/cm^2
- ❖ Higher current density result in faster removal rate
- ❖ Almost 100% removal after 12 h for all current densities
- ❖ With 0.5 mA/cm^2 , no removal was detected



The Effect of Initial Concentration on GenX Removal

- ➢ Current density 6 mA/cm^2
- ➢ Different initial GenX concentration 10 and 100 ppb
- ❖ Almost 100% removal after 12 h for all concentrations



GenX Removal Results

The Effect of Initial Concentration on GenX Removal

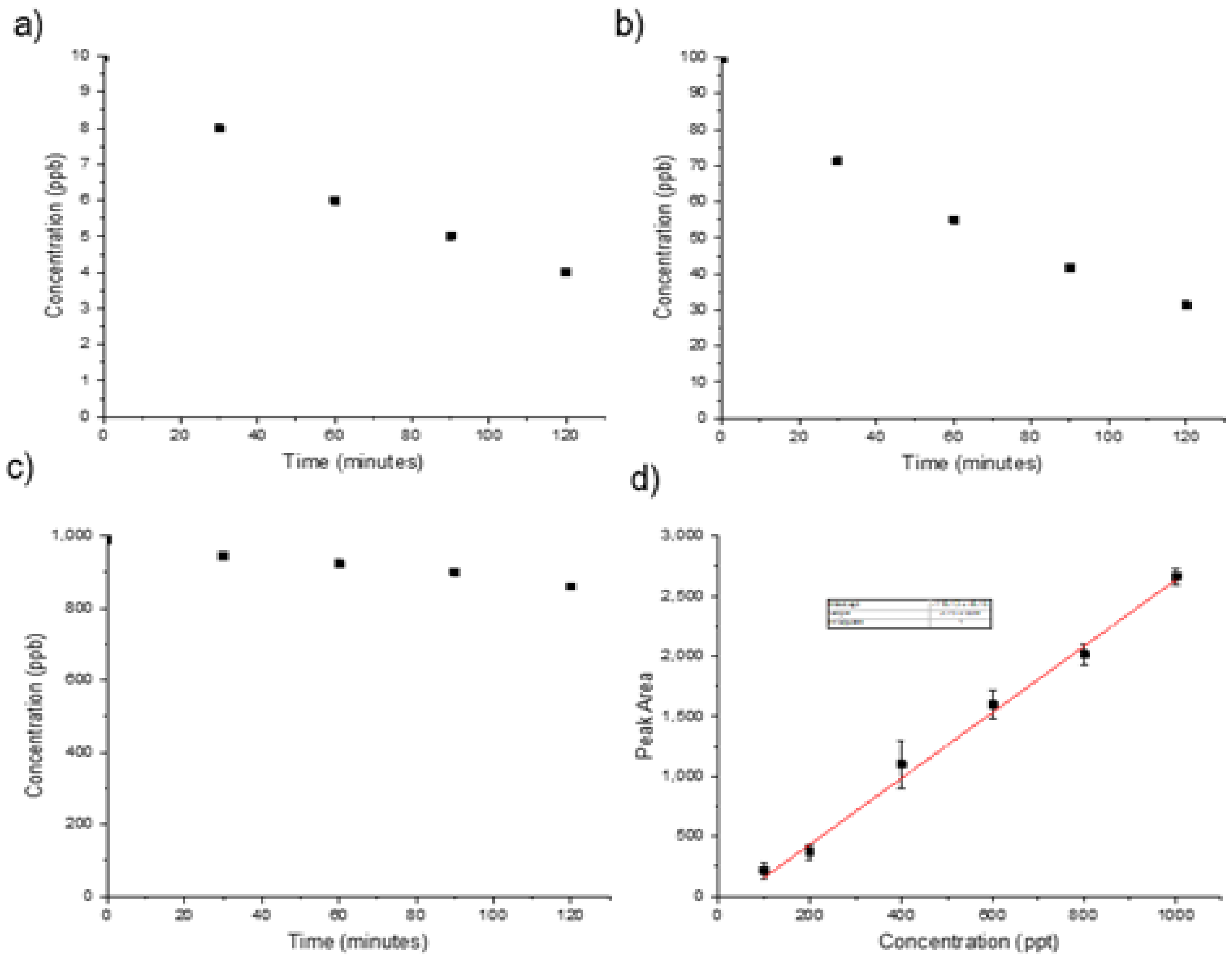
- ➢ Current density:
  15 mA/cm^2

- ➢ Different initial GenX concentration:
  10, 100, and 1000 ppb

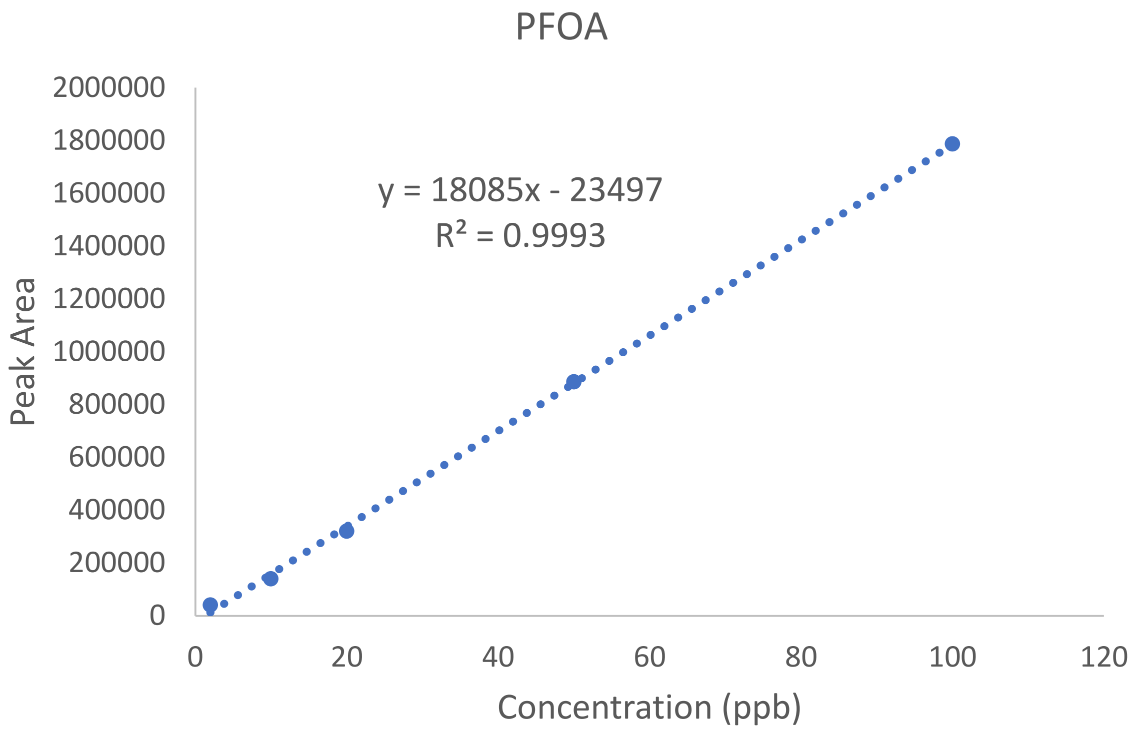
- ➢ Sampling:
  30-minutes intervals

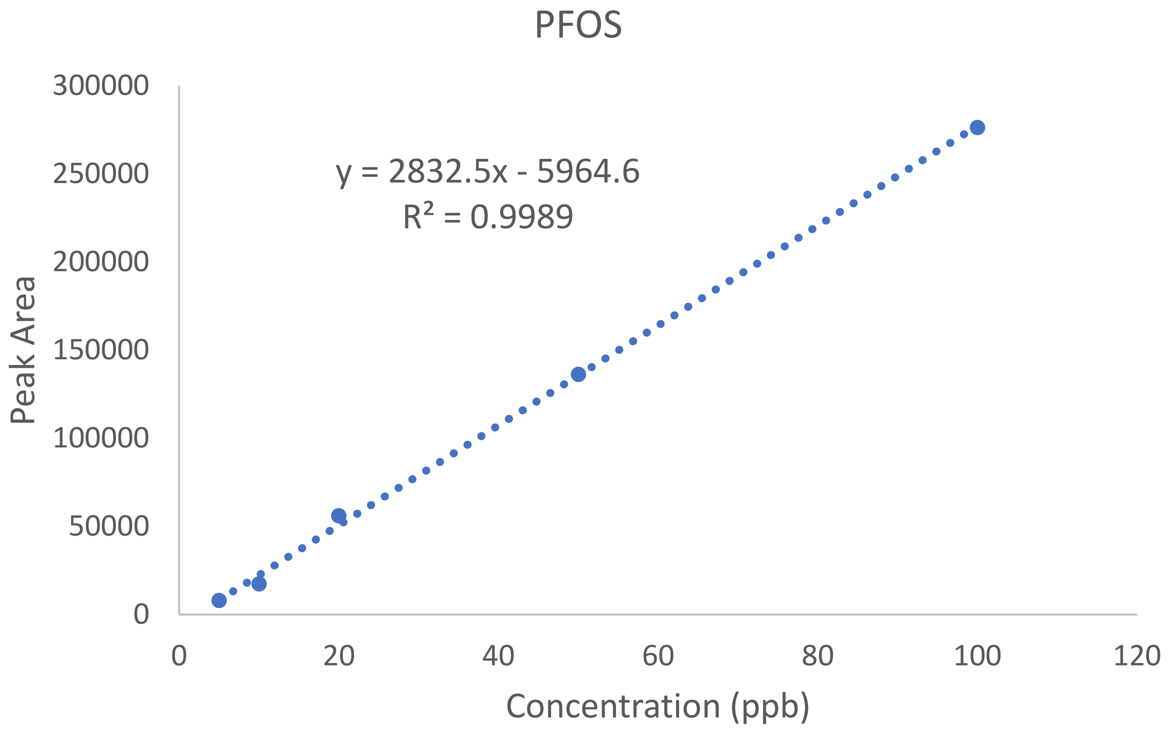
- ✓ For 100 ppb:
  Overall percent degradation of ~60% and ~70% respectively.

- ✓ For 1,000 ppb:
  Degradation of GenX slows down, resulting in ~13% degradation



PFOA and PFOS standard curves





Future Plans

- Modify the electrochemical cell setup to be able to capture gas phase samples and track degradation products
- Increase the efficiency
- Investigate the effect of pH, boron doping, natural organic matter, etc.