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Electrochemical Treatment of Perfluoroalkyl Acids in Ion Exchange Still Bottoms

Suzanne Witt, switt@fraunhofer.org

Fraunhofer USA Locations & Partner Universities

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- Automation
- Biomedical Manufacturing

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  East Lansing, Michigan
- Laser Applications
  Plymouth, Michigan

Center Mid-Atlantic CMA
- Software Systems Engineering
  Riverdale, Maryland
- Biotechnology
  Newark, Delaware
- South Carolina Alliance Office
  Columbia, South Carolina

Digital Media Technologies Office
San José, California

Headquarters
Plymouth, Michigan

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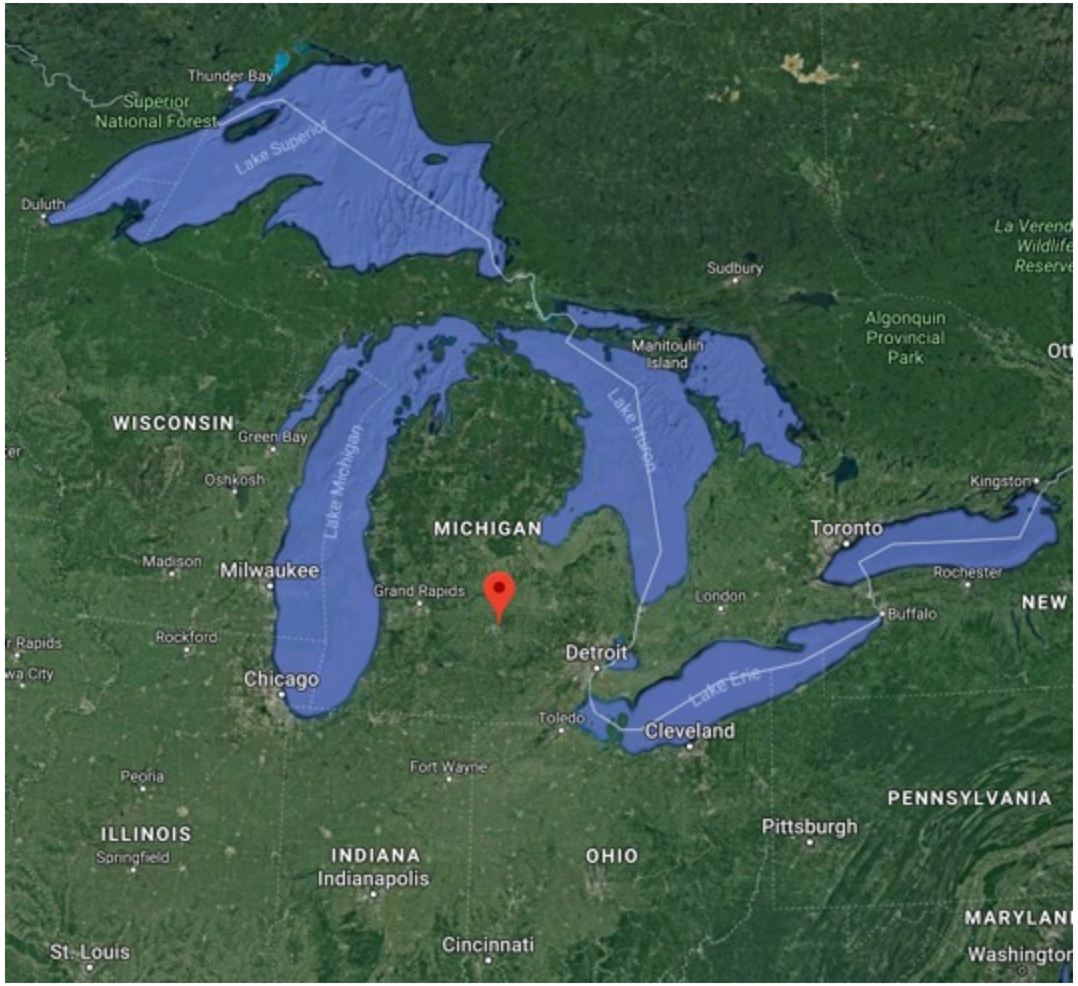
Location – East Lansing, Michigan



- Surrounded by 4 of the 5 Great Lakes
- ~20% of the worlds available fresh water
- Largest lake system by area (244.106 km^2)
- 3rd largest by volume (22.671 km^3)

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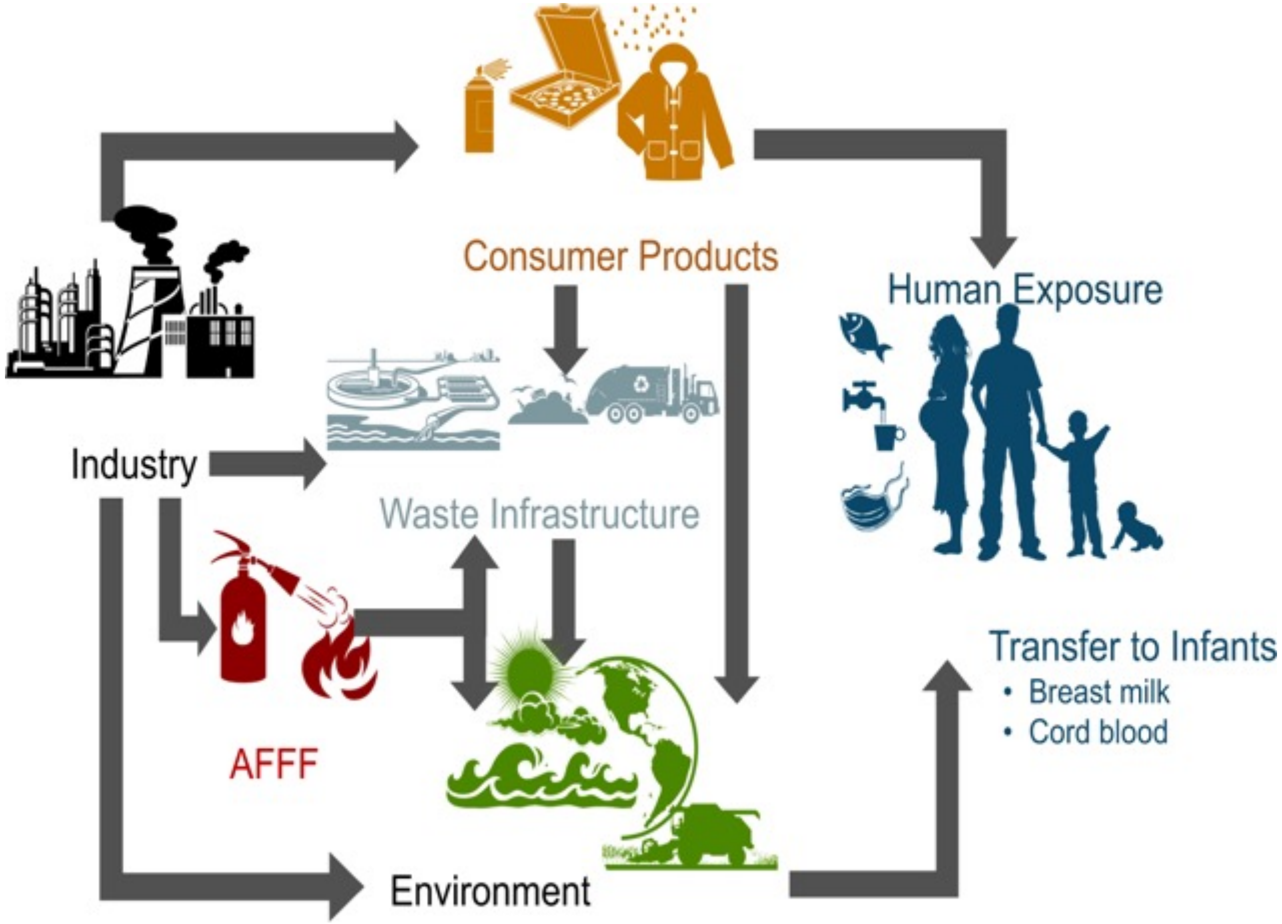
PFAS background



Sunderland et al. Journal of Exposure Science & Environmental Epidemiology 2019, 29, 131-147

- Regulations
  - USEPA Health Advisory Limit of **70 ppt** for PFOA and PFOS combined in drinking water
- Michigan drinking water regulations:
  - PFNA (6 ppt)
  - PFOA (8 ppt)
  - PFOS (16 ppt)
  - PFHxS (51 ppt)
  - GenX (370 ppt)
  - PFBS (420 ppt)
  - PFHxA (400,000 ppt)

Current remediation methods focus on filtration / adsorption

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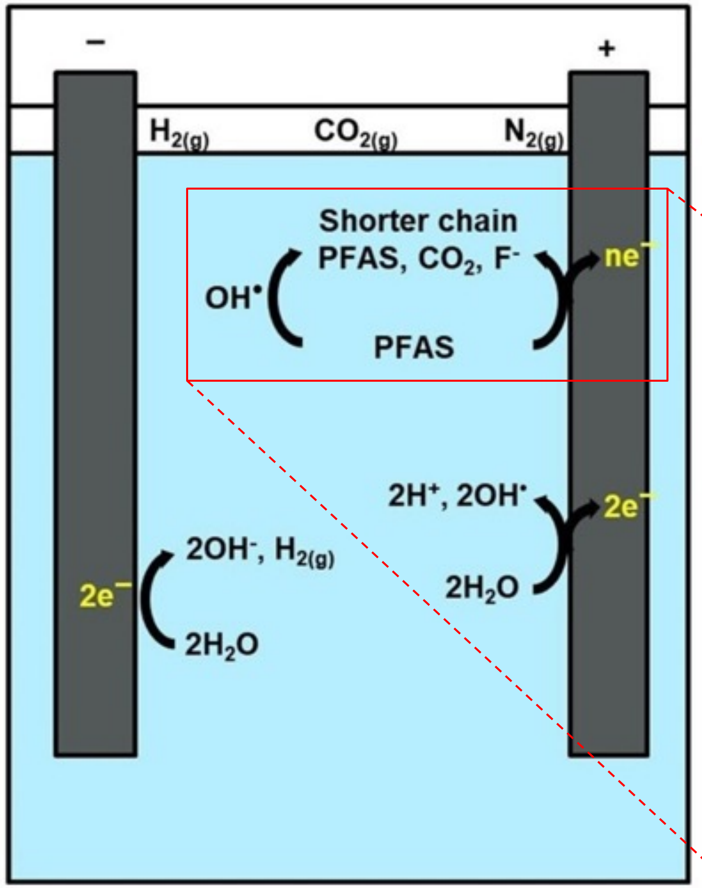
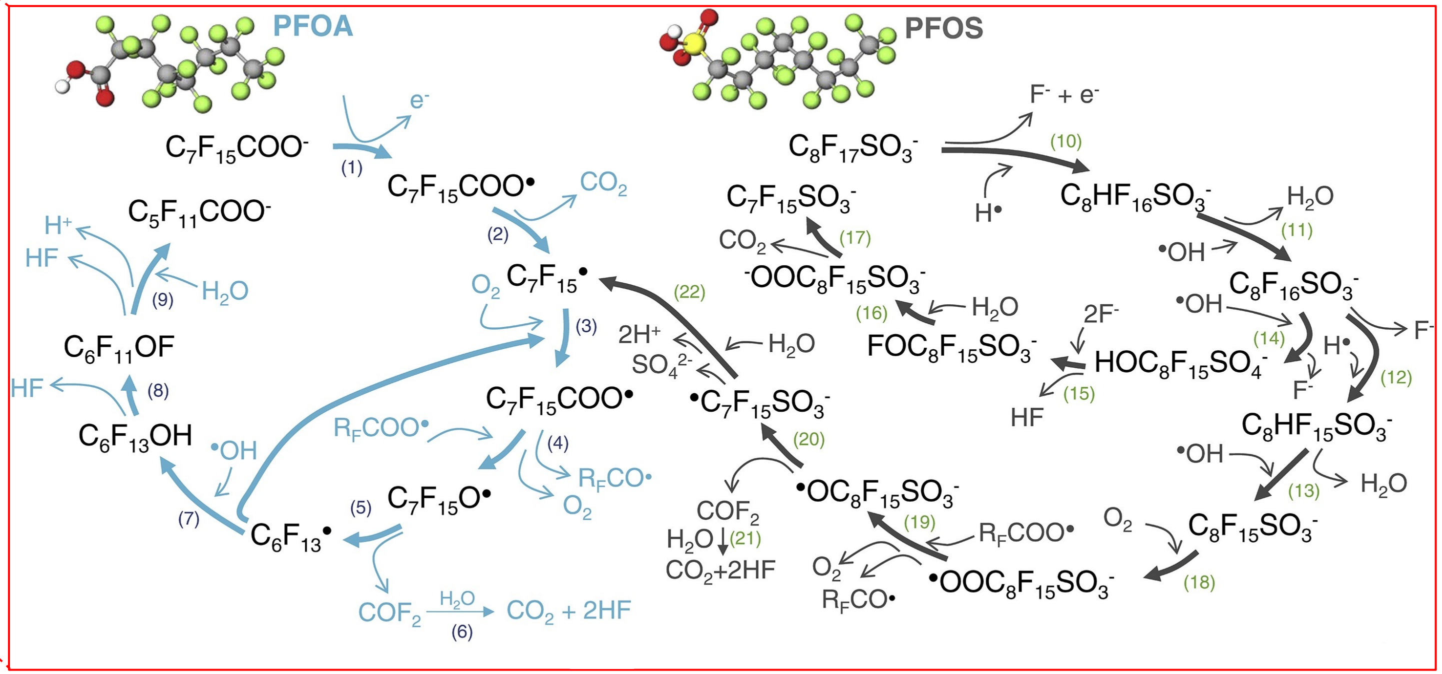
Electrochemical oxidation (EO) of PFAS

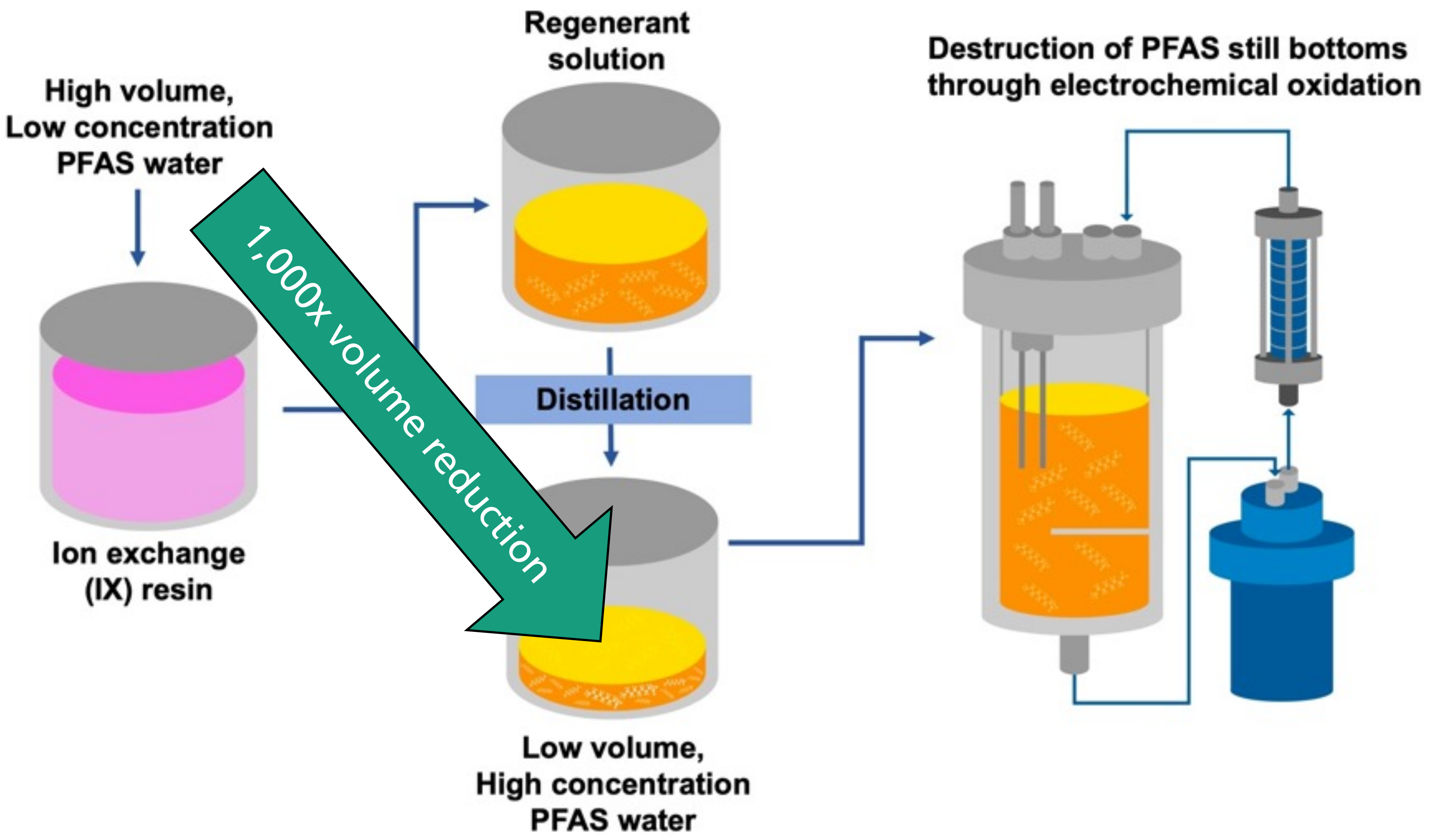


- Direct oxidation of analyte / contaminant at the electrode surface
- Generation of hydroxyl radicals (OH•) for indirect oxidation of analyte / contaminant in the bulk
- Electrode material = Boron doped diamond (BDD)



Pierpaoli et al., *J. Hazard. Mater.*, 2021, 403, 123606

Treatment of IX regenerate solutions (MTRAC†)

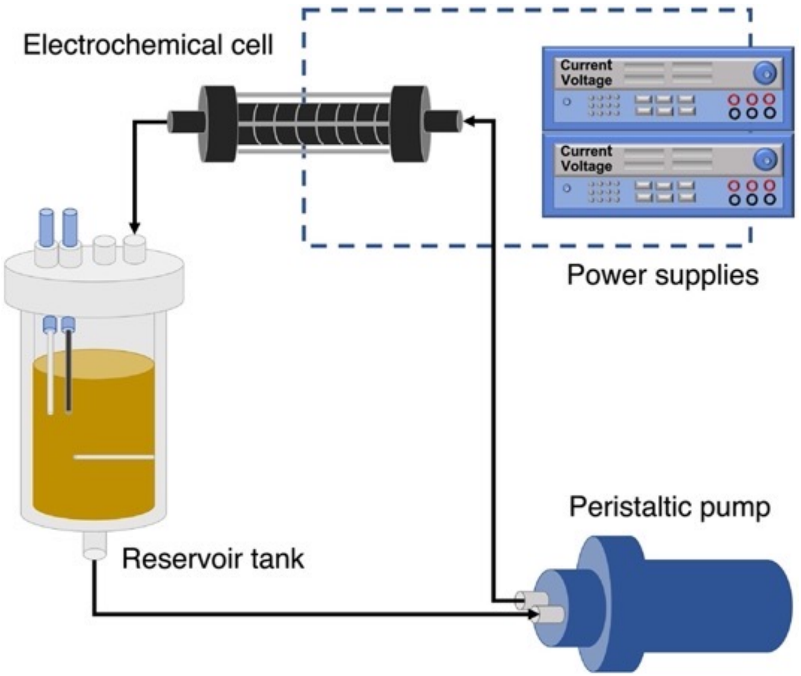


†Michigan Translational Research and Commercialization Innovation Hub for AgBio

Maldonado et al., *Water*, 2021, 13, 2873

BDD-based PFAS treatment systems

- Batch recirculation reactor systems
- Equipped with highly stable BDD electrode cells
- Built in-house with ability to scale up for higher treatment volumes



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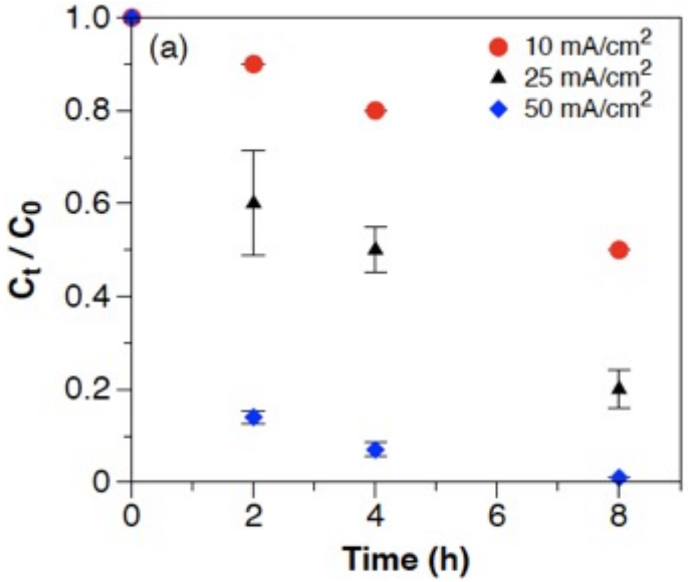
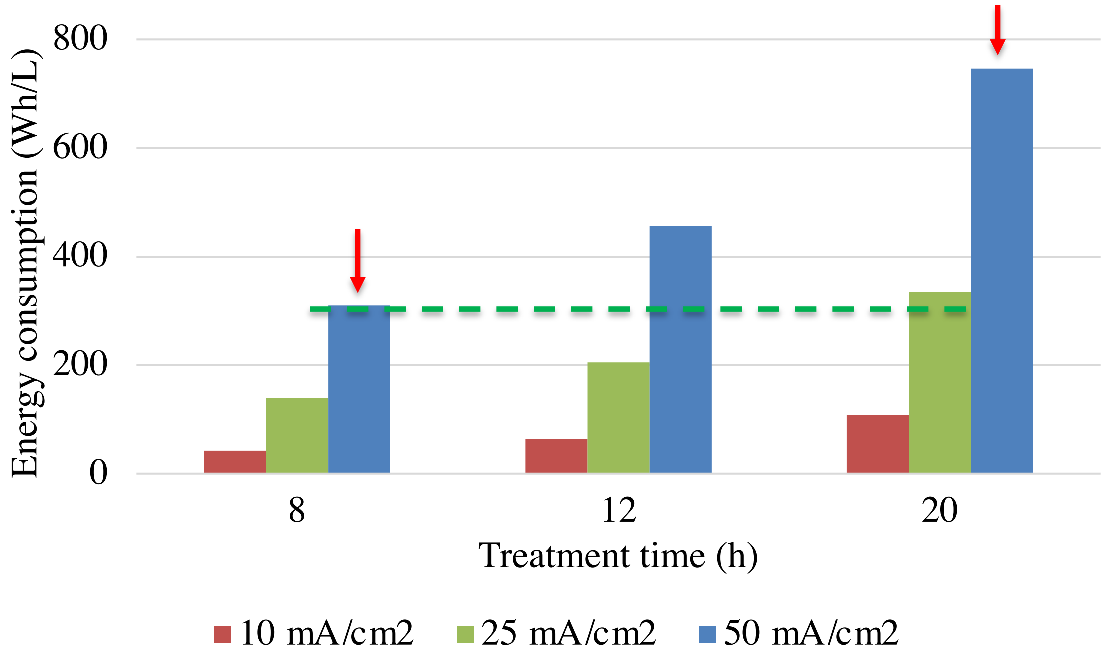
Maldonado et al., *J. Water Process Eng.*, 2021, 43, 102210

Treatment of IX solutions (MTRAC)

Synthetic still bottom solution composition

Compound	Value
pH	7.7
Conductivity (mS/cm)	110
PFBA (mg/L)	74
PFOA (mg/L)	86
PFHxS (mg/L)	87
PFOS (mg/L)	81
Chemguard C301 MS AFFF (%)	0.1
Chloride (mg/L)	41,670
Methanol (mg/L)	10,000
TOC (mg/L)	2400





- 50 mA/cm² led to the fastest total PFAS removal reaching >99% after 8h of treatment
- Extending the treatment with 50 mA/cm² only incrementally increased total PFAS removal

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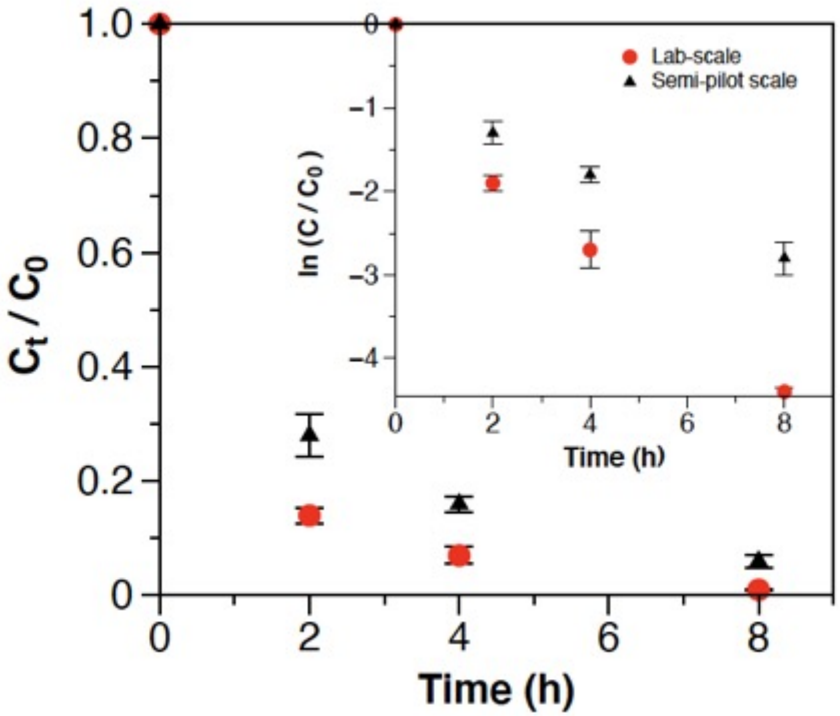
Maldonado et al., *Water*, 2021, 13, 2873

Lab scale *vs* semi-pilot scale treatment of synthetic IX solution



Lab scale: 2 L, ~200 cm^2 BDD anode area

Semi-pilot scale: 14 L, ~1400 cm^2 BDD anode area

Equivalent area/volume (A/V) ratio and current density (50 mA/cm^2)

- Lab scale: 99 % PFAA removal after 8 h
- Semi-pilot scale: 94 % PFAA removal after 8 h
- *Foam partitioning at both scales, but more significant at semi-pilot due to higher volume of gas generated*

To maintain current density at higher anode area, current must increase, therefore V_{gas} increases for semi-pilot scale

$V_{gas} = volume\ of\ gas\ (L)$

$I = current\ (A)$

$R = gas\ constant\ (0.08206\ L\ atm\ mole^{-1} K^{-1})$

$T = temperature\ (K)$

$t = treatment\ time\ (s)$

$n = moles\ of\ electrons$

$F = Faraday's\ constant\ (96485\ C\ mole^{-1})$

$P = pressure\ (atm)$

$$V_{gas} = \frac{IRTt}{nFP}$$

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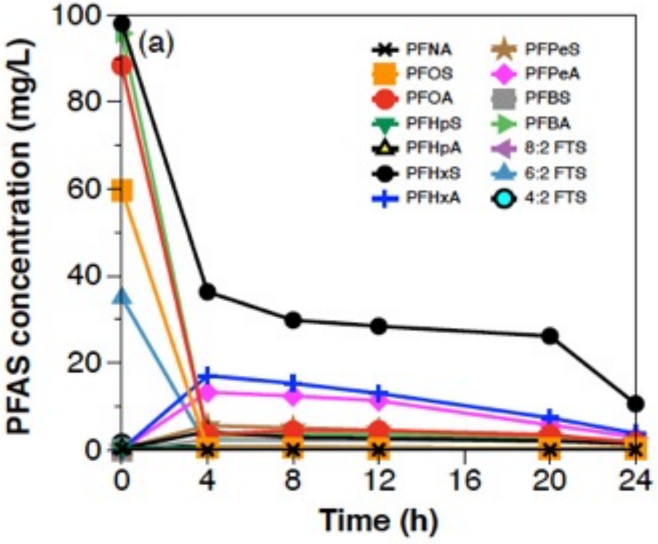
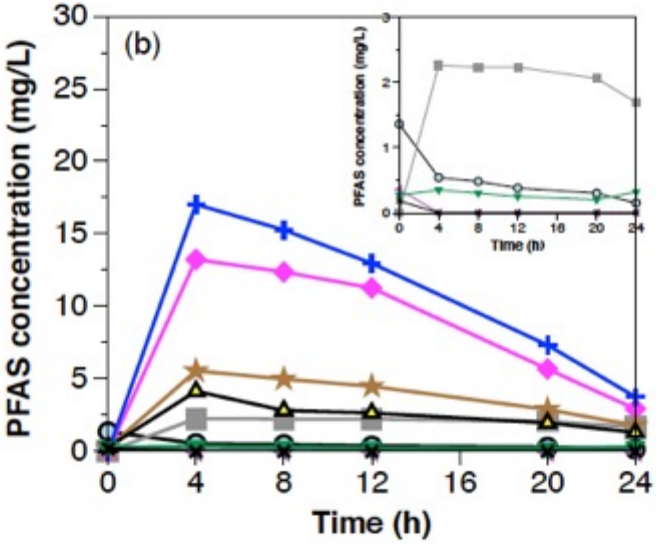
Maldonado et al., *Water*, 2021, 13, 2873

Lab scale treatment of real IX still bottom





Synthetic still bottom composition

Compound	Value
pH	7.7
Conductivity (mS/cm)	110
PFBA (mg/L)	74
PFOA (mg/L)	86
PFHxS (mg/L)	87
PFOS (mg/L)	81
Chemguard C301 MS AFFF (%)	0.1
Chloride (mg/L)	41,670
Methanol (mg/L)	10,000
TOC (mg/L)	2400

Real still bottom composition

Compound	Value
pH	9.7
Conductivity (mS/cm)	81.3
4:2 FTS (mg/L)	1.4
6:2 FTS (mg/L)	35.0
8:2 FTS (mg/L)	0.4
PFBA (mg/L)	95.8
PFPeS (mg/L)	0.3
PFHxS (mg/L)	98.0
PFHpA (mg/L)	0.3
PFHpS (mg/L)	0.3
PFOA (mg/L)	88.4
PFOS (mg/L)	59.3
Chloride (mg/L)	41,000
Methanol (mg/L)	28,000
TOC (mg/L)	14,050

- 93 % removal of PFAAs after 24 h treatment
- 3-fold slower degradation kinetics for PFAAs compared to synthetic solution
- Attributed to nearly 6x higher TOC content in real solution

Maldonado et al., *Water*, 2021, 13, 2873

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Energy consumption for treating IX still bottoms

$$E_{EO} = \frac{Pt}{V\, log(C/C_0)}$$

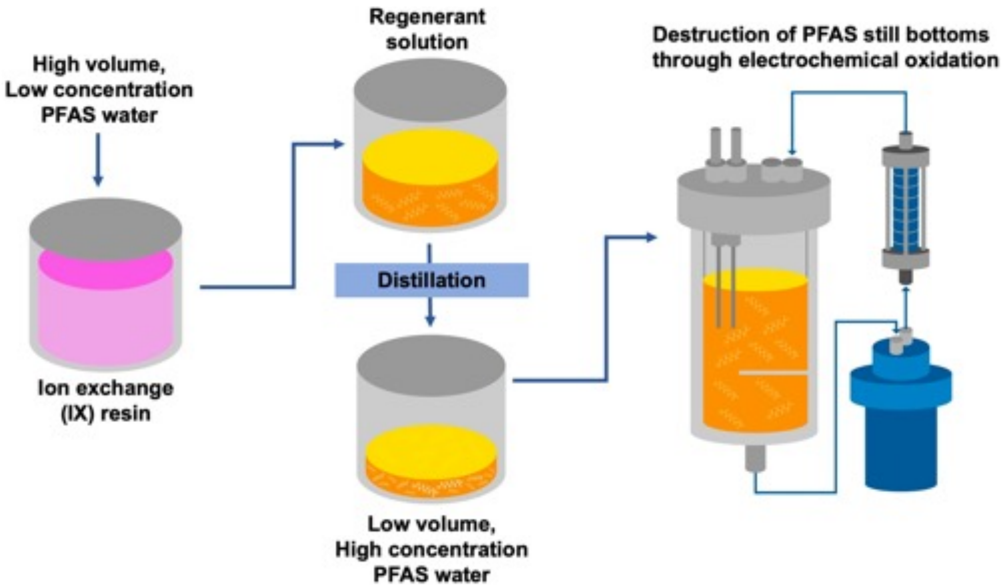
$E_{EO} = electric\ energy\ per\ order$

$P = power\ (W)$

$V = treatment\ volume\ (L)$

$t = treatment\ time\ (h)$

$C/C_0 = final\ PFAA\ concentration / initial\ PFAA\ concentration$



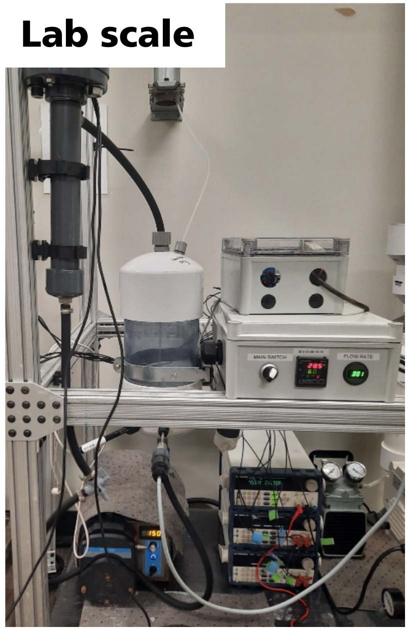
- E_{EO} for 90 % PFAA removal at lab and semi-pilot scales was 173 and 194 Wh/L, respectively
- IX still bottoms account for < 0.01% of total water pre-treated with IX resins
- *Therefore, pre-concentration with IX before electrochemical oxidation reduces energy consumption by > 99.9 % when compared to electrochemical treatment alone*

Maldonado et al., *Water*, 2021, 13, 2873

Summary of IX project

- Pre-treatment with IX is a viable way to decrease energy consumption during electrochemical degradation by drastically reducing solution volume
- High background TOC levels in IX still bottoms can decrease EO efficiency
- Increased foaming needs to be considered when scaling up systems to treat highly concentrated solutions

Lab scale



Semi-pilot scale

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- Michael Nickelsen

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