DEGRADATION OF PFAS BY ELECTROCHEMICAL OXIDATION

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"forever chemicals"

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- **Introduction**
- **Materials & Methods**
- **Results**
- **Conclusion**

Introduction | PFAS Sources | EO Process | Objectives

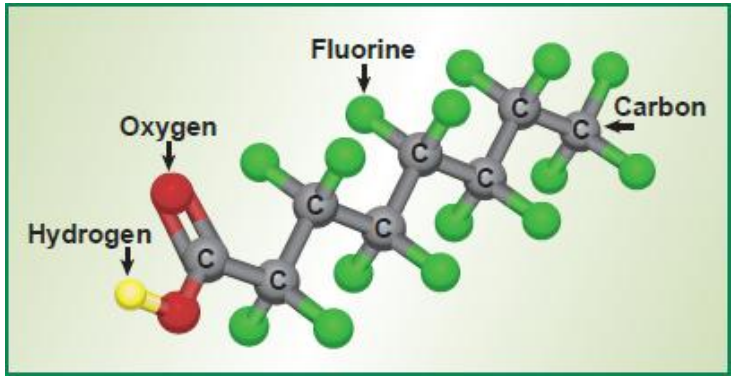
Per- and polyfluoroalkyl substances (PFAS) are anthropogenic fluorinated hydrocarbons (> 4,700 known PFAS chemicals were identified)

Technical properties: Thermal Stability, Surface activity, Chemical resistance

Applications: Industrial, medical and domestic uses

Benefit: Make products more resistant to stains, grease, and water

Exposure route: Food, soil, drinking water



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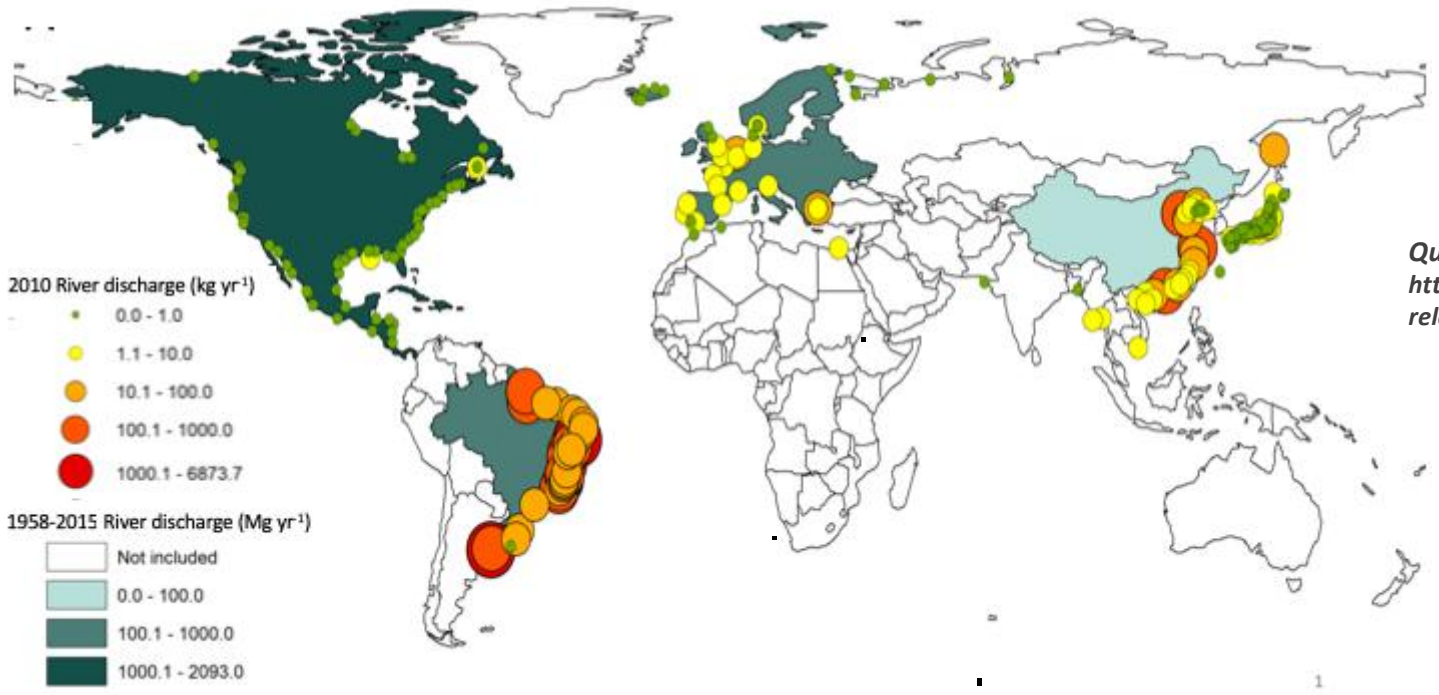


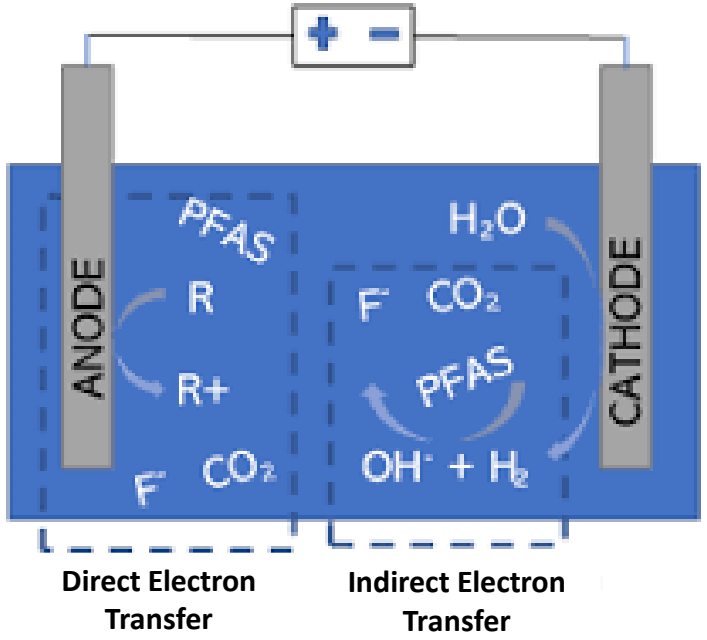
Quantifying global PFOS releases from rivers
https://scholar.harvard.edu/ccwagner/quantifying-global-pfos-releases%C2%A0-rivers

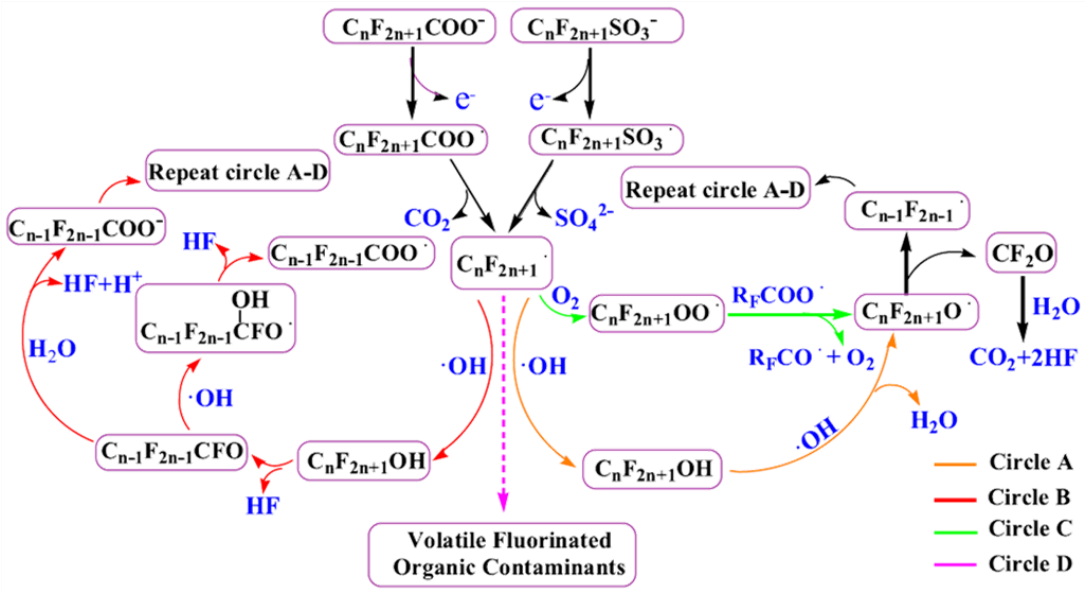
Widespread occurrence: PFAS are found in blood and urine

Health Effects: Cancer, liver damage, decreased fertility, thyroid disease, etc.

Persistent: PFAS remain in the environment for an unknown length of time and take many years to leave the body due to more PFAS being absorbed than eliminated (NIH).

Electrochemical Anodic Oxidation (EO)





Proposed pathways for electrochemical oxidation of PFCs in water
Lin et al., 2012, 2013; Niu et al., 2012, 2013; Zhuo et al., 2012, 2014

- Development of efficient decomposition technologies of PFAS in solution remains a challenge.

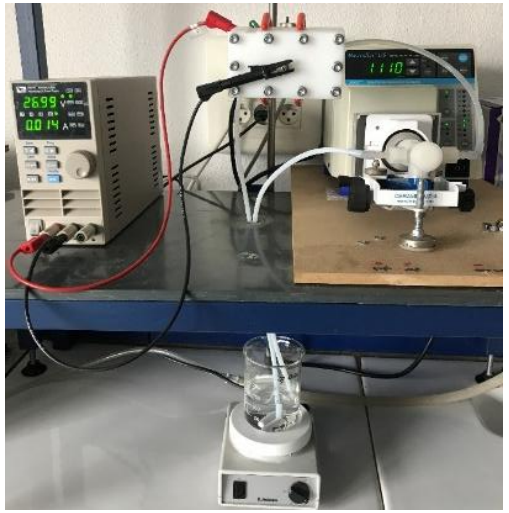
Introduction |

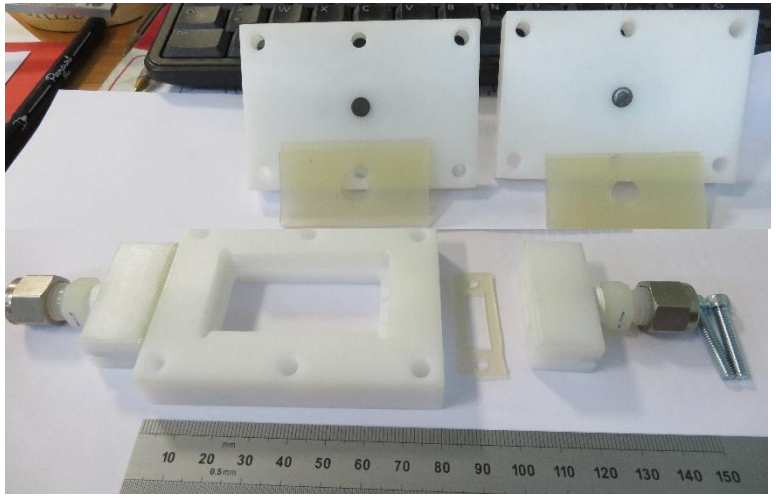
1
- Investigate the oxidative removal of PFAS at low concentration (µg/L), using Boron Dopped Damond (BDD) electrodes
- Study the effectiveness of different types of BDD electrodes (flat and wire mesh)
- Identify the by-products formed during degradation and study the molar balance

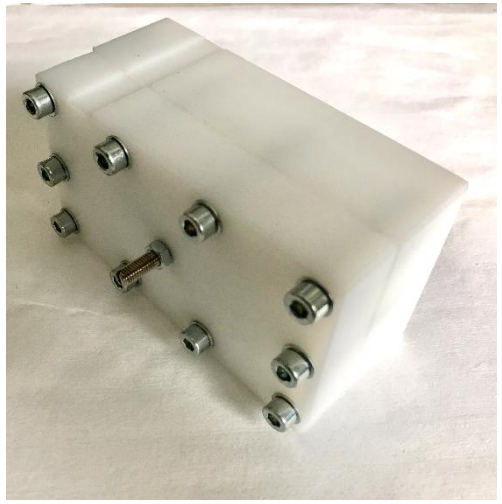
2 Impact of the Natural Organic Matter (NOM) on the degradation of PFAS

3 Impact of the electrolyte composition on the degradation of PFAS

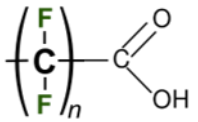
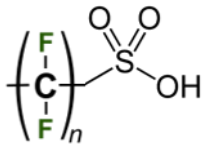
- Closed rectangular reactor containing two electrodes
- Beaker containing 200 mL target solution
- Pump with a constant flow
- DC power supply unit to supply electricity at constant current
- Magnetic stirrer at constant speed
- <u>Electrodes</u>:
  - *Type (anode & cathode):* BDD
  - *Dimension*: 5 cm X 2.5 cm
  - *Surface*: 12.5 cm^2





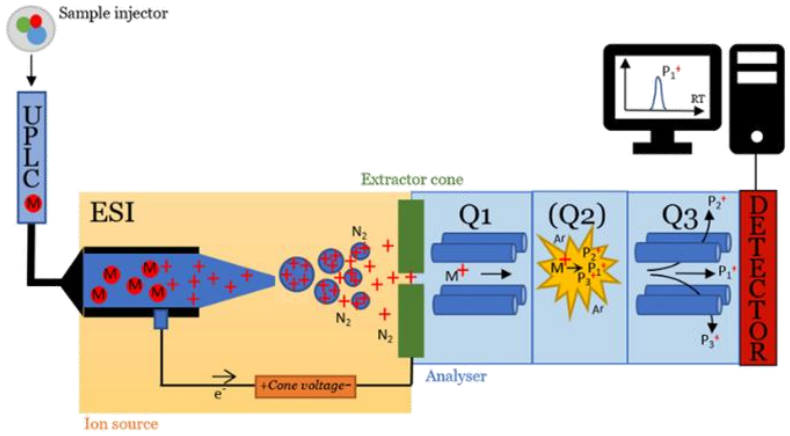


- **Chemicals**

Compounds		Abbreviation	Name of the molecule	Chemical Formula
Perfluorinated compounds	Perfluoro alkyls Carboxylates (PFCA)	PFBA – C4	Perfluobutanoic acid	 n=3-8
		PFPeA – C5	Perfluopentanoic acid	
		PFHxA – C6	Perfluohexanoic acid	
		PFHpA – C7	Perfluoheptanoic acid	
		PFOA – C8	Perfluooctanoic acid	
		PFNA – C9	Perfluorononanoic acid	
	Perfluoro alkyls Sulfonates (PFSA)	PFBS – C4S	Perfluorobutane sulfonic acid	 n=4,6,8
		PFHxS – C6S	Perfluorohexane sulfonic acid	
		PFOS – C8S	Perfluorooctane sulfonic acid	

- **Analytical Methods**

Measured compounds	Analytical Methods
PFAS compounds	**LC/MS/MS**
Fluorine Ion	Ion Chromatography **IC**



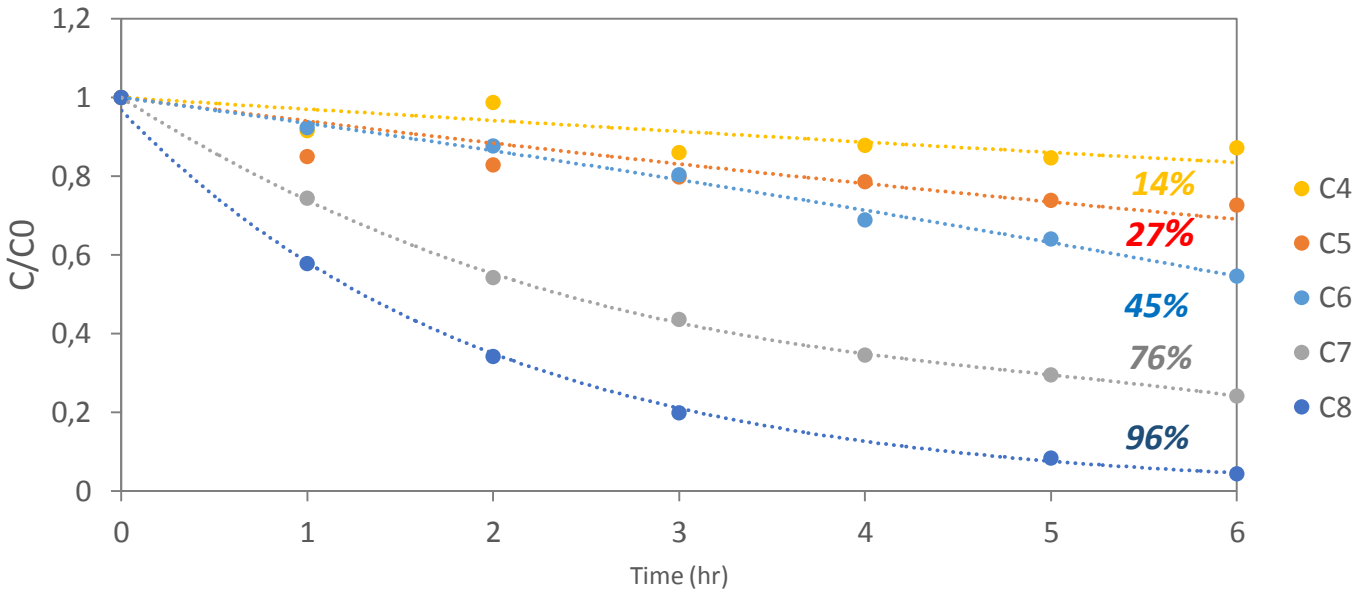
Results

1 Investigate the oxidative removal of PFAS of low concentration (µg/L)

- Effect of chain length on degradation of Perfluorocarboxylic acids (PFCA)

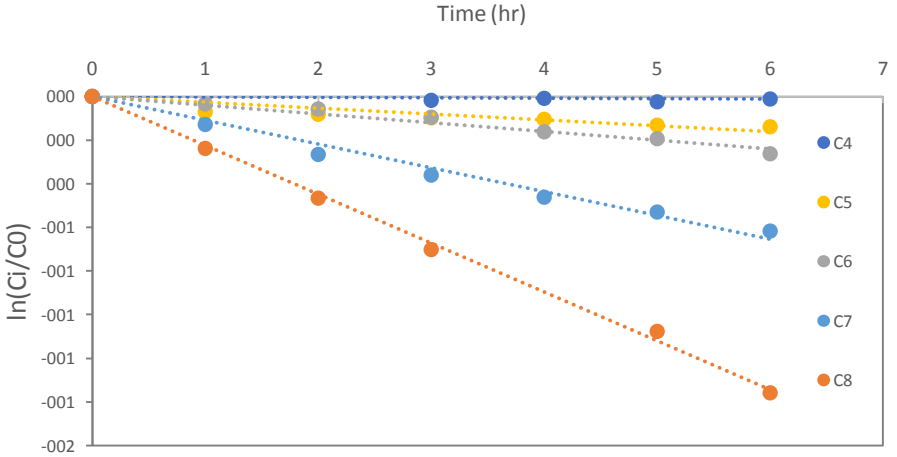
Experimental Conditions:

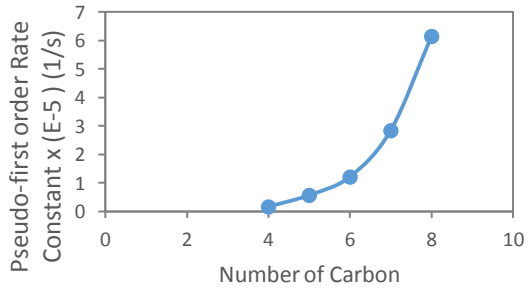
*PFCA **individually***
[PFCA]: 0.64 µM each
(C4 – C8: 137 – 265 µg/L)
Current Density: 8 mA/cm²
Voltage: 20-25 V
Electrolyte: 10 mM Na_2SO_4, pH=6



Observation:

- Electro oxidation rate increased with increasing chain length
- Water solubility decreases and hydrophobicity increases with increasing chain length of PFCA
- Pseudo-first order rate constants increased with increasing chain length





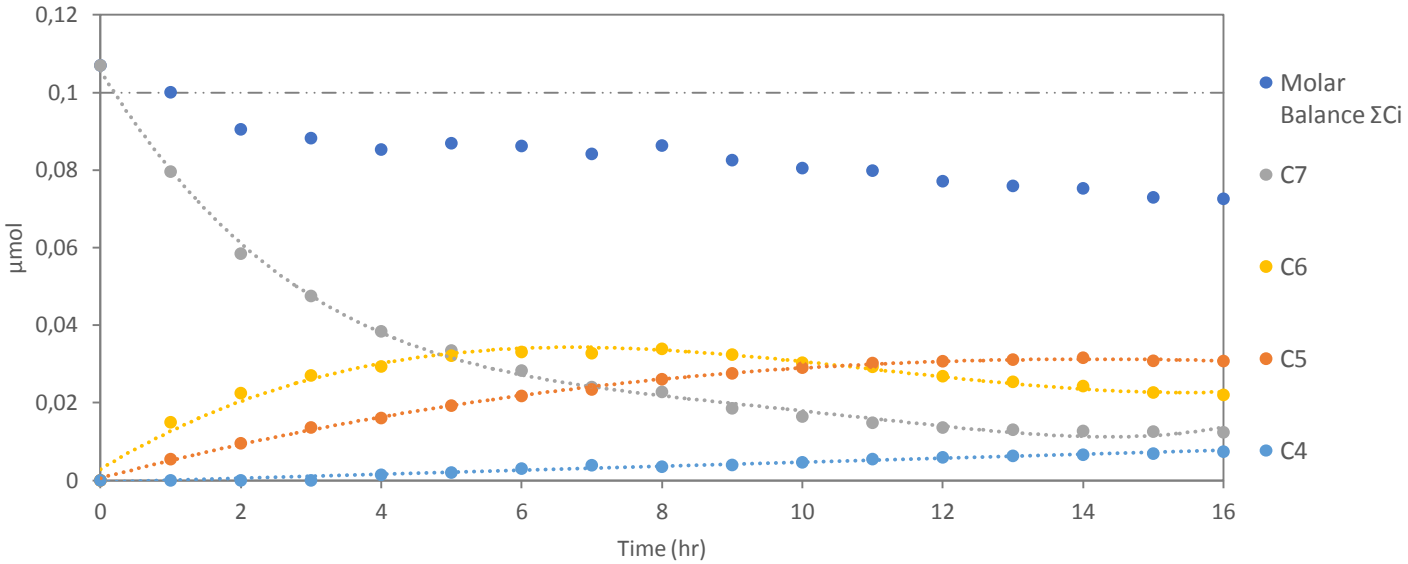
Results

1 Investigate the oxidative removal of PFAS at low concentration (µg/L)

- Decomposition of PFHpA-C7 and formation of by-products

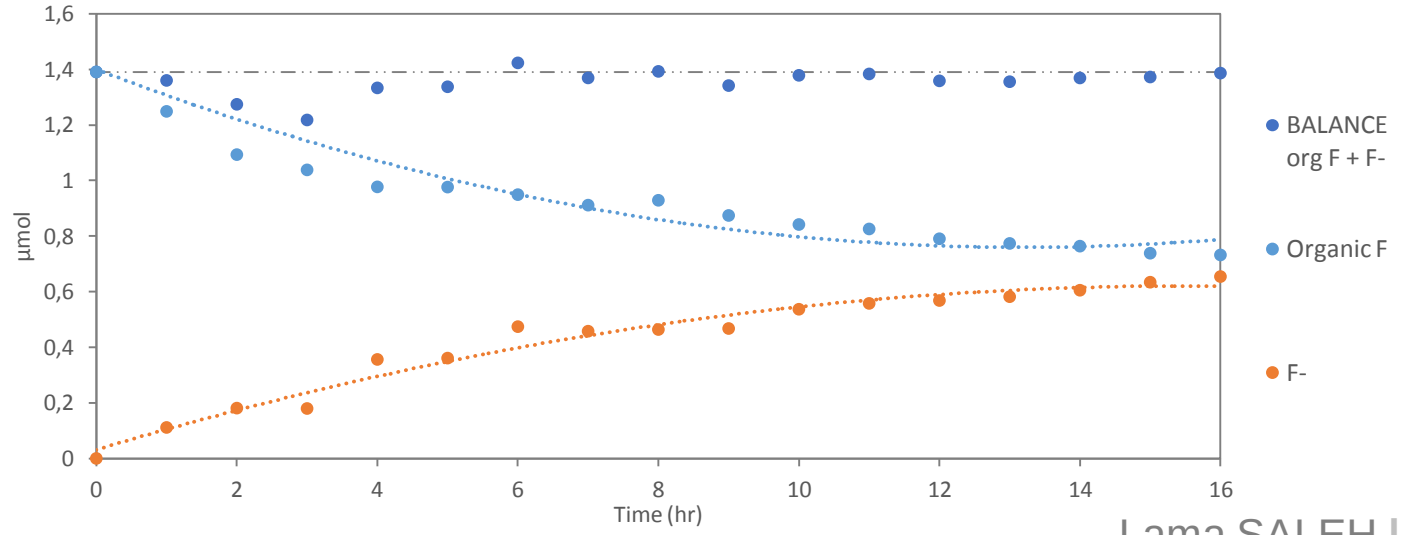
Experimental Conditions:

PFHpA-C7 ***individually***
[PFCA]: 0.64µM (233 µg/L)
Current Density: 8 mA/cm²
Voltage: 20-25 V
Electrolyte: 10 mM Na_2SO_4 , pH=6



Observation:

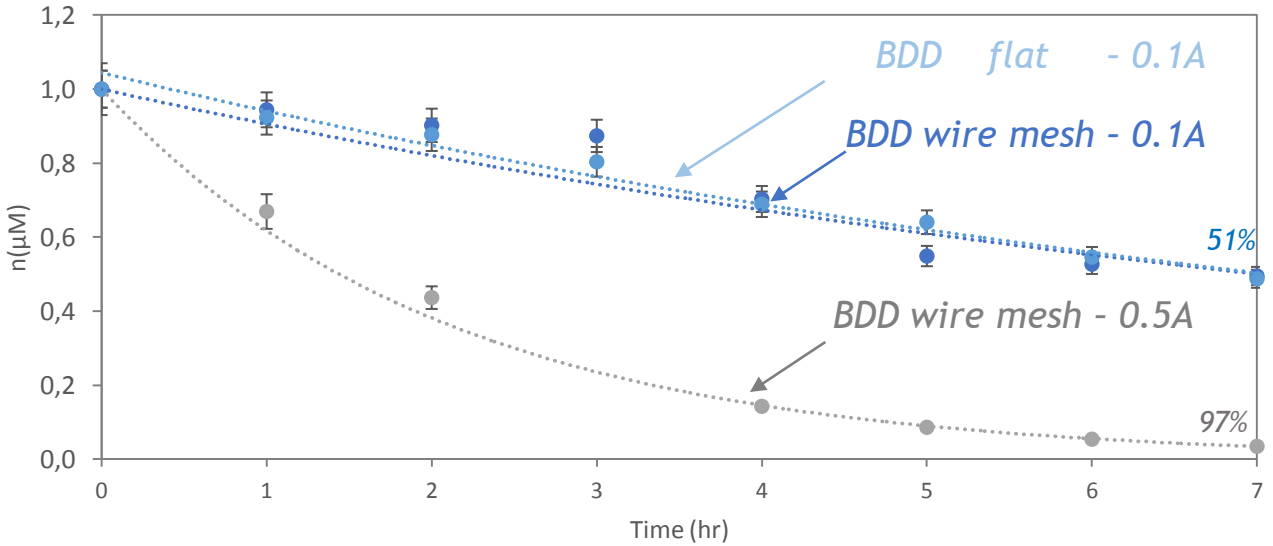
- C7 is transformed to C6, C5, and C4.
- Ultra short-chain (C2 and C3) may be formed
- 100% molar balance in terms of Fluoride



Results

1 Investigate the oxidative removal of PFAS at low concentration (µg/L)

- Study the effectiveness of different types of BDD electrodes (flat and wire mesh)



Experimental Conditions:

PFHxA-C6 ***individually***
[PFCA]: 0.64µM (200 µg/L)
Electrolyte: 10 mM Na_2SO_4 , pH=6

Observation:

- BDD wire mesh needs less voltage than BDD flat to apply the same current density
- BDD wire mesh supports high current density

Type of BDD	*Current Density (A)*	*Voltage (V)*
flat	***0.1***	***20-25***
Wire mesh	***0.1***	***6-8***
Wire mesh	***0.5***	***15-17***

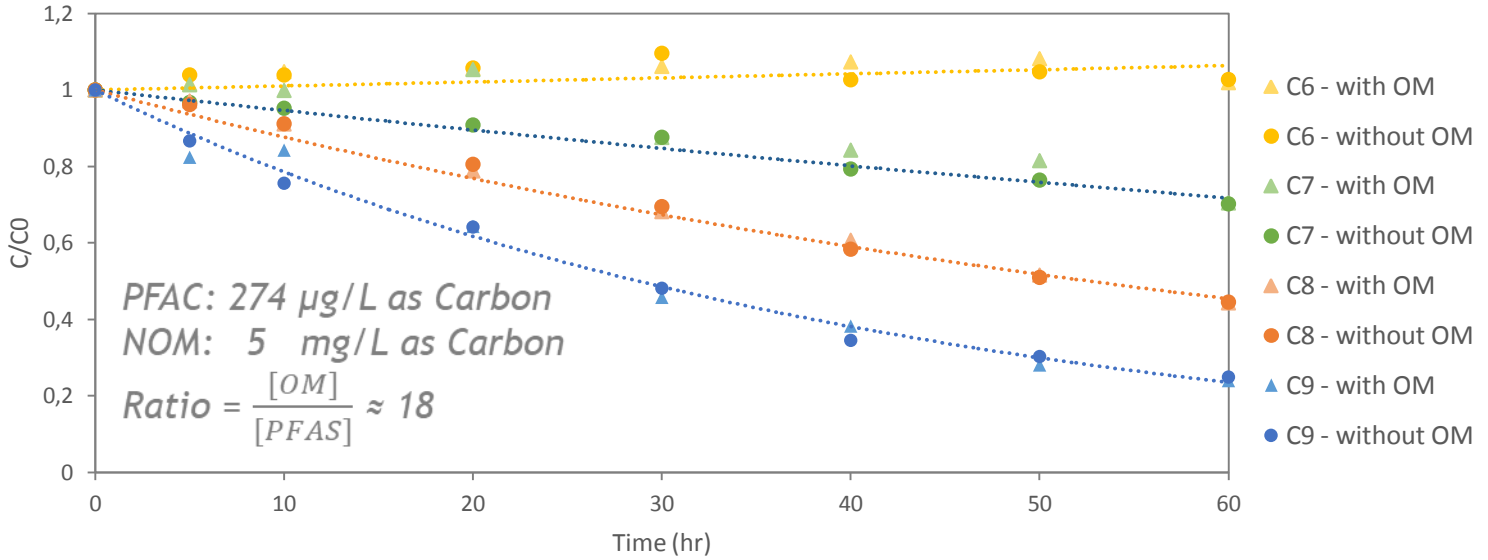
2 Impact of the natural organic matter on the degradation of PFAS

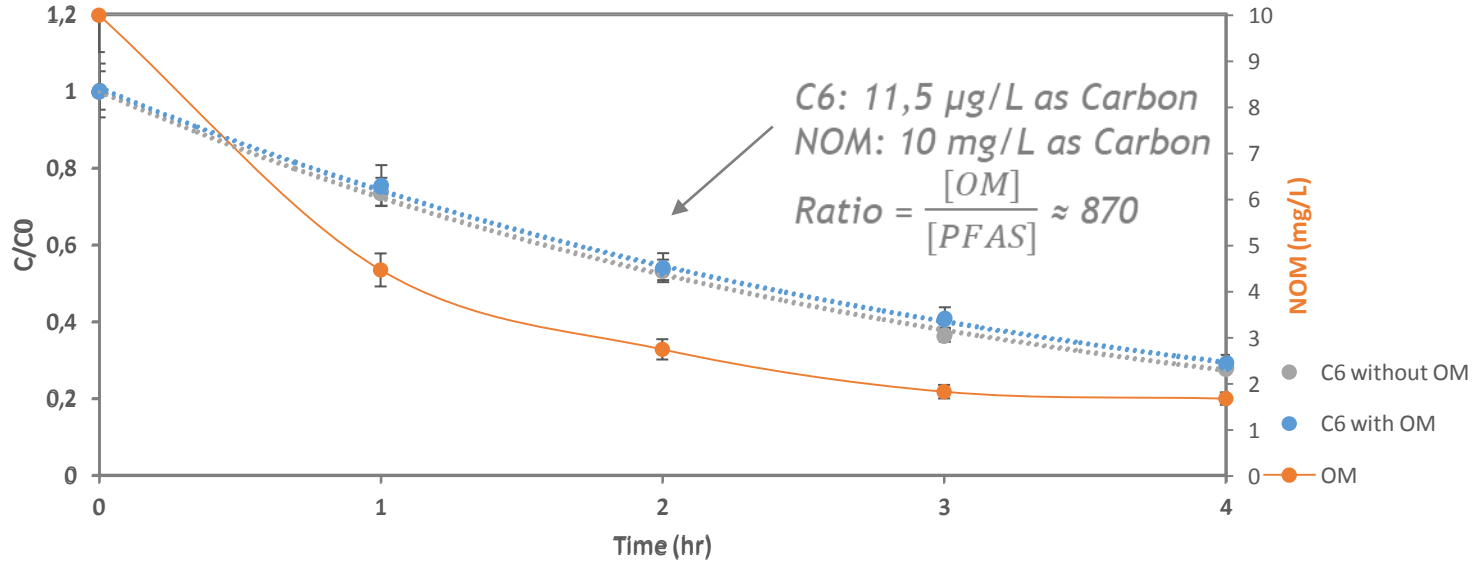
*Extracted Humic Substances – SUVA ≈ 5 L/(m*mg)*

Experimental Conditions:

*PFCA **in mixture***
[PFHxA]: 200 µg/L each
Current Density: 8 mA/cm²
Voltage: 20-25 V
Electrolyte: 10 mM Na_2SO_4 , pH=6

*PFHxA-C6 **individually***
[PFHxA]: 50 µg/L
Current: 0,5A
Voltage: 15-17 V
Electrolyte: 10 mM Na_2SO_4 , pH=6

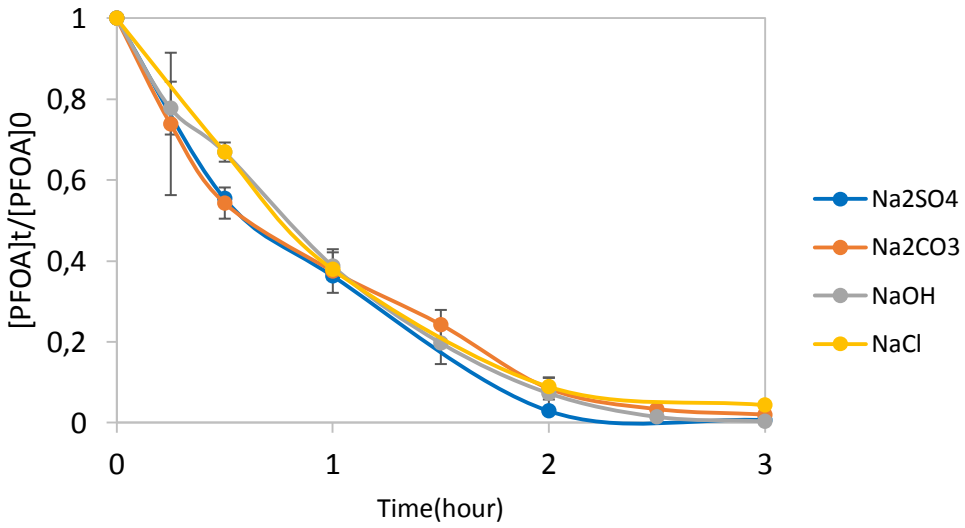


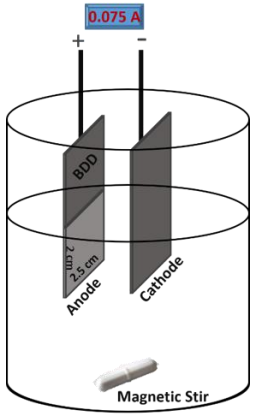


- No effect of NOM on the degradation of PFAS
- (Impact of NOM character under study)

3 Impact of the electrolyte composition on the degradation of PFAS

Anion: Sulfate Vs Carbonate Vs Hydroxide Vs Chloride



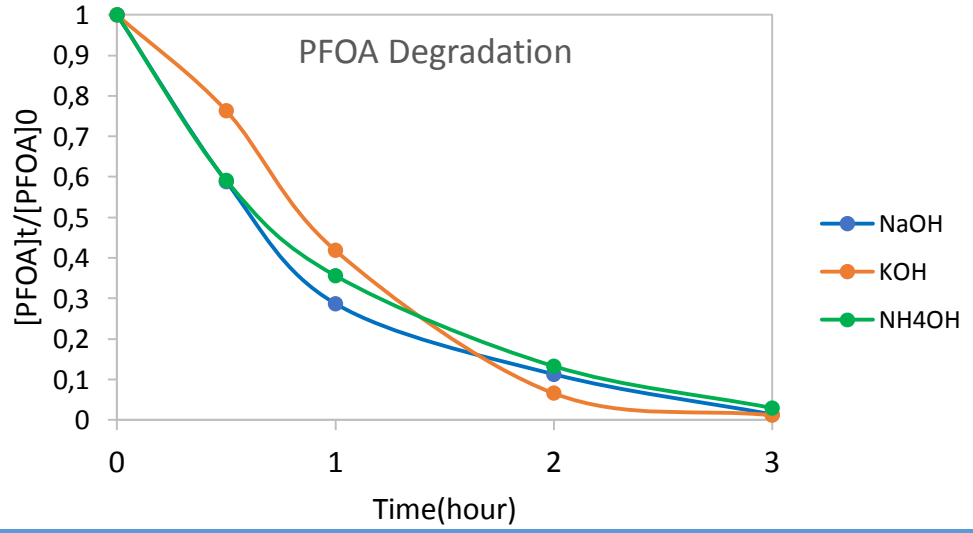


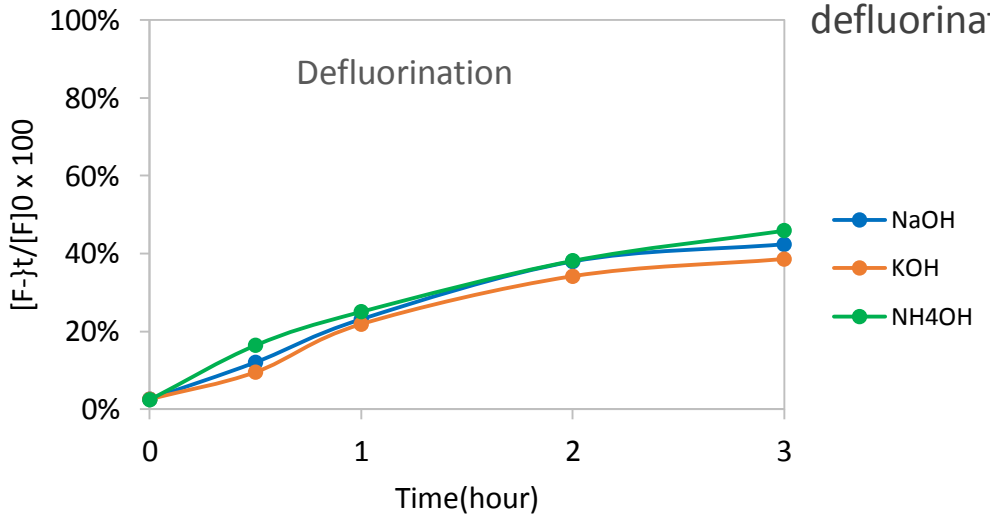
Experimental Conditions:

PFOA (C8) 1 mg/L
[Electrolyte]: 50 mM
pH=12
Surface Area: 5 cm²
Current Density = 15 mA/cm2

No impact of the type of cation or anion in the electrolyte solution on the degradation and defluorination of PFOA

Cation: Sodium Vs Potassium Vs Ammonium

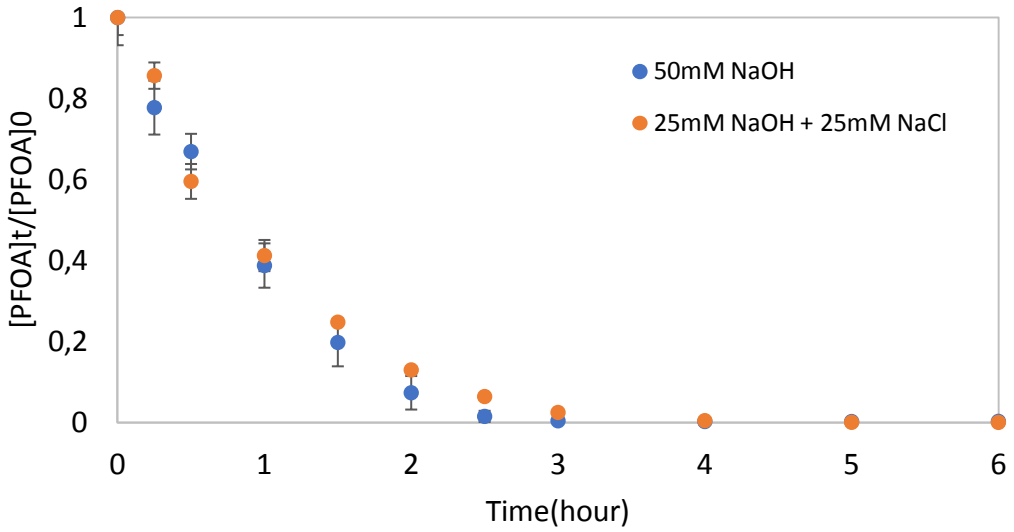


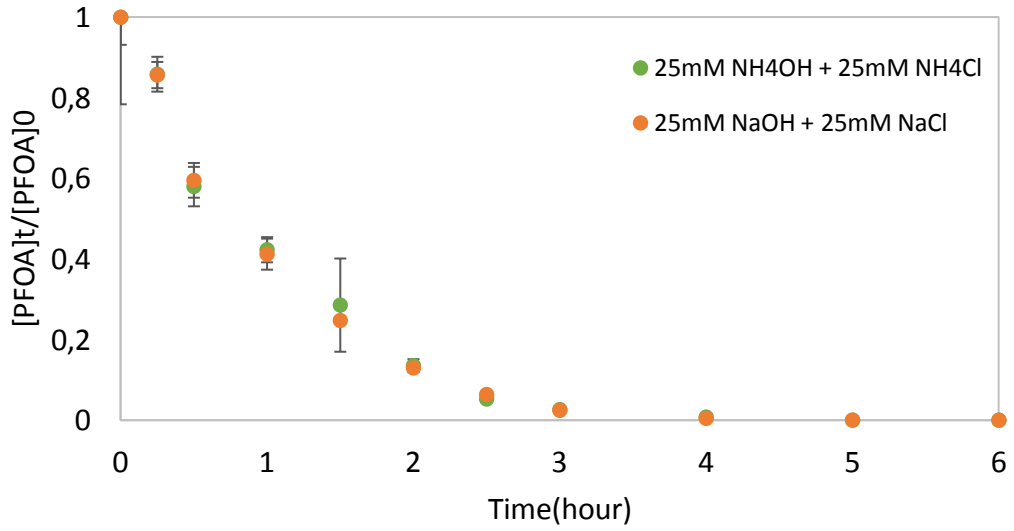


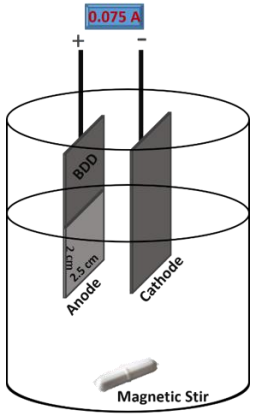
Results

3 Impact of the electrolyte composition on the degradation of PFAS

NaOH Vs **NaOH+NaCl** Vs **NH_4OH+ NH_4Cl**







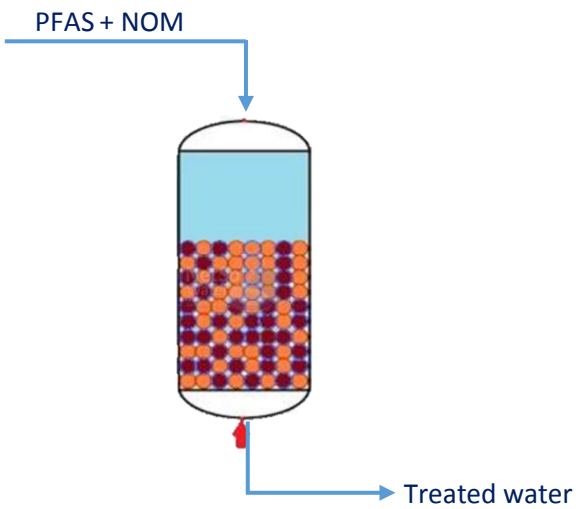
Experimental Conditions:

PFOA (C8) 1 mg/L
[Electrolyte]: 50 mM
pH=12
Surface Area: 5 cm^2
Current Density = 15 mA/cm2

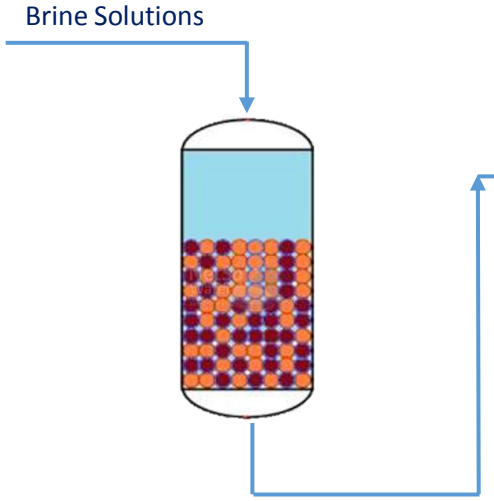
No impact on the electrolyte composition on the degradation of PFOA

- Efficient degradation of PFAS by BDD EO: The longer the carbon chain the faster the degradation
- Long C chain PFAS are degraded in lower molecular weight PFAS
- BDD wire mesh presents advantages over the BDD flat and presents promising results for a higher degradation of PFAS.
- No effect of the Natural Organic matter on the degradation of PFHxA
- No Impact of the composition of the electrolyte solutions on the degradation of PFOA

EO is mass transport limited and is not affected by the conditions of the bulk solution



STEP 1 : Ion Exchange Process

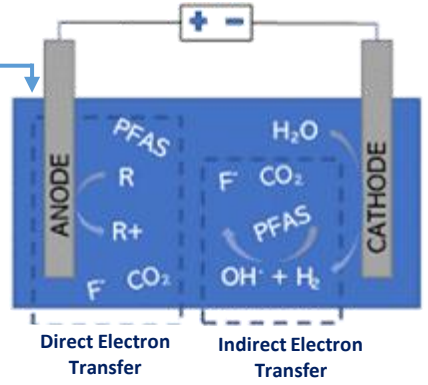


STEP 2 : Regeneration of resins

PFAS + NOM + Brine solutions

ADVANTAGE

Select any type of brine solution that enable the highest percentage of PFAS regeneration from the IX process



STEP 3: Electrochemical oxidation

PFAS

PER- AND POLY-FLUOROALKYL SUBSTANCES

THANK YOU

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Supplementary Data

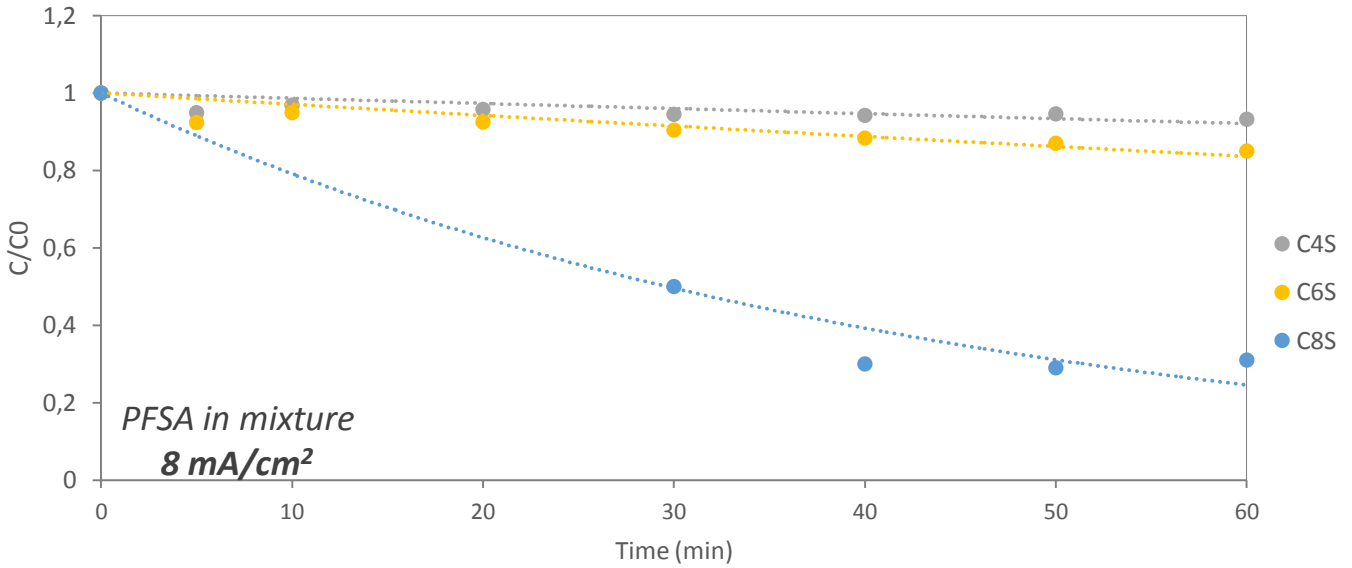
Results

1 Investigate the oxidative removal of PFAS of low concentration (µg/L)

- Effect of chain length on degradation of Perfluorosulfonic acids (PFSA)

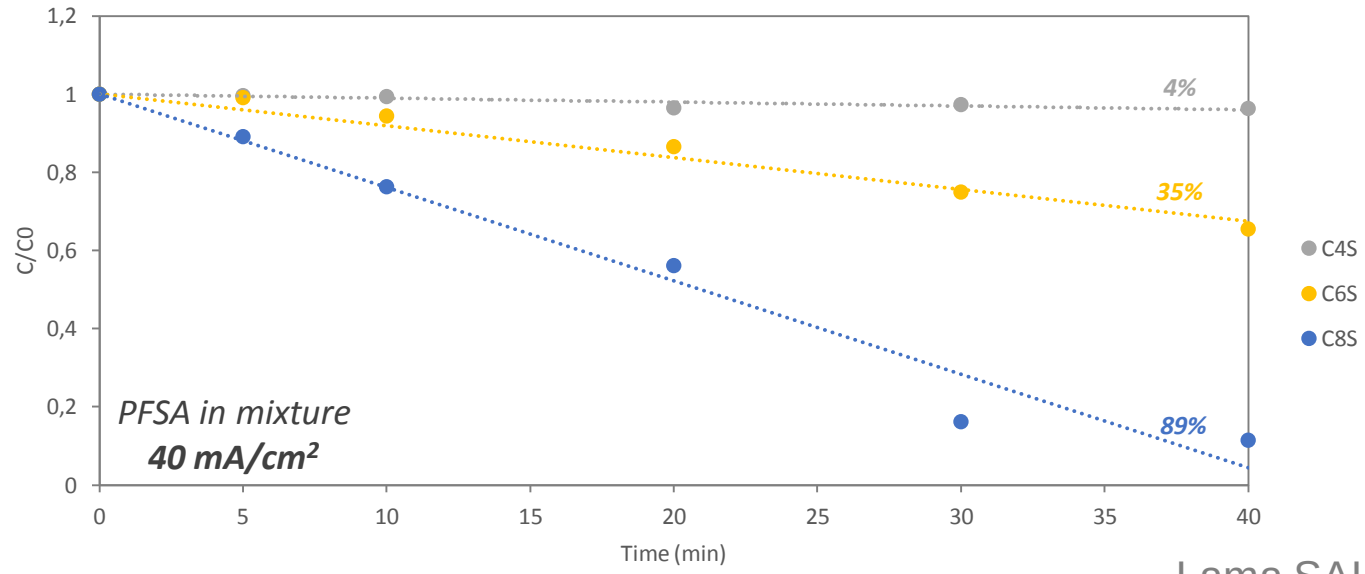
Experimental Conditions:

*PFSA in **mixture***
[PFSA]: 200 µg/L each
Electrolyte: 10 mM Na_2SO_4 , pH=6
Electrolyte: 10 mM Na_2SO_4 , pH=6



Observation:

- At a low current density (8 mA/cm2), the degradation of PFAS is fitted with a pseudo-first order
- At a high current density (40 mA/cm2), the degradation of PFAS is fitted with a zero order



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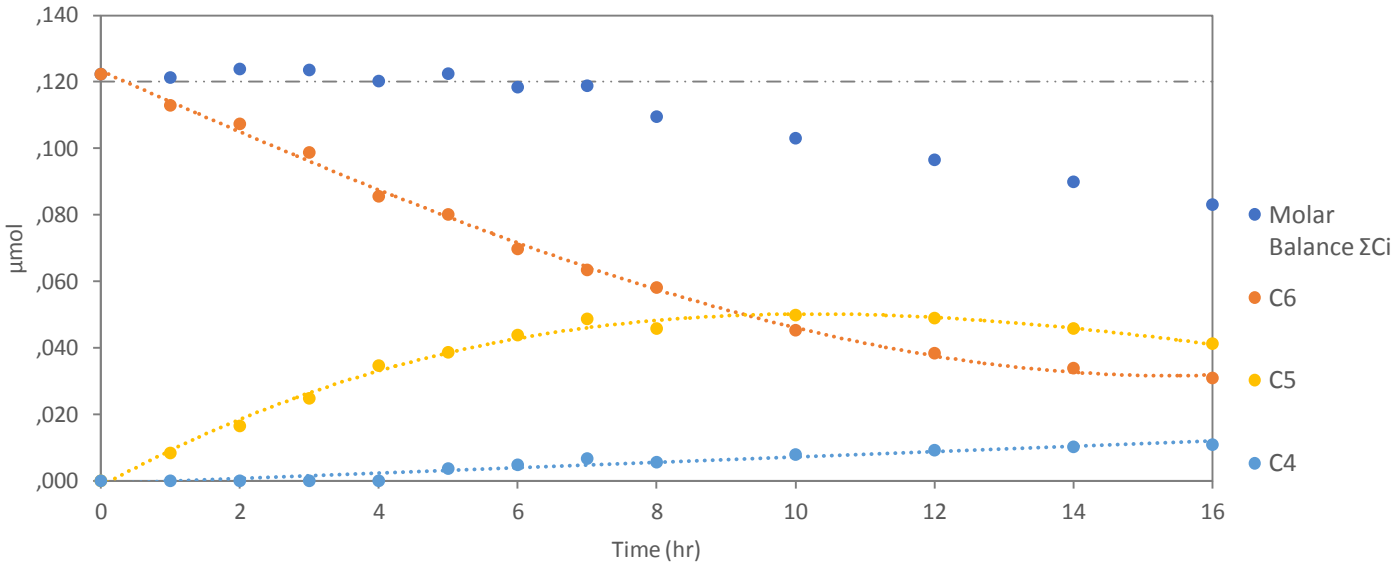
1 Investigate the oxidative removal of PFAS of low concentration (µg/L)

- Decomposition of PFHxA-C6 and formation of by-products

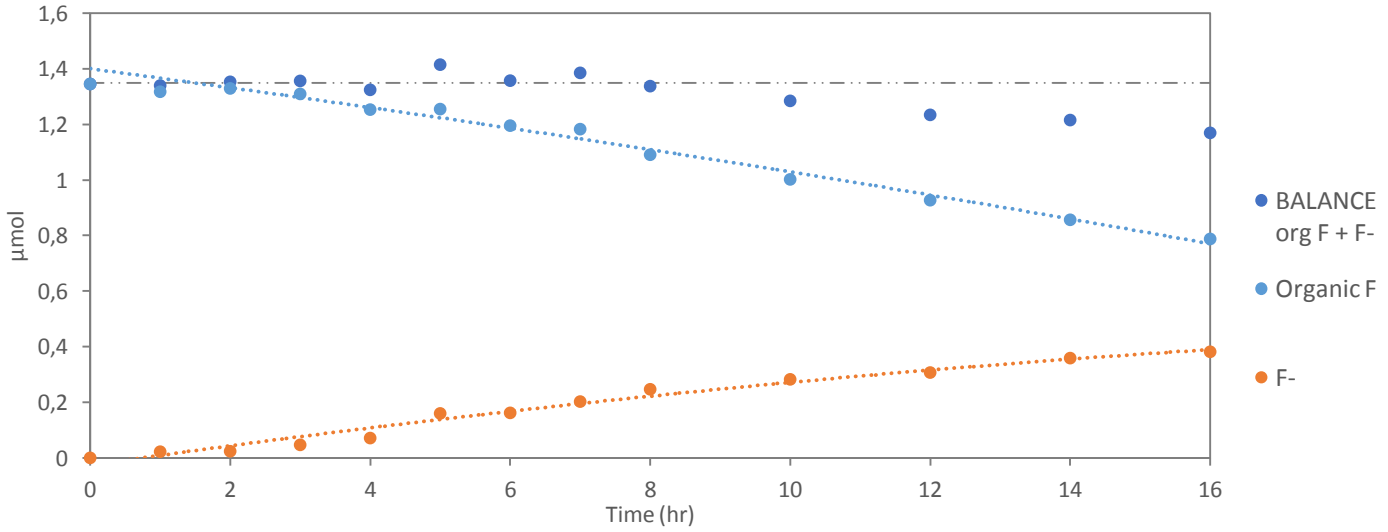
Experimental Conditions:

PFHxA-C6 ***individually***
[PFCA]: 0.64µM (200 µg/L)
Current Density: 8 mA/cm²
Voltage: 20-25 V
Electrolyte: 10 mM Na_2SO_4 , pH=6



Observation:

- C6 is transformed to C5, and C4.
- Ultra short-chain (C2 and C3) may be formed
- 100% molar balance in terms of Fluor




PFAS
contamination
TOXIC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