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Treatment of PFAS from industrial wastewater by advanced reduction process

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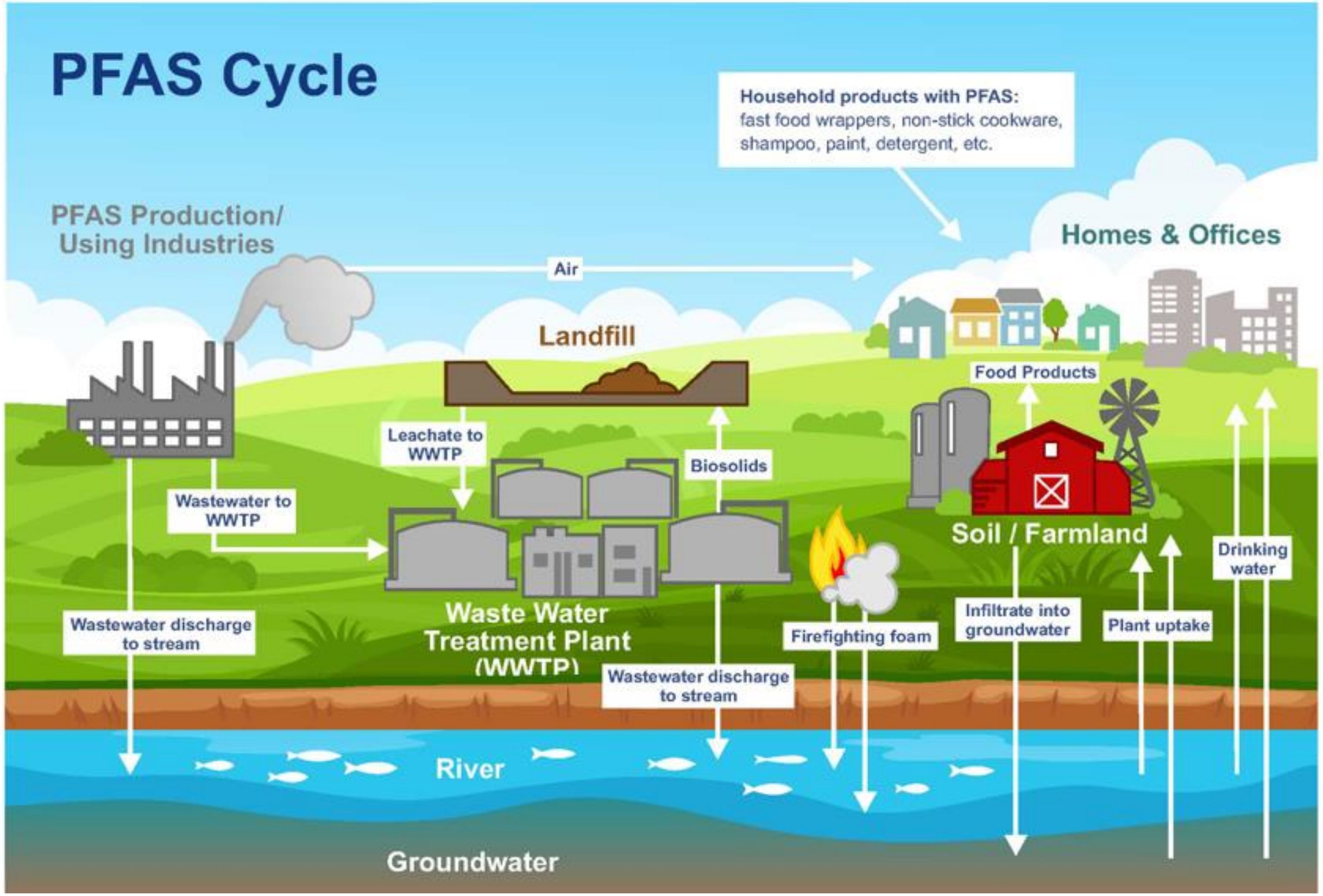
PFAS Cycle



www.dep.pa.gov/pfas

- Conventional Wastewater Treatment Plants (WWTPs) as a Vector of Environmental Pollution by PFAS: 70% of WWTPs worldwide with effluent concentrations ranging from 15 to 1500 ng/L
- Nearly 21,000 contaminated sites in Europe (Le Monde newspaper):
  - In situ treatment of wash waters allowing the extraction of contaminated soils
  - Treatment of groundwater before industrial processing
  - Source treatment of industrial effluents before discarding into the environment or into WWTPs

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Regulatory context

Industrial Regulatory Context in France:

- **PFAS (Per- and Polyfluoroalkyl Substances) Action Plan (ME) 2023-2027** -> Action Area 4: Significantly reduce emissions from industrial emitters
- **Ministerial Decree of June 20, 2023,** establishes the framework for monitoring these molecules in discharge waters for ICPEs subject to authorization (Classified Installations for Environmental Protection)
- **20 targeted PFAS** listed in DCE chemical surveillance and by the EDCH Directive of December 2020
- Every month for **3 consecutive months**, monitor all aqueous discharges for :
    - **Adsorbable Organic Fluorine (AOF)** within a limit of quantification (LOQ) of 2 µg/L
    - **Quantification of the 20 PFAS with an LOQ of 100 ng/L**
- Research and analysis of any other PFAS substance used, produced, treated, or discharged by an installation (8 additional PFAS + possible degradation products)

Treewater

- **Treewater in brief**
- Innovative young company founded in 2017
- 14 staff members in Lyon and Valence (France)
- Supplier of industrial **wastewater treatment/recycling** technology
    - Specialized in **advanced oxidation** technologies

- **Scope of work**
    - Elimination of pollutants to bring discharges into compliance
    - Zero pollutant discharge (targeting specific molecules)
    - Reuse of water in the industrial process

- **Partnership**
    - Expertise in photochemistry, analytical methods for PFAS

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PREFAS Project

Existing Treatments:

- Membranes (concentrate management)
- Activated carbon (low loading rates, particularly for short chains)
- Ion exchange resins (complex regeneration -> incineration)
- **Non-destructive processes**: Significant challenges for the development of a **destructive treatment** capable of **reaching regulatory thresholds** imposed on industries

➢ The **PREFAS project** (Processes for Remediation of PFAS) aims to develop a treatment solution for PFAS in complex industrial effluents

- ✓ Validate the treatment performance of a destructive process on simple and complex matrices
- ✓ Develop a semi-industrial pilot allowing continuous treatment of industrial effluent

Treatment by Advanced oxydation process (AOP) UV/H_2O_2

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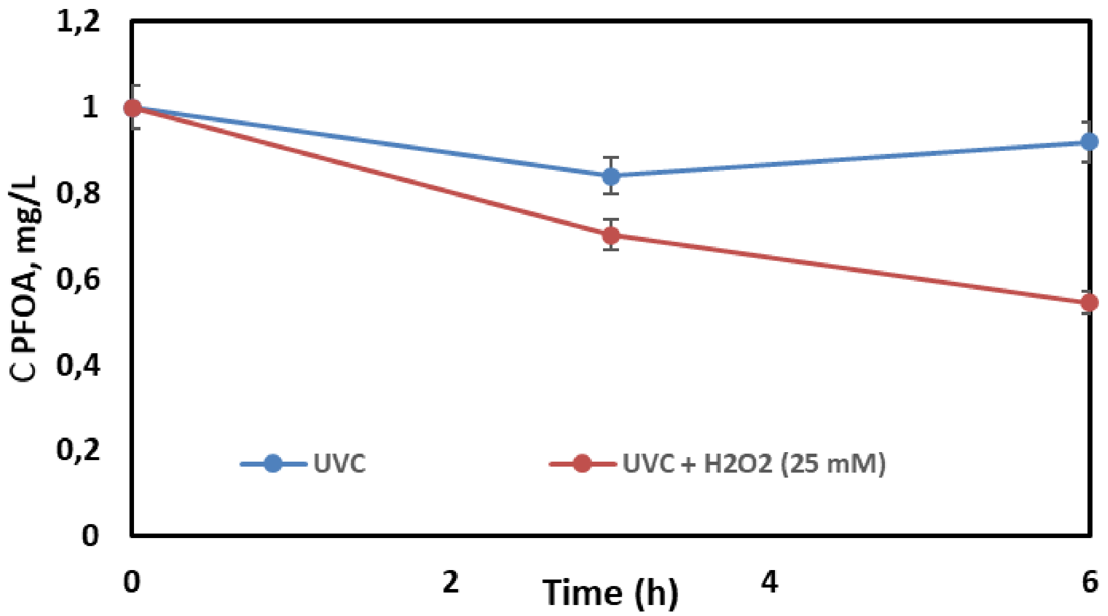
➢ Methodology:

- Goal: formation of OH· radicals
- Laboratory pilot tests (2L)
- Low-Pressure UVc Lamp, 24 W
- Treatment Parameters
  - Ultrapure spiked with 1 mg/L PFOA
  - $[H_2O_2]$ = 20 mM
  - Cumulative UV dose = kinetics

PFOA treatment by UV/H_2O_2

Results:

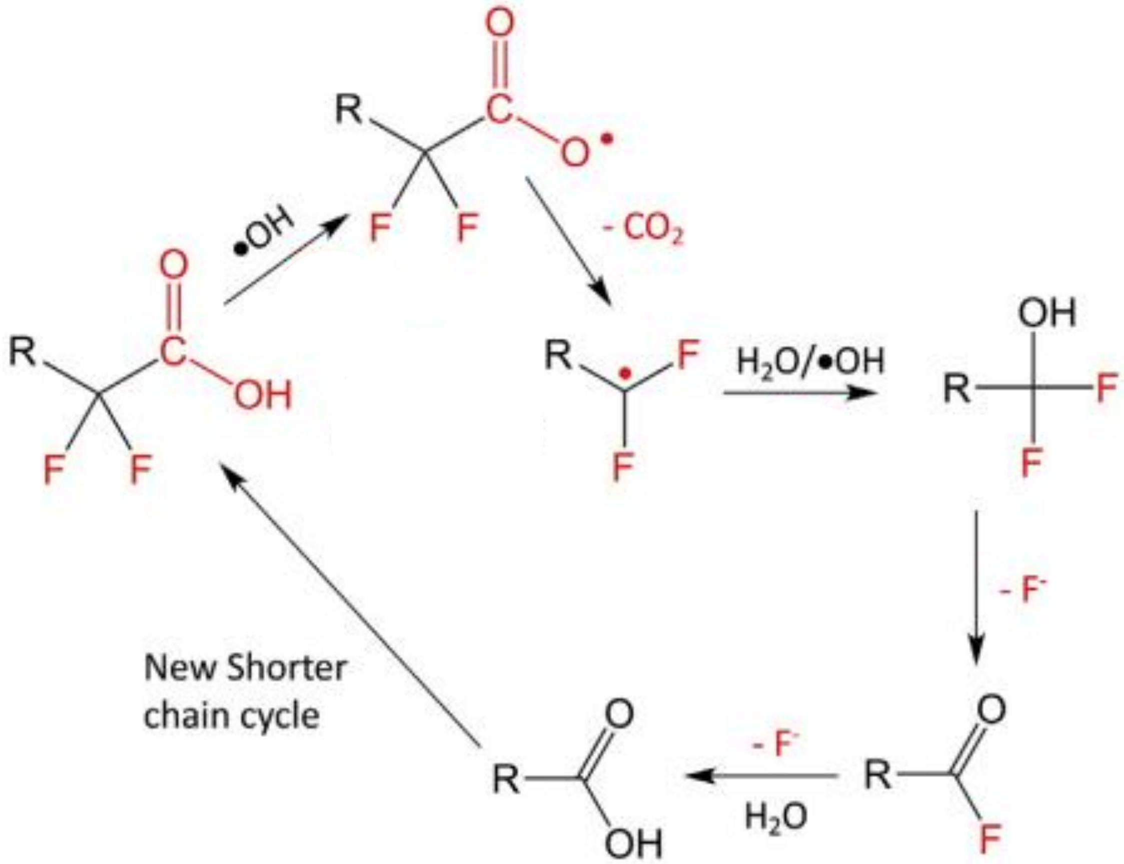


- PFOA photolysis low: 15% reduction
- AOP treatment (UV/H_2O_2): 45% reduction
- Low reduction rate depending on UV dose used (high energy cost > 100 kWh/m^3)
- What degradation mechanism?

PFOA treatment by UV/H_2O_2

- **Degradation Mechanisms by OH· Radicals :**
  - Hydrogen atom abstraction ❌
  - Electrophilic addition to double bonds ❌
  - **Electron transfer** ✅

- **What other « destructive » technology can prove effective ?**



Javed et al., 2020

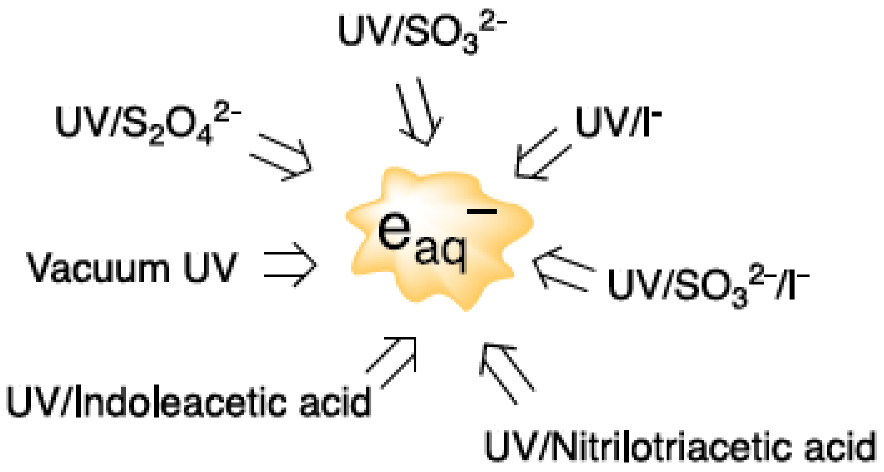
Advanced Reduction Process (ARP)

- ARP based on the production of reducing species: **hydrated electrons** (e^-_{aq}).

- There are several methods to generate these species: **UV**, ultrasound, electron beam, microwave.

- Production by adding a **reducing agent** (iodides, thiosulfate, sulfite, etc.).

- Highly reactive reducing species easily **scavenged by the matrix** of an effluent (dissolved O_2, H^+, nitrates, nitrites, halides, etc.).



Selection of studied ARP

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- Each reagent, have unique quantum yields (rate of aqueous electron formation) (Φ) and molar absorptivities (ε) (how strongly a chemical attenuates photons at a given wavelength)
  - **UV/Sulfites**

$$SO_3{}^{2-} \xrightarrow{hv} SO_3{}^{\cdot -} + e^-_{aq} \quad \Phi = 0.116 \quad \varepsilon = 18-20\ \mathrm{M}^{-1}cm^{-1}$$

  - UV/I$^-$

$$I^- + H_2O \xrightarrow{hv} I^{\cdot} + H_2O + e^-_{aq} \quad \Phi = 0.170-0.286 \quad \varepsilon = 162-220\ \mathrm{M}^{-1}\mathrm{cm}^{-1}$$

    - UV/I$^-$ generates more e-(aq) but forms reactive iodine species which scavenge iodide and e-(aq) reducing the overall effectiveness of the system

  - **UV/sulfites/I-**
    - Use of sulfite to scavenge oxygen and react with iodine species to regenerate the iodide

$$I^{\cdot} + SO_3{}^{2-} \rightarrow I^- + SO_3{}^{\cdot -}$$

ARP reaction mechanisms

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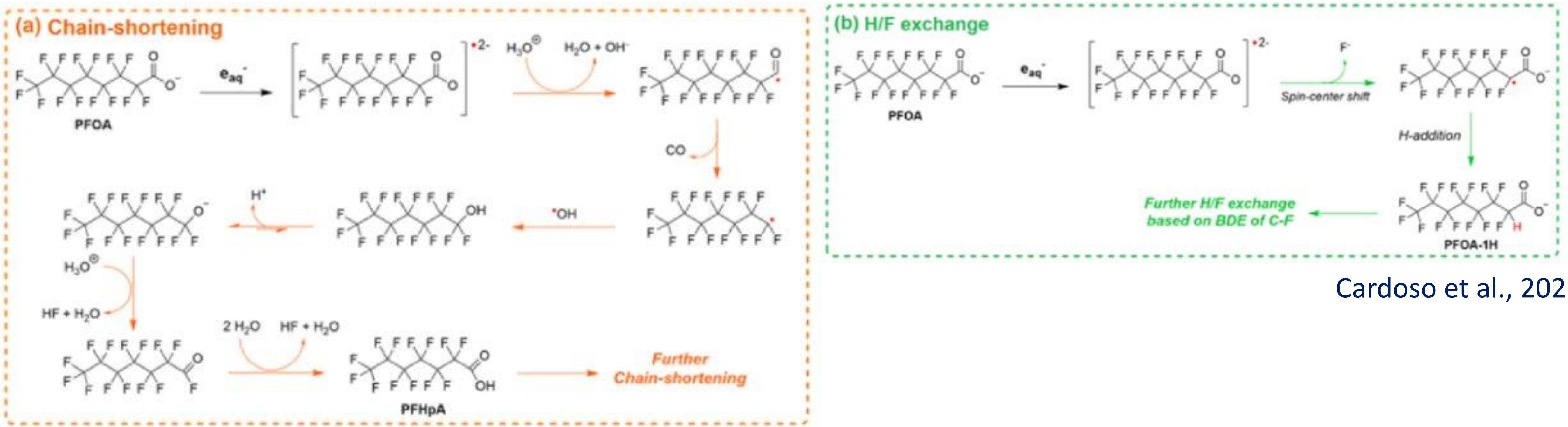


Cardoso et al., 2023

- (a): Mechanisms leading to the **highest defluorination rates**, favored at high pH
- Perfluorosulfonates cannot undergo this mechanism directly, only after desulfonation

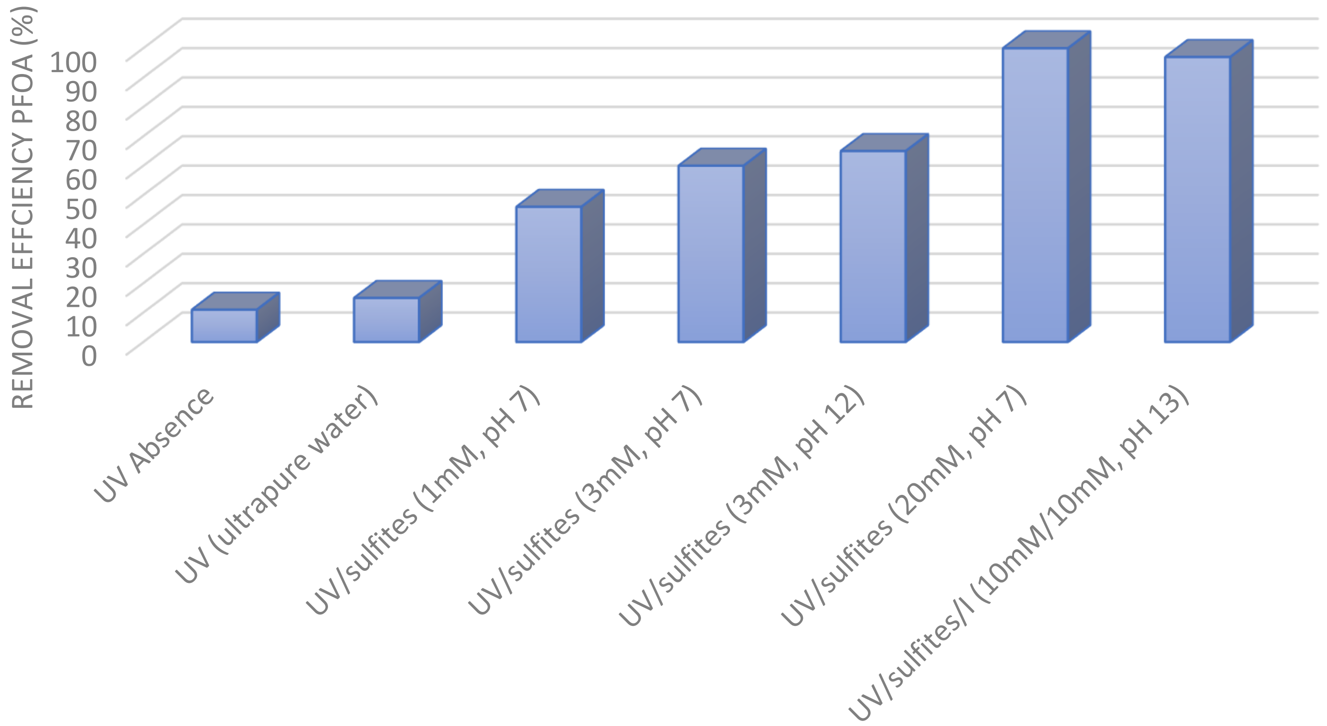
Treatment by ARP

➢Methodology:

- Goal: formation of e-(aq)
- Laboratory pilot tests (2L)
- Low-Pressure UVc Lamp, 24 W
- Treatment Parameters
  - Ultrapure water (UP) or wastewater spiked with 1 mg/L PFOA
  - [Sulfites] = 10 or 20 mM ; $[I^-]$= 10 mM
  - Cumulative UV dose = kinetics

Treatment by ARP (UP Water)

➢Results:



- The applied UV dose is similar
- UVc treatment is negligible
- pH increase to 12 -> slight performance increase (5 %)
- **Reduction > 97% for :**
  - ✓ **UV/sulfites (20 mM, pH 7)**
  - ✓ **UV/sulfites (10mM)/I (10mM), pH 13**
- Energy cost: 6 kWh/m^3
- What efficiency is achieved on real matrix?

Characterization of the effluents used

- Effluent from WWTP after primary treatment, at the inlet of biological treatment

	Units	WWTP
pH	/	7,85
Conductivity	mS/cm	0,984
COD	mgO2/L	181
UV Trans	%	11,5
TSS	mg/L	55,55
N-NO_3	mgN/L	0,308
N-NO_2	mgN/L	<0,6
HCO_3 -	mg/L	513,8
TOC	mg/L	60,6

- Effluent from a paper mill after treatment by coagulation/flocculation/filtration

	Units	Paper mill after Coag/floc
pH	/	7,91
Conductivity	mS/cm	2,2
COD	mgO2/L	1 829
UV Trans	%	14,8
TSS	mg/L	<10
N-NO_3	mgN/L	32,8
N-NO_2	mgN/L	<0,6
HCO_3 -	mg/L	1 400
TOC	mg/L	650

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Treatment by ARP (Wastewater)

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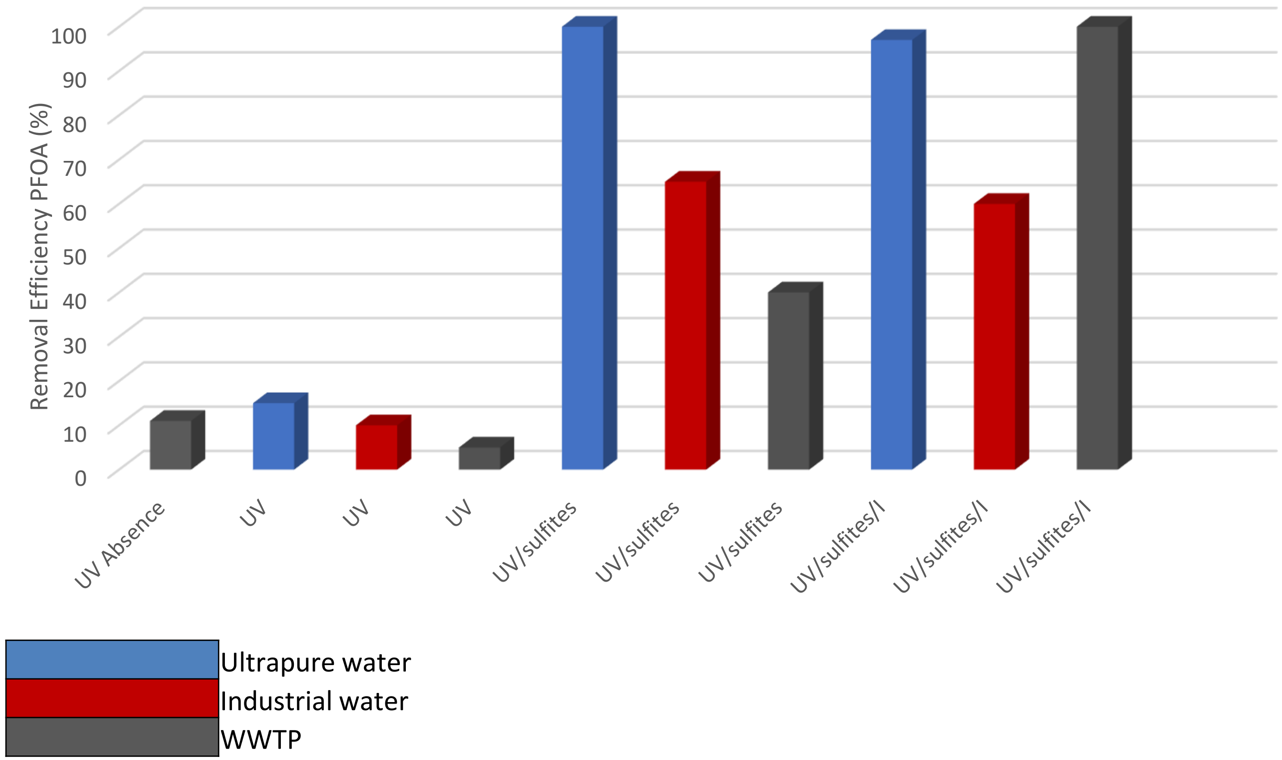
➢Results:



- Similar procedure for the 3 matrices.
- **99% PFOA** reduction with **UV/Sulfites/I on WWTP** effluent compared to **40% for UV/sulfites** -> Greater production of e-(aq) with longer lifetimes
- Similar performances on paper mill effluent (**around 60% reduction**) -> Reactions of I^- with effluent matrices (Coagulant + paper bleaching with Cl, ClO^-, H_2O_2)
- Energy cost: between 24 et 90 kWh/m^3

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Conclusions

- Destructive treatment of PFAS by **promising advanced reduction process.**
- **Excellent reduction results for PFOA in UP water** with UV/sulfites and UV/sulfites/I.
- **UV/sulfites/I highly effective on wastewater**, to be compared with a UV/sulfites experiment at pH 12?
- Lower performance on paper mill effluent: **consumption of e-(aq) and reducing agent by matrix** -> optimization needed.

Perspectives : combine AOP/ARP

➢ **Ongoing experiments on treatment by AOP/ARP sequence:**

- 1st Step: Electrochemical Advanced Oxidation Process or UV/H_2O_2
  - ➢ Removal of part of the effluent matrix -> decrease in interactions with e-aq
  - ➢ Chain shortening: Desulfonation, decarboxylation
- 2nd Step: Advanced Reduction UV/SO_3^{2-}
  - ➢ Chain shortening + H/F exchange
  - ➢ Defluorination, reduction of oxidation by-products
- 3rd Step: Advanced Oxidation UV/H_2O_2
  - ➢ Mineralization of by-products

➢ **Monitoring of AOF, F^-, PFOA+GenX+PFOS+PFDA; deployement of an in-situ pilot**