



Plasma Assisted Catalysis for Removal of Per- and Poly-Fluoroalkyl Substances (PFAS) from Water

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1. Introduction



- Per- and poly-fluoroalkyls are a group of 4,700 compounds which are toxic and classified as persistent organic pollutants
- The strong C-F bond is not degraded by any natural mechanism as nothing has evolved to degrade it & therefore they bioaccumulate
- Plasma is a state of matter which is characterised by radicals and free electrons
- Standard treatments are insufficient to degrade PFAS and plasma is a technique of research interest.



Fig 1: Natural plasma and uses for plasmas.

2. Objective

The aim of this project is to optimise degradation of PFAS *via* plasma assisted catalysis, investigate the mechanism of catalysis, and assess water quality post-plasma treatment.

Oxidative radical mechanism for PFAS degradation:

- Radicals are generated by the plasma

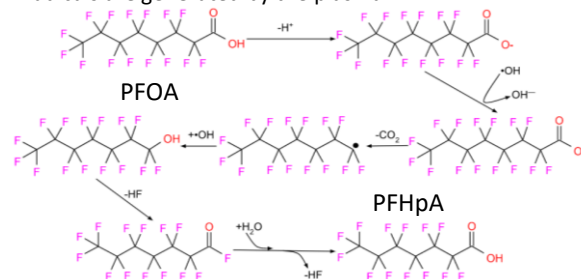


Fig 2: Proposed mechanism of plasma assisted catalysed degradation of PFOA.

Breakdown products

- Reduced chain length

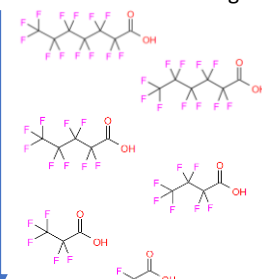


Fig 3: PFOA breakdown products.

3. Experimental

- The PFOA solution (1ppm) was treated in the plasma reactor
- Parameters studied: catalyst choice, catalyst loading, initial pH, tip distance, and voltage.

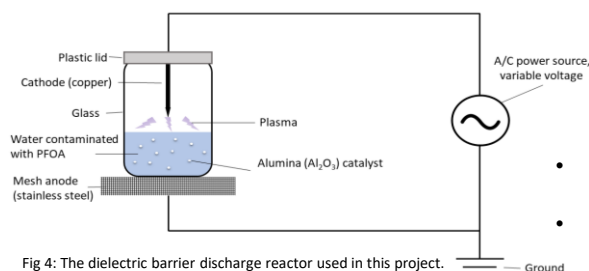


Fig 4: The dielectric barrier discharge reactor used in this project.

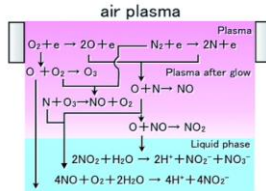


Fig 5: Reactive species generated in an air plasma.

- Initial and final concentrations of PFOA were determined by LC-MS
- Al₂O₃, the optimal catalyst, was characterised by UV-Vis DRS, XPS, & PXRD.

4. Watch H₂O₂!

- Radicals are generated in the plasma
H₂O → •OH + •H
- They react to form H₂O₂
•OH + •OH → H₂O₂
- Potassium Iodide (KI) reacts with H₂O₂ to form aqueous iodine (I₂)
H₂O₂ + 2KI → 2KOH + I₂(aq)



Fig 6: Images of water post-plasma treatment at various times.



I₂(aq) is yellow

5. Water Quality

- Post-treatment the water pH is 4.35, and H₂O₂, NO₂⁻ and NO₃⁻ are detected
- [NO₃⁻] is always below EU drinking water limits
- Breakdown products are present, some of which are also toxic and persistent.

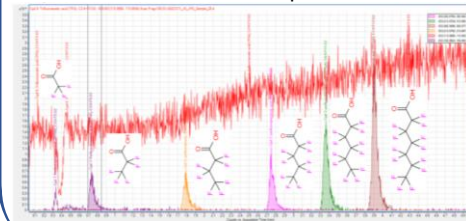


Fig 7: Chromatogram intensity vs/ retention time showing breakdown products of PFOA post-plasma treatment.

6. Al₂O₃ Characterisation

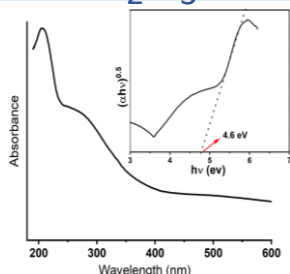


Fig 8: Tauc plot showing band gap of 4.6 eV transposed onto UV-Vis absorption spectrum of Al₂O₃.

- Band gap was 4.6 eV = 268 nm
- This is outside the range of wavelengths of light generated by the plasma
- Therefore, photocatalysis over Al₂O₃ is not taking place.

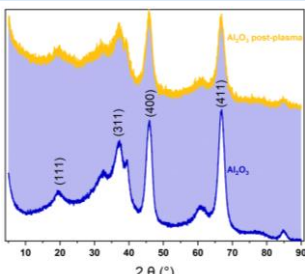


Fig 9: PXRD plot of Al₂O₃ and Al₂O₃ post-30 min of catalytic plasma treatment of aqueous PFOA.

- PXRD peaks are the same pre- and post-treatment
 - γ-Al₂O₃
- XPS spectra are also the same
- No changes to catalyst configuration measured.

7. Mechanism Studies

- Radical scavengers artificially lower concentrations of a particular radical in reaction mixture
- % degradation compared with radical-free system
- h⁺, •OH and O₂^{•-} are potentially relevant to PFOA degradation
- Unexpected increase in % degradation with scavenger
- Temperature remained below 36 °C during treatment
 - Combustion is not taking place.

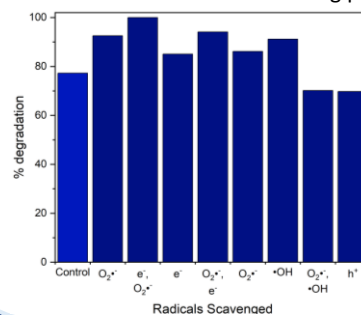


Fig 10: % degradation of PFOA after 5 min of catalytic plasma degradation with addition of various specific radical scavengers.

8. Optimised Parameters

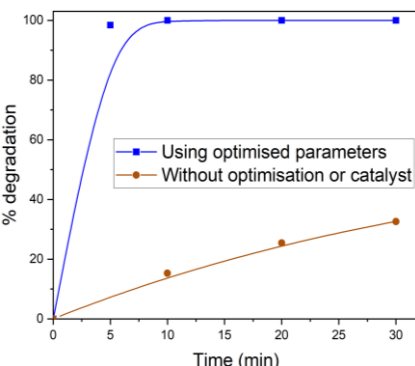


Fig 11: Plot of % degradation of PFOA vs/ time for the optimised process & process without optimisation or catalyst

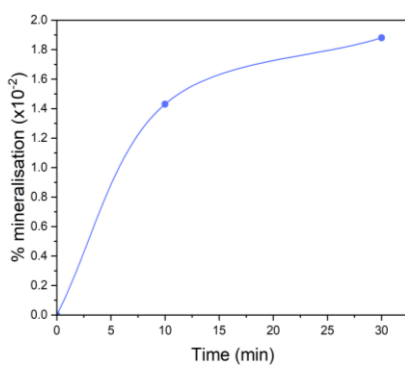


Fig 12: Plot of % mineralisation of PFOA vs/ time for the optimised process

Mineralisation – Ideal scenario
CF₃(CF₂)₆COOH → CO₂ + H₂O + F⁻

Optimised Parameters	
Catalyst	Al ₂ O ₃
Catalyst concentration	2 g/L
Starting pH	~7
Time	10 min
Voltage	2.95 V
Tip distance	5 mm
% degradation	99.9%

Table 1: Table of optimised parameters.

- 99.9% degradation of PFOA in 10 min**, compared to 15.2% without optimisation or catalyst
- However, only 0.014% mineralisation, measured by [F⁻] concentration in solution
- F⁻ adsorption onto the catalyst is also possible, this value is lower than the true extent of mineralisation
- Energy efficiency of the process (G50) = 10,400 mg/kWh, compared to literature 0.2- 90 mg/kWh.⁴
 - More PFOA is degraded per kWh of energy used in the optimised and catalysed process.

9. Conclusions

- 99.9% degradation of PFOA in 10 min using Al₂O₃ and the optimised parameters (Table 1)
- Poor mineralisation of PFOA is observed
 - Breakdown products generated
- Al₂O₃ is unchanged by the treatment & photocatalysis is not taking place
- Water quality is reduced by the treatment: acidity increased and NO₃⁻, NO₂⁻, H₂O₂ generated.

References

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