

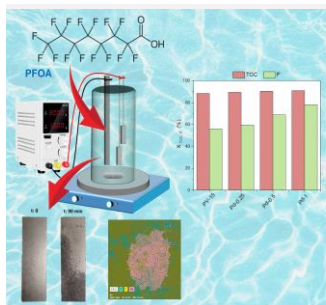
## Cathode modification for PFOA electrochemical degradation: boosting molecule defluorination

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Novel Pd-decorated cathodes were synthesized for PFOA abatement in aqueous phase through electrochemical degradation using Pd loads of 0.25, 0.5 and 1 mg. PFOA (100 mg/L) with 3.5 mM Na<sub>2</sub>SO<sub>4</sub> as electrolyte was subjected to electrochemical degradation using BDD anode and the synthesized cathodes. Under the optimized operating conditions (5 mA/cm<sup>2</sup>, pH<sub>0</sub>:4, T: 25°C), after 120 min practically complete PFOA degradation was reached with 90% mineralization and 76.4% fluoride release. Degradation mechanism follows a PFOA polymerization over the cathode followed by defluorination and pollutant release. Cathode stability was also tested in 10 consecutive cycles, without perceptible deactivation.

### Introduction

Concern about the widespread occurrence of perfluorinated alkyl substances (PFAS), such as perfluorooctanoic acid (PFOA) has increased over the past decade because of their carcinogenic and endocrine disruption properties.

In this sense, new regulations include these pollutants in the substances that must be monitored in drinking water. These pollutants are also known as forever chemicals, due to their high persistence related to the C-F bond. Hence, new technologies must be developed in order to eliminate efficiently these contaminants in aqueous phase.

Traditional advanced oxidation processes, such as the Fenton process, are not able to eliminate PFAS [1]. Only photocatalytic and electrochemical methods, which combine oxidation and reduction reaction mechanisms are able to degrade these pollutants [2].

Regarding electrochemical oxidation, a prior collaboration work demonstrated the importance of the cathode in PFOA abatement [3]. Reduction reactions involving the molecule defluorination take place in the cathode. These are crucial in the PFOA breakdown which follows a cascade reaction mechanism in which the terminal C needs to be defluorinated prior to its oxidation and cleavage on the anode's surface. Following this line of research, this work aims to improve PFOA defluorination using tailor made Pd decorated cathodes.

### Material and Methods

PFOA electrochemical oxidation runs were performed in a glass jacketed batch reactor, connected to a water circulating bath to keep constant temperature throughout the experiments. Inside the reactor, two bipolar BDD anodes with 2.5 cm<sup>2</sup> surface each, and one of the synthesized cathodes (10 cm<sup>2</sup>) were placed in the center of the reaction vessel with a 5 mm gap between them. The

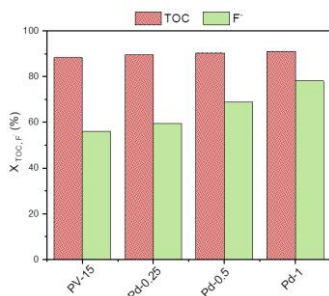
reactor was operated under galvanostatic conditions using an ELCAL 924 power supply. To avoid diffusional limitations, magnetic stirring was set at 450 rpm. In a typical reaction, 100 mL PFOA solution (100 mg/L) with 3.5 mM Na<sub>2</sub>SO<sub>4</sub> as electrolyte at the natural pH of the solution (pH:4) was loaded to the reactor. Afterwards, the power supply was turned on at the desired current density, representing this the reaction starting time.

Pd decorated electrodes were synthesized by incipient wetness impregnation on a commercial support (PV-15, SIGRACELL), followed by a calcination stage (250°C, 2h) and a subsequent reduction (H<sub>2</sub>: 50 mLN/min, N<sub>2</sub>:100 mLN/min, 250°C, 2h).

PFOA concentration along the reaction was measured using HPLC-DAD (Thermo-Fischer). Released fluoride was quantified by means of ionic chromatography (Metrohm) and total organic carbon (TOC) analyses were performed with a TOC analyzer (Shimadzu)

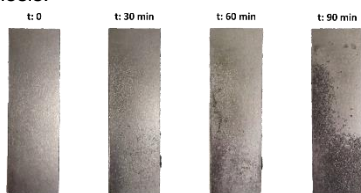
### Results and Discussion

Influence on the Pd load (0-1 mg) in PFOA electrochemical degradation was tested, as shown in Figure 1. PFOA decay was faster in presence of Pd. Still, differences between the different Pd loads tested was low (data not shown). Nonetheless, Pd load had a great influence in terms of PFOA defluorination after 120 min, as shown in Figure 1, reaching 76.4% defluorination with Pd-1 (1 mg Pd). In all cases TOC removal was around 90%, suggesting that the reaction mechanism goes through PFOA and/or reaction intermediates polymerization onto the cathode followed by its defluorination and release.



**Figure 1.** Influence of Pd load in PFOA degradation.

This polymerization was visible in the case of PV-15 bare electrode, in which there was a progressive residue build-up along the reaction, as shown in Figure 2. SEM and EDX mapping revealed an increase in fluorinated species over the anode surface, confirming the PFOA polymerization hypothesis.



**Figure 2.** Polymer build-up over PV-15 cathode.

To get a better understanding on the influence of anodic and cathodic reactions, separated cell tests were performed by inserting a Nafion membrane. Results, shown in Figure 3, show a greater PFOA degradation, related to the elimination of the terminal carboxylic group [3]. This is in agreement with the mineralization, which was only 5.3% after 120 min in the anodic cell. On the other hand, PFOA degradation in the cathode presents a lag phase of 30 min, after which the pollutant started polymerizing onto the cathodic surface, with a final 23.2% PFOA elimination, which matched the TOC removal (23.5%). Tests in the undivided cell reveal an incomplete PFOA degradation due to mass transfer limitations derived from a poor agitation. Still, in relation to the separated cell test, TOC elimination was higher (42.8%). This demonstrates that PFAS polymerization is exclusive to the cathode.

## Conclusions

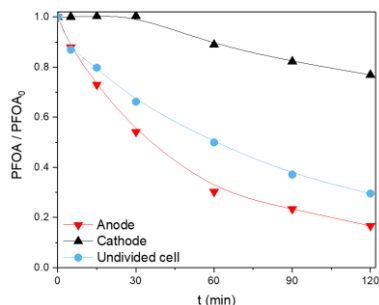
Novel Pd decorated cathodes are able to increase the defluorination and hence, the removal, of PFOA through electrochemical degradation. PFOA breakdown follows a complicated mechanism in which PFAS polymerize onto the cathode's surface, in which the Pd active centers carry out the molecule defluorination.

## Acknowledgments

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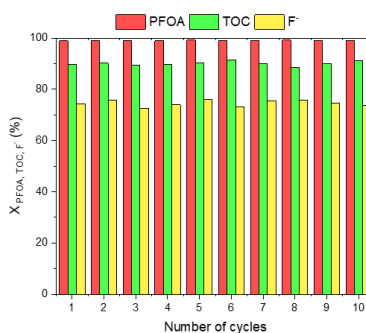
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**Figure 3.** Separated cells test.

Further experiments aimed to study the influence of the current density and the temperature in PFOA degradation. Regarding the current density, working above 5 mA/cm<sup>2</sup> resulted in an inefficient PFOA degradation in terms of energy consumption. Study on the influence of the temperature revealed an activation energy for PFOA removal of E<sub>a</sub>: 16.1 kJ/mol, significantly lower than those reported in the literature for both electrochemical and photochemical depletion of this pollutant. Finally, cathode stability (Pd-1) was tested in 10 consecutive reaction cycles, as depicted in Figure 4. In all cases there was a practically complete PFOA removal with mineralization rates around 90% and ≥ 75% defluorination.



**Figure 4.** Pd-1 stability over 10 reaction cycles.

Current efforts are dedicated to the analysis of reaction intermediates and elucidation of the complete degradation route.