On the role of the cathode for the electro-oxidation of perfluorooctanoic acid.

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Abstract

Perfluorooctanoic acid (PFOA), C7F15COOH, has been widely employed over the past fifty years, causing an environmental problem due to its dispersion and low biodegradability. Furthermore, the high stability of this molecule, conferred by the high strength of the C-F bond makes it very difficult to remove. In this work, electrochemical techniques are applied for PFOA degradation in view to study the influence of the cathode on defluorination. For this purpose, boron doped diamond (BDD), Pt, Zr and stainless steel have been tested as cathodes working with BDD anode at low electrolyte concentration (3.5 mM) to degrade PFOA at 100 mg/L. Among these cathodic materials, Pt improves the defluorination reaction. The electro-degradation of a PFOA molecule starts by a direct exchange of one electron at the anode and then follows a complex mechanism involving reaction with hydroxyl radicals and adsorbed hydrogen on the cathode. It is assumed that Pt acts as an electrocatalyst, enhancing PFOA defluorination by the reduction reaction of perfluorinated carbonyl intermediates on the cathode. The defluorinated intermediates are then more easily oxidized by HO• radicals. Hence, high mineralization (xTOC: 76.1%) and defluorination degrees (xF: 58.6%) were reached with Pt working at current density j = 7.9 mA/cm². This BDD-Pt system reaches a higher efficiency in terms of defluorination for a given electrical charge than previous works reported in literature. Influence of the electrolyte composition and initial pH are also explored.

Keywords: perfluorooctanoic acid, emerging contaminant, defluorination, platinum, electro-oxidation.
1. Introduction

Perfluoroalkyl substances (PFAS), such as perfluorooctanoic acid (PFOA, C\textsubscript{8}F\textsubscript{15}COOH) are widely used in the chemical industry due to their amphiphilicity, stability and surfactant property. They are employed in the synthesis of fluoropolymers and fluoroelastomers, as surfactants in fire-fighting foams, and in textile and paper industries to produce water and oil repellent surfaces\textsuperscript{1}. Nevertheless, despite their practical interest, these substances present a high toxicity due to their potential bioaccumulation, and common occurrence in water resources. PFOA has been recognized as an emerging environmental pollutant and has been included in the European Candidate List of Substances of Very High Concern (‘SVHC’)\textsuperscript{2}. Hence, the current challenge is to develop highly efficient and cost-effective processes for the elimination of perfluoroalkyl substances at source.

The main issue in PFOA degradation is to break the C-F bond, one of the strongest bonds known (≈460 kJ/mol)\textsuperscript{3}. This confers a high stability and resistance to PFAS which cannot be degraded by direct hydrolysis, photolysis or through conventional biological treatments\textsuperscript{4}. As a result, PFAS have been detected in natural water streams\textsuperscript{5}, sediments\textsuperscript{6} and even in tap and bottled water in concentrations up to 640 ng/L\textsuperscript{7}. So far, adsorption onto carbonaceous materials\textsuperscript{8}, alumina\textsuperscript{9} or other sorbents\textsuperscript{10} have been successfully applied for PFAS removal. Nonetheless, this technology implies the transfer of the pollutant to another phase, the sorbent, which becomes a new residue
after use. To overcome this drawback, Advanced Oxidation Processes (AOP) are being explored for PFAS removal. AOP are based on the use of strong oxidizing radicals to degrade, most commonly, organic pollutants in aqueous phase\textsuperscript{11}. The most extended AOP are those based on the use of hydroxyl radicals (HO\textsuperscript{•}) to attack organic pollutants by hydrogen abstraction. Consequently, the substitution of all organic hydrogen for fluorine in PFOA makes these compounds inert to AOP. The non-reactivity of PFOA to HO\textsuperscript{•} attack has been confirmed by various studies\textsuperscript{12,13,14}. As a matter of fact, Maruthamuthu et al. have shown that the reactivity of hydroxyl radicals on acetate decreases considerably with increasing halogen substitution\textsuperscript{12}. Using the Fenton process, known to generate hydroxyl radicals by the action of Fe (II) on hydrogen peroxide, no degradation was observed when the Fenton reagent (0.2 mM, Fe\textsuperscript{2+}: H\textsubscript{2}O\textsubscript{2}, molar ratio = 1:1) was mixed with PFOA (0.02 mM) at room temperature\textsuperscript{13}. Similar results were obtained by Santos et al. with only 10\% PFOA removal without any C-F bond cleavage\textsuperscript{15}.

More recently, photocatalytic treatments have been applied for PFOA degradation. This technology achieved high PFOA removal ($x_{PFOA} > 90\%$) when using modified TiO\textsubscript{2} photocatalysts such as Cu-TiO\textsubscript{2}\textsuperscript{16}, Pb-TiO\textsubscript{2}\textsuperscript{17} and rGO-TiO\textsubscript{2}\textsuperscript{18}.

Besides PFOA removal, defluorination ($x_{F^{-}}$) is a very important parameter to evaluate the process efficiency. $x_{F^{-}}$, defined as the ratio of the fluoride concentration ($C_{F^{-}, \text{measured}}$) released by PFOA degradation with respect to the initial content of fluoride in the initial amount of PFOA molecule ($C_{F,PFOA_{0}}$), is expressed in percentage as shown in Eq. 1.

$$x_{F^{-}} = \frac{C_{F^{-}, \text{measured}}}{C_{F,PFOA_{0}}} \cdot 100 \quad \text{Eq. 1}$$

In photochemical oxidation of PFOA, defluorination is usually low ($x_{F^-} < 25\%$), with the average $x_{F^{-}}/x_{PFOA}$ ratio around 0.26\textsuperscript{19}.

Another technique for PFAS remediation is electrochemical degradation. PFOA electrooxidation has been successfully carried out in different systems using Boron Doped Diamond (BDD) as anode (Table 1). Under the studied conditions, PFOA removal ranged from 60\% to 100\%. It should be noted that defluorination values were very different, suggesting that either the operating conditions (electrolyte, pH, etc.) or the cathode reduction reactions may play a key role in the PFOA degradation mechanism. The cleavage of the C-F bonds to form F\textsuperscript{–} ions is interesting because F\textsuperscript{–} ions...
readily combine with \( \text{Ca}^{2+} \) to form environmentally harmless \( \text{CaF}_2 \), as reported by Hori et al.\(^3\)

\( x_F^- \) and \( x_{\text{PF}O\text{A}} \) ratios obtained by electrochemical treatment (up to 80-85 %, Table 1) are higher than those reported in photo-oxidation (< 25%). Nonetheless, all previous electrooxidation studies were conducted employing a high supporting electrolyte concentration, which makes difficult to dispose the treated wastewater after reaction. Therefore, this work aims to gain knowledge on the role of the cathode as electrocatalyst in PFOA electrooxidation working at low electrolyte concentration (3.5 mM). For this purpose, BDD was chosen as anode and BDD, Pt, Zr and stainless steel were tested as cathodes in the degradation of 100 mg/L PFOA.

### Table 1. PFOA electrooxidation with BDD anode.

| Electro-oxidation system | Operating conditions | Results | Remarks | Ref |
|--------------------------|----------------------|---------|---------|-----|
| Anode: BDD              | [PFOA]_0: 15 mg/L    | \( x_{\text{PF}O\text{A}}\): 60-100\% \( x_F^-\): 30-80\% | No apparent influence of \( \text{Cl}^- \) in the process | 20 |
| Cathode: W              | Electrolyte: 1500 mg/L Na\(_2\)SO\(_4\) or 1500 mg/L Na\(_2\)SO\(_4\) + 167 mg/L NaCl | T: 20°C, j: 3, 15, 50 mA/cm\(^2\), V: 250 mL, t: 480 min | | |
| Area: 38 cm\(^2\)       |                      |         |         | |
| Spacing: 4 mm           |                      |         |         | |
| Anode: BDD              | [PFOA]_0: 100 mg/L   | \( x_{\text{PF}O\text{A}}\): 93\% \( x_{\text{TOC}}\): 95\% \( x_F^-\): 38\% | In the tested conditions, SO\(_4^{2-}\) did not produce additional oxidants. ↑j, ↑ degradation | 21 |
| Cathode: W              | Electrolyte: 1.4 – 8.4 g/L NaClO\(_4\), 5 g/L NaSO\(_4\) | T: 20°C, j: 50, 100, 200 mA/cm\(^2\) | | |
| Area: 42 cm\(^2\)       | V: not specified, t: 360 min | | | |
| Spacing: 8 mm           |                      |         |         | |
| Anode: BDD              | [PFOA]_0: 50 mg/L    | \( x_{\text{PF}O\text{A}}\): 100\% \( x_F^-\): 58\% | Slightly better results obtained at pH\(_0\) 3 than pH\(_0\) 9 | 22 |
| Cathode: BDD            | Electrolyte: 1.4 g/L NaClO\(_4\) | pH: 3, 9, 12, T: 32°C, j: 23.24 mA/cm\(^2\), V: 40 mL, t: 120 min | | |
| Area: 85 cm\(^2\)       |                      |         |         | |
| Spacing: 30 mm          |                      |         |         | |
| Anode: BDD              | [PFOA]_0: 50 mg/L    | \( x_{\text{PF}O\text{A}}\): 85\% | F\(^-\) deposition on the BDD surface. | 23 |
| Cathode: Pt             | Electrolyte: 1.2 g/L NaClO\(_4\) | T: not specified, j: 0.04-1.2 mA/cm\(^2\), V: 300 mL, t: 480 min | | |
| Area: 77.4 cm\(^2\)     |                      |         |         | |
| Spacing: 10 mm          |                      |         |         | |
| Anode: BDD              | [PFOA]_0: 200 mg/L   | \( x_{\text{PF}O\text{A}}\): 95\% \( x_{\text{TOC}}\): 90\% \( x_F^-\): 90\% | High temperature process greatly enhances the PFOA degradation in relation to the room temperature system. | 24 |
| Cathode: Pt             | Electrolyte: 7.1 g/L Na\(_2\)SO\(_4\) | P: 0.3 MPa, T: 80-120°C, j: 20 mA/cm\(^2\), V: 400 mL, t: 360 min | | |
| Area: 5.5 cm\(^2\)      |                      |         |         | |
| Spacing: 20 mm          |                      |         |         | |
2. Results

Figure 1. Influence of the cathode material in a) PFOA removal (symbols: experimental data, lines: kinetic fitting), b) TOC depletion, c) released fluorine (symbols: experimental data, lines: kinetic fitting). Operating conditions: [PFOA]₀: 100 mg/L, j: 7.9 mA/cm², electrolyte: 3.5 mM Na₂SO₄, T: 25°C, pH₀: 4.
Figure 2. PFOA electrooxidation mechanism.
Figure 3. Variation of fluorine ions (full symbols) and carbon removal (empty symbols) during electrolysis with respect to carbon removal and degraded PFOA. Operating conditions: [PFOA]₀: 100 mg/L, j: 7.9 mA/cm², electrolyte: 3.5 mM Na₂SO₄, T: 25°C, pH₀: 4.

Figure 4. Ratio of fluorine and carbon atoms in the chemical intermediates. Operating conditions: [PFOA]₀: 100 mg/L, j: 7.9 mA/cm², electrolyte: 3.5 mM Na₂SO₄, T: 25°C, pH₀: 4.
Figure 5. Influence of the electrolyte in PFOA a) degradation b) mineralization and c) defluorination in electrooxidation using BDD/Pt electrodes. Operating conditions: [PFOA]₀: 100 mg/L, j: 7.9 mA/cm², electrolyte: 3.5 mM, T: 25°C, pH₀: 4.
Figure 6. Influence of the pHo in PFOA a) degradation, b) mineralization and c) defluorination and d) pH evolution in electrooxidation using BDD/Pt electrodes. Operating conditions: [PFOA]0: 100 mg/L, j: 7.9 mA/cm², Na2SO4: 3.5 mM, T: 25ºC.

Figure 7. Process comparison in terms of defluorination against electric charge for PFOA electrooxidation with BDD anodes. Cathodes: Schaefer et al. – W20, Urtiaga et al. – W21, Zhuo et al. – BDD22, Ochiai et al. – Pt23, this work - Pt.

Table 2. PFOA degradation and fluoride release kinetics.

|     | k_{PFOA}·10³(min⁻¹) | r²  | k_F·10³(min⁻¹) | r²   |
|-----|----------------------|-----|----------------|------|
| BDD | 8.22 ± 0.68          | 0.973 | 8.97 ± 0.28    | 0.999 |
| Pt  | 11.86 ± 0.32         | 0.994 | 10.36 ± 0.44   | 0.997 |
| Zr  | 8.91 ± 0.58          | 0.971 | 6.23 ± 0.86    | 0.982 |
| Steel | 8.64 ± 0.42        | 0.983 | 4.70 ± 0.78    | 0.982 |
3. Discussion

In order to test the influence of the cathode material on the degradation process, a BDD anode was successively coupled with cathodes made of BDD, Pt, Zr and stainless steel. Results of electrolysis runs conducted at 7.9 mA/cm², at 25°C, for the treatment of 100 mg/L PFOA solutions (namely, 0.242 mol/m³), are presented in Fig. 1(a). For each couple of electrodes, the curves show that PFOA concentration followed, from \( C_{\text{PFOA,0}} = 100 \text{ mg/L} \) to \( C_{\text{PFOA,t}} \approx 25 \text{ mg/L} \), a similar decrease, characteristic of a pseudo-first order kinetics. For experiments presented in Fig. 1(a) the applied current density was higher than the limiting current density. Indeed, considering a pure mass transport controlled reaction for the first exchange of charge between a molecule of PFOA and the anode surface, the limiting current density calculated using the equation established from the Nernst diffusion model:

\[
j_{\text{lim}} = n \cdot F \cdot k_m \cdot C_{\text{PFOA,0}}
\]

equals to 0.63 A/m² (for \( n = 1 \), \( F = 96485 \text{ C/mol} \), \( k_m = 2.7 \cdot 10^{-5} \text{ m/s} \), \( C_{\text{PFOA,0}} = 0.242 \text{ mol/m³} \)). This value of the limiting current density is more than 100 times lower than that applied during electrolysis (\( j = 79 \text{ A/m²} \)). Under these conditions, the decay of concentration from \( C_{\text{PFOA,0}} \) to \( C_{\text{PFOA,t}} \) depends upon the mass transfer coefficient \( k_m \), the surface area (A) of the electrode and the volume (V) of electrolyte, as follows:

\[
C_{\text{PFOA,t}} = C_{\text{PFOA,0}} \cdot e^{-\frac{t}{\tau}}
\]

Where the constant of time, \( \tau \), is defined by: \( \tau = V / (k_m \cdot A) \). With the following values: \( V=10^{-3} \text{ m³} \), \( A=63 \cdot 10^{-4} \text{ m²} \) and the mass transfer coefficient \( k_m=2.7 \cdot 10^{-5} \text{ m/s} \) (for a flow rate of 0.360 m³/h)²⁶, the time constant \( \tau \) is equal to 5800 s. According to Eq. 2, the PFOA theoretical concentration at \( t = 2h \) is around 29 mg/L, which is in agreement with the experimental results (\( \approx 25 \text{ mg/L} \)), as shown in Fig. 1(a).

The excess of charge over the need for the first oxidation step of PFOA is used for other electron transfers and by the action of HO• radicals during the degradation of the numerous intermediates. PFOA removal after 6 h was 100%, 98.1%, 97.9% and 97.6% for Pt, Steel, Zr and BDD, respectively. Values of the rate constants and regression coefficients are collected in Table 2. It should be noted that the Pt cathode has the best results with a PFOA degradation rate 39% faster than the other tested materials, which exhibit a similar behavior between them. This enhancement is also reflected in the mineralization (Figure 1b), with a 76.1% TOC removal with the BDD-Pt system.
As previously explained, one of the main challenges in PFOA oxidation is the effective breakdown of the C-F bond. PFOA defluorination was followed along the reaction by means of ionic chromatography, as depicted in Figure 1.c. The trend for defluorination was Pt > BDD > Zr > Steel. In this case, the cathode also played an important role, reaching a 58.6% in the case of Pt, against 42-49% for BDD, Zr and steel. Moreover, fluoride release in the first stages of reaction follows a first order, as reflected in Figure 1 and Table 2, where the function of Pt as electrocatalyst is confirmed.

Pt is a common catalyst in hydrodehalogenation reaction of organic molecules, due to its capacity to adsorb hydrogen, providing a catalytic site were the dehalogenation takes place. H2 generation by water electrolysis on the cathode’s surface may be responsible for PFOA hydrodefluorination, following the reaction mechanism shown in Figure 2.

Because PFOA is inert to hydroxyl radicals, its degradation is initiated on the anode by a direct electron transfer reaction to form a perfluoro radical C7F15COO• (Eq.3). This radical loses its carboxylic group (Eq. 4) and reacts with HO• leading to the generation of C7F13CF2OH (Eq. 5), as previously described by Zhang et al.28

\[
\begin{align*}
    BDD + C_7F_{15}COO^- & \rightarrow BDD + C_7F_{15}COO^* + e^- \quad \text{Eq. 3} \\
    C_7F_{15}COO^* & \rightarrow C_7F_{15}^* + CO_2 \quad \text{Eq. 4} \\
    C_7F_{15}^* + HO^* & \rightarrow C_7F_{15}OH \quad \text{Eq. 5}
\end{align*}
\]

This alcohol then reacts according to three pathways, (for clarity reasons, only the first one (i) is illustrated in Fig.2):

(i) with adsorbed hydrogen generated by water electro-reduction at the cathode, releasing 2 F− (Eq 6)

\[
C_6F_{13}CF_2OH + 4 H_{ads} \rightarrow C_6F_{13}CH_2OH + 2 HF \quad \text{Eq. 6}
\]

As the first carbon in the alkyl chain is now defluorinated, HO• can attack it once again leading the formation of C6F13COOH. This mechanism is similar to that presented for PFOA photocatalytic degradation by Wang et al.19 and theoretic quantum calculations and experimental data collected by Trojanowicz et al.29 Hence, this step depends strongly on the cathode material.
with hydroxyl radicals leading to the formation of COF$_2$, as related by Niu et al.$^{31}$ and Zhang et al.$^{28}$, following Eqs 7-9:

$$C_7F_{15}OH + HO^* \rightarrow C_7F_{15}O^* + H_2O \quad \text{Eq. 7}$$
$$C_7F_{15}O^* \rightarrow C_6F_{13}^* + COF_2 \quad \text{Eq. 8}$$
$$COF_2 + H_2O \rightarrow CO_2 + 2HF \quad \text{Eq. 9}$$

According to George et al.$^{30}$, hydrolysis of carbonyl fluoride COF$_2$ in the aqueous phase is extremely fast since its half-life is 0.7 s at $T = 273$ K.

Giving the perfluorocarbonyl fluoride (Eq. 10) for which hydrolysis leads the formation of perfluorocarboxylic acid and HF (Eq. 11)$^{28,31}$

$$C_7F_{15}OH \rightarrow C_6F_{13}COF + HF \quad \text{Eq. 10}$$
$$C_6F_{13}COF + H_2O \rightarrow C_6F_{13}COO^- + HF + H^+ \quad \text{Eq. 11}$$

Considering this complex reaction mechanism, it should be noted that TOC decay was faster within the first hour of reaction, then it slowed down (Figure 1b). This is related to the generation of short-chain fluorinated acids (decarboxylation step), which are less active to electro-oxidation processes. In fact, pH value in the Pt system decreased from 4 to 3.2 in 120 min, maintaining this pH until the end of the reaction, which evidences the generation of these acidic species.

Data displayed in Fig. 1 allows to determine the fluoride concentrations produced with respect to the degraded carbon in the form of CO$_2$ (F/CO$_2$) or with respect to the PFOA eliminated over time (F/PFOA). Fig. 3 shows that the PFOA defluorination leads to the formation of 1 to 1.5 fluorine ions per removed atom of carbon in the first three hours of electrolysis. According to the proposed mechanism, this value close to one at the beginning of the electrolysis is related to decarboxylation until the formation of Rf-COF. The kinetic of this step is probably faster than the defluorination stages according to Eqs. 6-9. Besides, part of the process can be attributable to the electrocatalytic hydrogenation of the perfluorocarbonyl fluoride C$_6$F$_{13}$COF that form simultaneously the hydrofluoric acid and the 1,1-dihydroperfluoroalkyl alcohol C$_6$F$_{13}$CH$_2$OH which is stable but easily oxidizable on the BDD anode (cf. Fig. 2). This process is slowed down by the diffusion of the species to the cathode. Not all molecules
undergo the loss of two fluoride atoms, which would explain the value of 1.5 instead of the usual ratio 1.9 present in the initial PFOA molecule.

In addition, Fig. 3 shows the variation of the ratio between the concentration of fluoride ions released and the concentration of the removed PFOA. This ratio varies from 7.7 to 9 for 360 minutes of electrolysis. These values highlight the high, yet incomplete PFOA defluorination. Finally, the ratio between the carbon loss (in the form of CO₂) and the removed PFOA (CO₂/PFOA) is in the order of 6-7, slightly less than 8, i.e. the theoretical value for C₇F₁₅COOH, confirming the formation of reaction intermediates. This ratio decreases during electrolysis, degradation being faster at the beginning until 150 minutes of electrolysis. At this time more than 85% of PFOA has been eliminated. PFOA depletion slows down defluorination and carbon skeleton breaking. In addition, shorter molecular chains could display slower kinetics.

Fig. 4 shows the ratio of fluorine and carbon atoms contained in the chemical intermediates. The molar concentration of F and C atoms contained in the intermediates are defined respectively as follows:

\[ C_{F,\text{intermediates}} = 15 \cdot (C_{PFOA,0} - C_{PFOA,t}) - C_{F^-t} \]  \hspace{1cm} \text{Eq. 12}

\[ C_{C,\text{intermediates}} = TOC_t - TOC_{PFOA,t} \]  \hspace{1cm} \text{Eq. 13}

\( C_{PFOA,0} \) and \( C_{PFOA,t} \) refer to the molar concentration of PFOA at initial time and at time \( t \), respectively; \( C_{F^-t} \) is the molar concentration of fluorine ions at \( t \); \( TOC_t \) and \( TOC_{PFOA,t} \) are the total carbon molar concentration and the carbon molar concentration in the PFOA, respectively.

From Fig. 1, after 360 minutes of electrolysis, the defluorination rate is 59% whereas more than 98% of PFOA and 76% of TOC have been eliminated. Fig. 4 highlights that at this time, the intermediates still contain 24% of carbon and 41% of fluorine. Xiao et al. reached a 90% defluorination and mineralization working at high temperature (T: 80-120ºC), meaning they managed to degrade the short-chain acids. This is in agreement with the results for degradation of phenol in heterogeneous Fenton at high temperature, where maleic, malonic, oxalic and formic acids can be completely degraded, in contrast with room temperature processes. Aiming to verify Xiao et al.’s results, an electrooxidation run at 80ºC was performed using Pt cathode. After 30 min reaction there was an overvoltage on the cell due to damage on the cathode, probably due to HF.
attack (Figure S1 of the Supplementary Material). Hence, high temperature electrooxidation could not be performed in our system and further runs were conducted at 25ºC.

After selecting Pt as the best cathode, within the tested materials, different salts were used as electrolyte, NaClO₄, KNO₃, Na₂SO₄, Na₂S₂O₈ at 3.5 mM. Results for these experiments can be found in Figure 5. As previously reported by Schaefer et al.²⁰, the influence of the electrolyte type on PFOA degradation is very low. Still, significant differences were found for TOC removal where the removal efficiency followed this order Na₂SO₄ (76.1%) > Na₂S₂O₈ (72.6%) > KNO₃ (70.5%) > NaClO₄ (67.1%). Sulfate achieved both a slightly higher mineralization degree and defluorination. This can be explained by the fact that sulfate anions behave as an active electrolyte via the electrochemical generation of the strong oxidizing sulfate radicals SO₄²⁻ on a BDD anode³³,³⁴. Indeed, the oxidation of water at the anode greatly increases locally the pH at the surface leading the formation of HSO₄⁻ from SO₄²⁻. Then HSO₄⁻ reacts with HO⁻ radicals to form sulfate radicals³³,³⁵.

\[
HSO_4^- + HO^* \rightarrow SO_4^{2-} + H_2O \quad k = 6.9 \cdot 10^5 \text{ M}^{-1}\text{s}^{-1} \quad \text{Eq.14}
\]

SO₄²⁻ radical participates in electron transfer reactions and promotes the decarboxylation of carboxylic acids, contrary to HO⁻ which rather acts in hydrogen abstraction or addition³⁶. In addition, sulfate radicals are more stable than hydroxyl radicals (their half-life is 30-40 µs and 10⁻³ µs, respectively).

Considering PFOA degradation with sulfate radicals, the literature review by Yang et al. highlights that the decomposition and defluorination efficiencies increase with a decrease in PFOA chain-length³⁷. Besides, the major role of hydroxyl radicals on PFOA oxidation, the presence of sulfate radicals helps to improve the degradation of the generated intermediates. Qian et al.³⁸ estimated the constant rate of PFOA with sulfate radicals to be 2.59 10⁵ M⁻¹s⁻¹. This is consistent with the highest TOC removal observed in our experiments in presence of sulfate radicals.

Furthermore, sulfate is a more environmentally friendly electrolyte, in comparison to perchlorate and nitrate, which can be considered pollutants by themselves. Thus, the rest of experiments were carried out using Na₂SO₄ 3.5 mM.
Influence of initial pH (pH$_0$) on PFOA degradation was also evaluated working at the natural pH of PFOA solution (pH: 4) and at pH values of 7 and 9. Results for these experiments are shown in Figure 6. As it may be seen in Figure 6d, reaction media is quickly acidified. This is related to both the generation of short chain acids and the reaction between sulfate radicals and water to produce hydroxyl radicals, which also generates protons, as depicted in Eq 2. PFOA decay (Figure 6a) was similar for all the runs. However, pH$_0$ had a great influence in the initial rate for TOC abatement, related to the higher oxidation potential of sulfate radicals in alkaline media$^{39}$. Despite achieving a higher mineralization degree at pH$_0$: 9, the highest defluorination was reached when starting in acidic media.

$$\text{SO}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{HO}^- + \text{SO}_4^{2-}$$  

Eq. 15

So far, the role of the cathode as electrocatalyst in the degradation and defluorination of PFOA has been proved. Also, the influence of several operating conditions has been tested, demonstrating an overall great decontamination working at low electrolyte concentration at mild temperature. Nonetheless, in order to compare the obtained results to that reported in literature we have compared the defluorination degree against the energetic requirements, measured as the applied charge, as shown in Figure 7. As may be seen, both Shaefer et al.$^{20}$ and Urtiaga et al.$^{21}$ boosted the defluorination degree when increasing the applied charge. However, the results presented in this work using Pt cathode at 7.9 mA/cm$^2$, 3.5 mM Na$_2$SO$_4$ at pH$_0$:4 and T:25$^\circ$C are the most competitive in terms of PFOA defluorination against electric charge. In this sense, cathode selection becomes a key point for both increasing the activity and reducing the energy requirements in PFOA electrooxidation.
4. Materials and Methods

4.1. Reactants

Perfluorooctanoic acid (95 wt.%), Na₂SO₄, KNO₃, NaClO₄, Na₂S₂O₈, acetonitrile (ACN), H₂SO₄ and NaOH were supplied by Sigma-Aldrich. All reagents are analytical grade and they were used as received without further purification. Working standard solutions of PFOA and fluoride (NaF from Sigma-Aldrich) were prepared for calibration.

4.2. Experimental set-up

The electrochemical oxidation system consists in a 1-liter thermoregulated glass reservoir connected to the cell through a centrifugal pump. PFOA solution was recycled in the system at 360 L/h flow rate and the temperature was set at 25±1°C. The electrochemical cell is a one-compartment flow filter-press reactor which was operated under galvanostatic conditions using an ELCAL 924 power supply. Electrodes present a 63 cm² active surface and the gap between them was set at 10 mm. All experiences were performed with a BDD anode from Adamant Technologies (Switzerland), which was elaborated by chemical vapor deposition on a conductive substrate of silicium. Zirconium, stainless steel, BDD and Pt (5µm) on Titanium substrate were employed as cathodes. Before each electrolysis, the working electrodes were anodically pretreated (40 mA/cm² for 30 min in 0.1 M H₂SO₄) to clean their surfaces of any possible adsorbed impurities. Then, the system was rinsed by ultrapure water.

In a typical reaction 1 L PFOA solution (100 mg/L) with 3.5 mM Na₂SO₄ as electrolyte at the natural pH of the solution (pH:4) was loaded to the reservoir, preheated to 25°C and recycled through the system. Once the selected temperature was reached, the power supply was turned on and current intensity was set at 0.5 A, representing this the reaction starting time. Samples were taken at regular intervals in the tank. The global volume of samples was less than 10% of the total volume.

4.3. Analytical methods

Samples were periodically withdrawn from the reactors and immediately analyzed. PFOA concentration was measured by high performance liquid chromatography connected with an ultraviolet–visible spectrometry detector (HPLC-UV Agilent 1200 Series HPLC). An ion-exclusion column (ZORBAX Eclipse Plus C18, 100 mm, 1.8µm)
was used as stationary phase. As mobile phase mixture of ACN/4mM H₂SO₄ aqueous solution with a ratio: 3/2 was employed and the column temperature was set to 50 °C. A 60% ACN – 40% mixture was employed at 0.5 mL/min. The detection UV wavelength was set to 206 nm. Total Organic Carbon was quantified using a TOC analyzer (Shimadzu TOC-VSCH). Fluoride was analyzed in an ion chromatograph with chemical suppression (Metrohm 790 IC) using a conductivity detector. A Metrosep A supp 5-250 column (25 cm long, 4 mm diameter) was used as stationary phase and 0.7 mL/min of a 3.2 mM/1 mM aqueous solution of Na₂CO₃ and NaHCO₃, respectively, as mobile phase.

5. Conclusions

PFOA electro-degradation follows a complex mechanism which involves both oxidation reactions on the anode surface and reduction reactions, responsible for the molecule’s defluorination, which take place over the cathode. Electrocatalytic hydrogenation of the unsaturated acyl fluoride R₇COF can be a route for the degradation process. Atomic hydrogen produced in situ at the catalyst surface can form simultaneously the alcohol RFCH₂OH and hydrofluoric acid.

In this work, different cathodes have been used, finding that it plays a key role on PFOA degradation. In this sense, Pt acts as an electrocatalyst due to its higher capacity to produce in situ atomic hydrogen, which seems efficient in hydrodefluorination. It has been also demonstrated that working at low electrolyte concentration (3.5 mM Na₂SO₄), complete PFOA removal can be reached with up to 76.1% TOC abatement and 58.6% defluorination working at the natural pH of the solution (pH₀: 4). The kind of electrolyte employed did not have a significant impact on the overall reaction. Still, slightly better results were achieved using sulfate due to the generation of sulfate radicals. Regarding the influence of the starting pH, higher TOC removal was obtained working at pH₀: 9, whilst at higher pH values PFOA mineralization was hindered. When comparing the results obtained in this work with those reported in literature, it must be remarked that the employed BDD-Pt system allows a higher defluorination degree with a lower energy consumption. In view to render the process economically viable to treat dilute solutions, further experiments are planned to combine the electrochemical process with a preconcentration step (such as filtration or adsorption).
Supplementary material:

Figure S1. Damaged Pt cathode after high temperature PFOA electrooxidation (T:80ºC)

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Juan A. Zazo: supervision, writing: review.

Andre Savall: supervision, data curation, validation, writing: review.

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Jose A. Casas: formal analysis, funding acquisition, supervision, validation, writing: review.
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