



# Kinetics of the electrochemical mineralization of perfluorooctanoic acid on ultrananocrystalline boron doped conductive diamond electrodes



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## ABSTRACT

This work deals with the electrochemical degradation and mineralization of perfluorooctanoic acid (PFOA). Model aqueous solutions of PFOA (100 mg/L) were electro-oxidized under galvanostatic conditions in a flow-by undivided cell provided with a tungsten cathode and an anode formed by a commercial ultrananocrystalline boron doped diamond (BDD) coating on a niobium substrate. A systematic experimental study was conducted in order to analyze the influence of the following operation variables: (i) the supporting electrolyte, NaClO<sub>4</sub> (1.4 and 8.4 g/L) and Na<sub>2</sub>SO<sub>4</sub> (5 g/L); (ii) the applied current density,  $j_{app}$ , in the range 50–200 A/m<sup>2</sup> and (iii) the hydrodynamic conditions, in terms of flowrate in the range  $0.4 \times 10^{-4}$ – $1.7 \times 10^{-4}$  m<sup>3</sup>/s and temperature in the range 293–313 K. After 6 h of treatment and at  $j_{app}$  200 A/m<sup>2</sup>, PFOA removal was higher than 93% and the mineralization ratio, obtained from the decrease of the total organic carbon (TOC) was 95%. The electrochemical generation of hydroxyl radicals in the supporting electrolyte was experimentally measured based on their reaction with dimethyl sulfoxide. The enhanced formation of hydroxyl radicals at higher  $j_{app}$  was related to the faster kinetics of PFOA removal. The fitting of experimental data to the proposed kinetic model provided the first order rate constants of PFOA degradation,  $k_c^1$  that moved from  $2.06 \times 10^{-4}$  to  $15.58 \times 10^{-4}$  s<sup>-1</sup>, when  $j_{app}$  varied from 50 to 200 A/m<sup>2</sup>.

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## 1. Introduction

Among emerging water contaminants, perfluoroalkyl substances (PFASs) are particularly problematic because they are highly persistent, bio-accumulative and have been detected ubiquitously in the abiotic environment, biota, food items and humans, all over the planet (Cornelis et al., 2012; Johansson et al., 2014). PFASs exhibit the special physical–chemical characteristics of chemical and thermal stability, low surface free energy and surface active properties (Lehmeler, 2005). These features have promoted their utilization as water and oil repellents, fire retardants, reactants in polyurethane production and vinyl polymerization, herbicide and insecticide formulations, cosmetics, greases and lubricants, paints, polishes and adhesives. The wide-spread use of PFAS has resulted in an important release of these compounds into the environment, which was estimated at 3200–7300 tons during the period 1950–2004 by direct and indirect emissions (Prevedouros et al., 2006).

Among the PFASs, perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA), are subjected to increasingly intense research. Taking into account their potential toxicity and the extent of their environmental distribution, these compounds have started to be regulated by various international bodies. PFOS is part of the OSPAR List of Chemicals for Priority Action (Ospar, 2011). PFOS and its salts are also included in the Annex B of the Stockholm Convention on Persistent Organic Pollutants (Stockholm-Convention-Secretariat, 2009) and it has been included as a priority substance in the field of European water policy according to Directive 2013/39EC. PFOA is still produced and used, however it is listed in the Candidate List of Substances of Very High Concern under the European regulation REACH (ECHA, 2013).

The scientific community is facing the challenge of developing clean technologies for the treatment at source of the emissions of PFASs and for the abatement of the existing water polluted sites. Among others, literature reports the use of membrane (Thompson et al., 2011), adsorption (Carter and Farrell, 2010; Eschauzier et al., 2012) and/or ion exchange processes (Ochoa-Herrera and Sierra-Alvarez, 2008; Xiao et al., 2012). However, these technologies imply the transfer of the contaminants to a second phase and the generated waste must be managed in

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order to avoid the impact of its disposal on the receiving environment.

The destructive methods aim at the cleavage of the C–F bonds to form  $F^-$  ions. The electrochemical oxidation is a technology that has demonstrated its capacity to degrade refractory organic contaminants such as emerging contaminants contained in the secondary effluents of wastewater treatment plants (Pérez et al., 2010; Urtiaga et al., 2013), polychlorinated dibenzo-p-dioxins and dibenzofurans (Vallejo et al., 2013) and organic pollutants in industrial wastewaters (Urtiaga et al., 2014). Electro-oxidation is presented as a clean alternative since its main reactants are electrons. Furthermore, robustness, versatility and the easy automation are other advantages (Anglada et al., 2009). The anodic material plays a key role, and previous studies have shown the effectiveness of boron doped diamond (BDD),  $SnO_2$  and  $PbO_2$  in the degradation and mineralization of perfluorocarboxylic and perfluorosulfonic acids (Carter and Farrell, 2008; Ochiai et al., 2011; Zhuo et al., 2011; Lin et al., 2012; Niu et al., 2012; Zhao et al., 2013) in model solutions. Whereas the use of electrodes based on tin and lead can be questioned because of the leaching of these toxic metals into the treated waters, the stability and effectiveness of boron doped diamond electrodes make this material an excellent candidate for the effective degradation of PFASs in contaminated waters (Xiao et al., 2011; Zhuo et al., 2012). So far, the effect of electro-oxidation parameters on the PFASs degradation ratio has not been considered in depth and controversial results are found for the studied variables namely, current density, electrolyte solution, pH, initial compound concentration, background electrolyte, temperature and fluid-dynamics. Although some researchers (Ochiai et al., 2011; Lin et al., 2012; Niu et al., 2012, 2013; Zhao et al., 2013; Zhuo et al., 2011) have studied the degradation mechanisms of PFOA, no final pathway is stated.

Usually, BDD electrodes are composed of a boron doped microcrystalline diamond rough film with relatively large grain size (0.5–10  $\mu m$ ) that can contain pinholes and defects (Chaplin et al., 2011). The thickness of the diamond film needs to be of several microns to reduce the number of pinholes (Gruen, 2006). Some examples of microcrystalline BDD commercial electrodes can be found in previous electro-oxidation studies of PFASs (Fryda et al., 2003; Liao and Farrell, 2009).

In the present study a new ultrananocrystalline boron doped conductive diamond (UNCD) electrode provided with a thin film coating and nanoscale grain size was tested in the electro-oxidation of perfluorooctanoic acid. Towards that end, a commercial electro-oxidation flow-by undivided cell was used. The influence of the main process variables on the PFOA degradation kinetics, i.e.: applied current density, electrolyte composition, recirculation flow rate and temperature, the mineralization degree and the fluoride generation, is presented. Moreover, the generation of oxidant species, e.g.: hydroxyl radicals and hydrogen peroxide, is related to the process variables and to the kinetic analysis of PFOA degradation.

## 2. Materials and methods

### 2.1. Materials

All chemicals used in the experiments were reagent grade or higher and were used as received without further purification. Perfluorooctanoic acid (PFOA) (96%) was purchased from Sigma Aldrich Chemicals. Dihydrogen phosphate (99%), sodium sulfate (99%) and methanol were obtained from Panreac (Spain), while sodium perchlorate monohydrate (98%) was purchased to Merck. PFOA was dissolved in ultrapure water (Q-POD Millipore) to prepare feed solutions with an initial concentration of  $100 \text{ mg L}^{-1}$

( $0.24 \text{ mol m}^{-3}$ ). Sodium perchlorate 1.4 and  $8.4 \text{ g L}^{-1}$  ( $10 \text{ mol m}^{-3}$  and  $60 \text{ mol m}^{-3}$ ) and sodium sulfate  $5 \text{ g L}^{-1}$  ( $35.2 \text{ mol m}^{-3}$ ) were used as electrolytes.

### 2.2. Electrochemical experiments

Fig. 1 shows a diagram of the experimental set-up used in the electro-oxidation experiments. It consisted of a tank in which the feed solution was stored before it started to circulate through the electrochemical cell by means of a magnetic pump. All experiments were carried out in discontinuous mode, i.e. the PFOA solution was continuously circulated from the reservoir to the cell and back to the tank in a closed loop. The recirculation flowrate was set at  $1.11 \times 10^{-4} \text{ m}^3 \text{ s}^{-1}$ , unless otherwise stated. The temperature was maintained at  $293 \pm 2 \text{ K}$  by circulating a cooling fluid through the jacket of the feed tank, unless otherwise stated. The single compartment electrochemical cell (Diamonox 40) was supplied by Advanced Diamond Technologies (Romeoville, U.S.A.). The cell is comprised of two rectangular electrodes disposed in parallel with a surface area of  $42 \times 10^{-4} \text{ m}^2$  each. The anode is made of a boron doped ultrananocrystalline diamond (UNCD) coating (2  $\mu m$  film thickness and 3–5 nm of average grain size) on a niobium substrate while tungsten was employed as cathodic material. The distance between electrodes was  $8 \times 10^{-3} \text{ m}$ . The electric power required during the electro-oxidation experiments was provided by a laboratory power supply (75-H-Y3005D Vitrico) with a maximum output of 5 A and 30 V. The experiments were performed at constant current density. Samples were withdrawn from the feed tank at regular time intervals and preserved in the refrigerator at  $4 \text{ }^\circ\text{C}$  until analysis.

### 2.3. Analytical methods

The concentration of PFOA was determined using a HPLC-DAD system (Waters 2695) equipped with a X Bridge C18 column (5  $\mu m$ ,  $250 \text{ mm} \times 4.6 \text{ mm}$ , Waters) and UV-Visible spectrophotometric detector. The separation column was set in an oven at  $40 \text{ }^\circ\text{C}$ . A mixture of methanol (65%) and di-hydrogen phosphate (35%) was used as mobile phase in an isocratic mode with a flow rate of 0.5 ml/min. The variable wavelength of the detector was set at 204 nm. The limit of quantification was  $7.4 \text{ mg L}^{-1}$ .

TOC analyses were performed using a TOC-V CPH (Shimadzu). The concentration of fluoride ion was measured by ion chromatography using an ICS-1100 system (Dionex) equipped with an Ion-Pac-AS9HC column and a conductivity detector. A solution of sodium carbonate ( $9 \text{ mol m}^{-3}$ ) was used as mobile phase and the flow rate was set at  $1 \text{ mL min}^{-1}$ .

The determination of hydrogen peroxide was performed by using a specific kit, Merckoquant Peroxide Test (118789 Spectroquant), suitable for determining  $H_2O_2$  concentrations in the range  $0.0001\text{--}0.18 \text{ mol m}^{-3}$ . The method for the hydroxyl radicals determination was adapted from Tai et al. (2004). The method is based on the reaction between hydroxyl radicals and dimethyl sulfoxide to produce formaldehyde quantitatively, which then reacts with 2,4-dinitrophenylhydrazine (DNPH) to form the corresponding hydrazone that is finally analyzed by HPLC-UV.

## 3. Results and discussion

### 3.1. Influence of the electrolyte

Preliminary experiments were performed in order to select an adequate supporting electrolyte. Previous studies (Liao and Farrell, 2009; Ochiai et al., 2011; Zhuo et al., 2012) reported the use of sodium perchlorate as it is an inert compound towards

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