Highlights

- Electrochemical degradation and mineralization of perfluorooctanoic acid is achieved
- Novel ultrananocrystalline boron doped conductive diamond electrode is applied
- Increasing the applied current density enhanced the kinetics of PFOA mineralization
- Hydroxyl radical formation is related to the kinetics of PFOA degradation

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, $NaClO_4$ (1.4 and 8.4 g/L) and Na_2SO_4 (5 g/L); ii) the applied current density, j_{app}, in the range 50-200 A/m^2 and iii) the hydrodynamic conditions, in terms of flowrate in the range 0.4×10^{-4} -1.7×10^{-4} m^3/s and temperature in the range 293-313 K. After 6 hours of treatment and at j_{app} 200 A/m^2, 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 2.06×10^{-4} to 15.58×10^{-4} s^{-1}, when j_{app} varied from 50 to 200 A/m^2.

Keywords

perfluorooctanoic acid, ultrananocrystalline boron doped diamond anode, electrochemical oxidation, perfluoroalkyl susbtances, hydroxyl radicals

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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; Johanson et al., 2014). PFASs exhibit the special physical-chemical characteristics of chemical and thermal stability, low surface free energy and surface active properties (Lehmler, 2005). These features have promoted their utilization as water and oil repellents, fire retardants, reactants in polyurethane production and vinyl polimerization, 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 2013/39/EC. 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 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 (Ochiai et al., 2011; Zhuo et al., 2011; Zhao et al., 2013; Lin et al., 2012; Carter and Farrell, 2008; Niu et al., 2012) 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 (Lin et al., 2012; Niu et al., 2012, 2013; Ochiai et al., 2011; 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 μm) 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 phospate (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 mg/L (0.24 mol/m^3). Sodium perchlorate 1.4 and 8.4 g/L (10 mol/m^3 and 60 mol/m^3) and sodium sulfate 5 g/L (35.2 mol/m^3) were used as electrolytes.

2.2 *Electrochemical experiments*

Figure 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 electrolytic 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 1.11×10^{-4} m^3/s, unless otherwise stated. The temperature was maintained at 293 ± 2 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 42×10^{-4} m^2 each. The anode is made of a boron doped ultrananocrystalline diamond (UNCD) coating (2 μm 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 8×10^{-3} 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 ºC 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 (5µm, 250 mm x 4.6 mm, Waters) and UV-Visible spectrophotometric detector. The separation column was set in an oven at 40 ºC. 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 mg/L.

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 IonPac-AS9HC column and a conductivity detector. A solution of sodium carbonate (9 mol/m^3) was used as mobile phase and the flow rate was set at 1 mL/min.

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 - 0.18 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 (Zhuo et al., 2012; Ochiai et al., 2011; Liao and Farrell, 2009) reported the use of sodium perchlorate as it is an inert compound towards oxidation at conductive diamond electrodes. Fig. 2a shows the evolution of PFOA concentration with the electrolysis time for two different concentrations of sodium perchlorate, 1.4 and 8.4 g/L. The measured conductivities of the two initial solutions were 0.11 and 0.57 Sm^{-1}, respectively. A small, although significant increase of the PFOA degradation kinetics is observed at the lowest electrolyte concentration. This positive kinetic effect could be related to the higher cell voltage, depicted in Fig. 2b, obtained as a consequence of the lower conductivity of the electrolyte, which is inversely proportional to the system resistance and according to the Ohm`s law, a higher voltage is expected. Although the anode voltage could not be directly measured in this type of experimental set-up, it is hypothesized that at the higher cell voltage obtained for sodium perchlorate 1.4 g/L, the electrode voltage was also higher and the oxidation potential was increased, resulting in the observed increase of the PFOA degradation rate. However, $NaClO_4$ should be avoided in the treatment of real wastewaters, since this compound is considered as a contaminant itself, that is, perchlorate may have an adverse effect on the health of persons (EPA, 2011). Sodium sulfate is a safer electrolyte that is widely employed in the electrochemical practice (Niu et al., 2013; Xiao et al., 2011; Zhao et al., 2013). Fig. 2a compares the degradation of PFOA using sodium sulfate (5 g/L) and sodium perchlorate (8.4 g/L) as electrolytes. The conductivity of the initial sodium sulfate solution was 0.63 Sm^{-1}. It is observed that PFOA degradation rates were not influenced by the type of electrolyte, as the experimental trends of concentration and voltage are practically overlapped. Moreover,

PFOA electro-oxidation kinetics were not enhanced by the use of sulfate as electrolyte, thus it is concluded that at the conditions applied in the present study, the use of sodium sulfate did not promote the generation of secondary oxidants that could contribute to the degradation of PFOA.

3.2. Influence of the applied current density

The effect of the applied current density on the degradation rates of PFOA was investigated in the range of j_{app} values of 50, 100 and 200 A/m^2. Experimental data of the change of PFOA, TOC and fluoride concentrations are shown in Fig. 3. It is observed that the kinetics of PFOA degradation was significantly enhanced when increasing the applied current density from 50 to 100 A/m^2, although the effect of a further increase of j_{app} to 200 A/m^2 was less significant.

The influence of current density on the electro-oxidation of PFASs on conductive diamond electrodes has been previously studied by several authors, with differing conclusions. Zhuo et al. (2012) reported the PFOA degradation (50 mg/L) on non-commercial Si/BDD; the authors observed that the applied current density in the range 5.9-58.8 A/m^2 exerted a small influence on the first order degradation rate; similar outcomes were found by Carter & Farrell (2008) when dealing with the degradation of perfluorooctane sulfonate (PFOS) using commercial BDD anodes purchased to Adamant Technologies in the range $10 < j_{app} < 200$ A/m^2, although they observed zeroth order PFOS degradation kinetics. On the contrary, Ochiai et al. (2011) showed that PFOA removal using commercial BDD anodes obtained from Condias was enhanced at higher j_{app}, although the decomposition rate was saturated for current densities over 6 A/m^2; Liao & Farrell (2009) also reported that the perfluorobutane sulfonate (PFBS)

electro-oxidation rates were enhanced at increasing values of j_{app} in the range 5-200 A/m^2.

TOC was measured as an indicator of PFOA mineralization. Fig. 3b shows that TOC decreased in a similar manner as PFOA concentration did. However, TOC evolution is slightly slower than PFOA degradation, and the effect of the applied current density is more significant when changing j_{app} from 100 to 200 A/m^2, as it also happens in the generation of fluoride anions (Fig. 3c). This is an evidence of the formation of intermediate oxidation products, smaller perfluorocarboxylic compounds (Lin et al., 2013). Nevertheless, at j_{app} = 200 A/m^2 the low values of TOC obtained after 6 hours of treatment indicate that electro-oxidation with UNCD anode succeeds to mineralize PFOA.

To evaluate the effectiveness of the treatment in terms of PFOA mineralization, the mineralization index (M.I.) was defined (Eq. 1),

$$M.I. = \frac{\Delta TOC_{exp}}{\Delta TOC_{calculated\ from\ PFOA}} \cdot 100 = \frac{TOC_{exp,0} - TOC_{exp,t}}{TOC_{c,0} - TOC_{c,t}} \cdot 100 \qquad (Eq.1)$$

where TOC_{exp} is the experimental value of TOC and TOC_c is the value of TOC calculated from the concentrations of PFOA. The subscripts 0 and t refer to the initial value and to the value at a given experimental time, respectively. The values of M.I. obtained during the course of the electro-oxidation experiments for the different applied current densities are listed in Table 1. It is shown that increasing the applied current density and the electrolysis time provided an increase in the values of the M.I. of PFOA, ranging from 55.8 to 94.9% for 50 and 200 A/m^2, respectively after 6 hours of experiment. This indicates the successful conversion of PFOA into CO_2 and can be

explained due to the enhanced formation of hydroxyl radicals at higher current densities (Kapalka et al., 2008).

It has been referenced (Michaud et al., 2003) that the first step of water oxidation on conductive diamond anodes is the formation of hydroxyl radicals (Eq. 2),

$$H_2O \rightarrow OH\bullet + H^+ + e^- \qquad (Eq.\ 2)$$

In this work, the generation of hydroxyl radicals at different applied current densities was measured. Duplicate experiments (S.D. < 5%) were performed in the absence of PFOA, and the average results are shown in Fig. 4a. It is observed that the increase in the applied current density enhanced the formation of hydroxyl radicals.

According to Michaud et al. (2003) the electro-generated hydroxyl radicals can be involved in four parallel reactions:(i) Oxidation of supporting electrolyte; ii) O_3 formation, iii) BDD combustion and (iv) H_2O_2 formation, electro-generated hydroxyl radicals may react with each other forming hydrogen peroxide near the electrode (Eq. 3); this then diffuses into the bulk of the electrolyte (Eq. 4) or is oxidized to oxygen (Eq. 5),

$$2\ OH\bullet \rightarrow H_2O_2 \qquad (Eq.\ 3)$$

$$H_2O_{2\ electrode} \rightarrow H_2O_{2\ solution} \qquad (Eq.\ 4)$$

$$H_2O_{2\ solution} \rightarrow O_2 + 2\ H^+ + 2\ e^- \qquad (Eq.\ 5)$$

Figure 4b shows the trend of H_2O_2 concentration in the electrolyte during electrolysis in Na_2SO_4 at the three values of the applied current density, j_{app} 50, 100 and 200 A/m^2. The set of reactions (Eqs. 2-5) explains both the presence of hydrogen peroxide in the

electrolyte and the trend of its concentration towards a limiting value that was comprised in the range 0.060-0.070 mol/m^3.

3.3. Effect of the flowrate and temperature

In order to analyze the influence of the hydrodynamic conditions on the kinetics of PFOA removal, the effects of varying the feed flowrate in the range 0.4×10^{-4} -1.7×10^{-4} m^3/s and temperature in the range 293-313 K were experimentally studied (Fig. SM-1 and Fig. SM-2 in Supplementary Material (SM)). Even though the Reynolds number changed from the laminar regime when operating at the lowest flowrate (*Re* = 1371) to the turbulent regime at the highest flowrate (*Re* = 5894) no significant effect was observed either in the removal of PFOA or in the generation of fluoride. Similarly, the effect of changing the process temperature in the studied range did not exert any influence on the evolution of both response variables. This behavior indicates that the kinetics of PFOA degradation by electro-oxidation with UNCD anodes is not limited by mass transfer, regardless the low concentrations employed in the present work.

3.4. Kinetic analysis

The mass balances for the concentration of PFOA applied to the two main elements of the experimental system are written as follows,

Electro-oxidation cell

$$\frac{\partial C_a}{\partial t} = -\frac{Q}{A} \cdot \frac{\partial C_a}{\partial z} - r_a \qquad (Eq.6)$$

Recirculation feed tank

$$V \cdot \frac{dC_{out}}{dt} = Q \cdot C_{a_{in}} - Q \cdot C_{a_{out}} \qquad (Eq.7)$$

Where Q is flow-rate (m^3/s), V is the volume of treated dissolution (m^3), A is the cross section of the fluid circulation channel ($A= d \cdot M$, m^2), C_a is the PFOA concentration (mol/m^3), r_a is the reaction rate of the electro-oxidation process ($mol/m^3/s$), z is the axial position along the cell and t is time (s).

Several assumptions were made for the integration of the mass balances. Firstly, it was considered that in the electro-oxidation cell the variation with time of PFOA concentration was negligible compared to its variation along the axial position $\frac{\partial Ca}{\partial t} \ll \frac{\partial Ca}{\partial z}$, and $\frac{\partial Ca}{\partial t} = 0$. Secondly, first order kinetics is considered for the electro-oxidation process, Eq. (8)

$$r_a = k_c^1 \cdot C_a \qquad (Eq. 8)$$

where k_c^1 is the kinetic constant (s^{-1}). Then Eq. (6) was integrated along the cell length (from z=0 to z=L) and substituted into Eq. (7) by means of Eq. (9) and Eq. (10),

$$C_{a_{z=L}} = C_{a_{in}} \qquad (Eq. 9)$$

$$C_{a_{z=0}} = C_{a_{out}} \qquad (Eq. 10)$$

The resulting mass balance was integrated between the beginning of the experiment (t=0) and a certain time t. The final integrated equations is presented in Eq. (11),

$$V \cdot Ln\left(\frac{C_{a_0}}{C_a}\right) = Q \cdot \left[1 - exp\left(-\frac{k_c^1\, V^{cell}}{Q}\right)\right] t \qquad (Eq. 11)$$

The experimental data of PFOA development given in Fig. 3 were satisfactorily fitted to Eq. (11) as it is shown in Fig. 5. A summary of the results is presented in Table 2. The observed values of the kinetic constant k_c^1 were compared to the mass transport

coefficient (k_m) calculated for the mass transfer of PFOA through the liquid boundary layer within the cell. A standard correlation (Perry, 2007), Eq. (12), for Newtonian fluids circulating in closed channels, was applied,

Turbulent flow regime (2000 <Re< 35000) $$Sh = 0.023 \cdot Re^{0.83} \cdot Sc^{0.44} \quad (Eq. 12)$$

where *Sh*, *Re* and *Sc* are the Sherwood number, Reynolds number and Schmidt number, respectively. Water density and viscosity were used to calculate the diffusion coefficient according to the Wilke-Chang correlation for diffusion of organic compounds in liquids (Perry, 2007), and the obtained value was 5.1×10^{-10} m^2 s^{-1}.Taking into account the surface to volume ratio of the electrochemical cell (A/V = 8.4 m^{-1}), the k_m value for the experiments performed at Q = 1.11x 10^{-4} m^3/s would correspond to a kinetic constant of 2.02×10^{-4} s^{-1}. The value of k_c^1 obtained at j_{app}=50 A/m^2 is 2.06×10^{-4} s^{-1} , that is very close to the theoretical value derived from k_m. Increasing the applied current densities results in values of the apparent kinetic constant of 8.63×10^{-4} s^{-1} (at j_{app}=100 A/m^2) and 15.58×10^{-4} s^{-1} (at j_{app} =200 A/m^2). The difference is assigned to the enhanced secondary oxidation processes in the bulk derived from the higher concentration of electro-generated oxidants at higher current densities. This excludes mass transport limitations in the experimental system. At the same time, the enhancement of PFOA electro-oxidation kinetics by higher applied current densities points to the higher generation of hydroxyl radicals and supports the mechanism that involves the role of hydroxyl radicals in PFOA degradation.

4. Conclusions

This work presents an experimental study on the electrochemical treatment of perfluorooctanoic acid (PFOA) in aqueous solutions using a novel commercial

ultrananocrystalline boron doped diamond anode. The following conclusions can be withdrawn:

1. PFOA degradation and mineralization ratios higher than 90% were easily achieved.

2. First order PFOA degradation rates were observed. The operating variable that exerted the most positive kinetic effect was the applied current density.

3. Increasing the applied current density positively influenced on the hydroxyl radical generation in the electrochemical system. At the same time, the kinetic analysis of the system showed that PFOA degradation rate was not limited by mass transfer. Therefore it was concluded that hydroxyl radicals play a predominant role in PFOA degradation using ultrananocrystalline BDD electrodes.

It is concluded that electro-oxidation with BDD anodes is a promising technology for the treatment of perfluoroalkyl substances in polluted waters.

Appendix A. Supplementary material

Supplementary data on the kinetic evolution of PFOA and fluoride concentrations at variable flowrate and temperature are included.

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Table 1

Table 1. Mineralization index at different current densities

	M.I. (%)		
	j_{app}		
Time (h)	50 A/m^2	100 A/m^2	200 A/m^2
1		57.8	93.4
2	94.9	70.6	81.8
3	87.6	68.7	83.2
4	64.2	75.4	86.1
5	77.5	77.1	85.8
6	55.8	84.1	94.9

Table 2

Table 2. Kinetic parameters that characterize PFOA electrochemical removal. Influence of the applied current density. PFOA 100 mg/L, T=293 K, Na_2SO_4 5 g/L.

j_{app} (A/m^2)	***Q*** (L/min)	***Re***	***Flow regime***	***k_m*** (m/s)	***$k_m(A/V)$*** *(s^{-1})*	***Slope Fig. 5*** (L/h)	***K_c^1 Eq. (11)*** *(s^{-1})*
50	6.67	3838	Turbulent	2.4×10^{-5}	2.02×10^{-4}	0.0249	2.06×10^{-4}
100						0.1101	9.10×10^{-4}
200						0.1896	15.68×10^{-4}

Figure 1

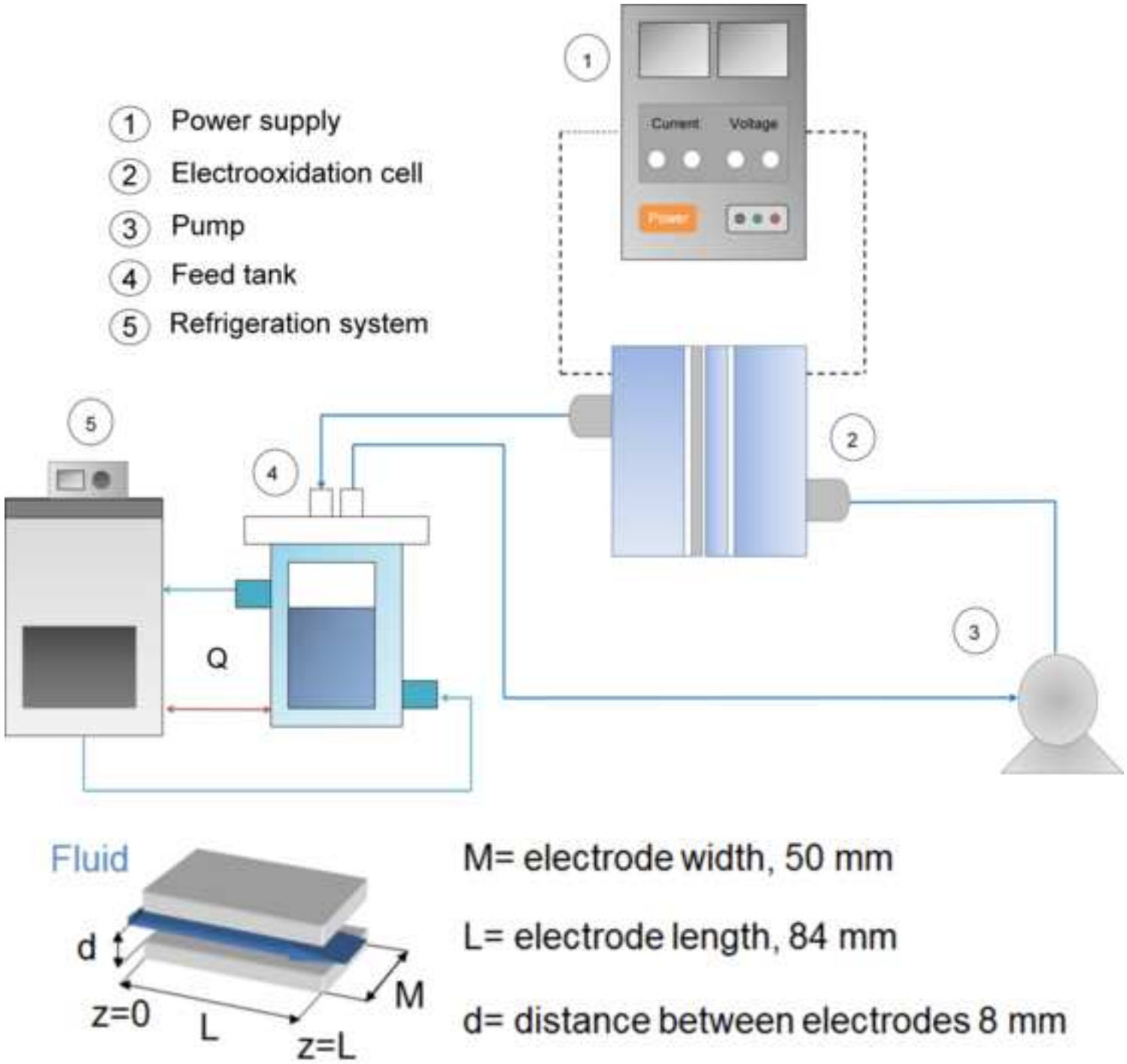
1 Power supply
2 Electrooxidation cell
3 Pump
4 Feed tank
5 Refrigeration system
Current
Voltage
Power
Q
Fluid
d
z=0
L
z=L
M
M= electrode width, 50 mm
L= electrode length, 84 mm
d= distance between electrodes 8 mm

Figure 2

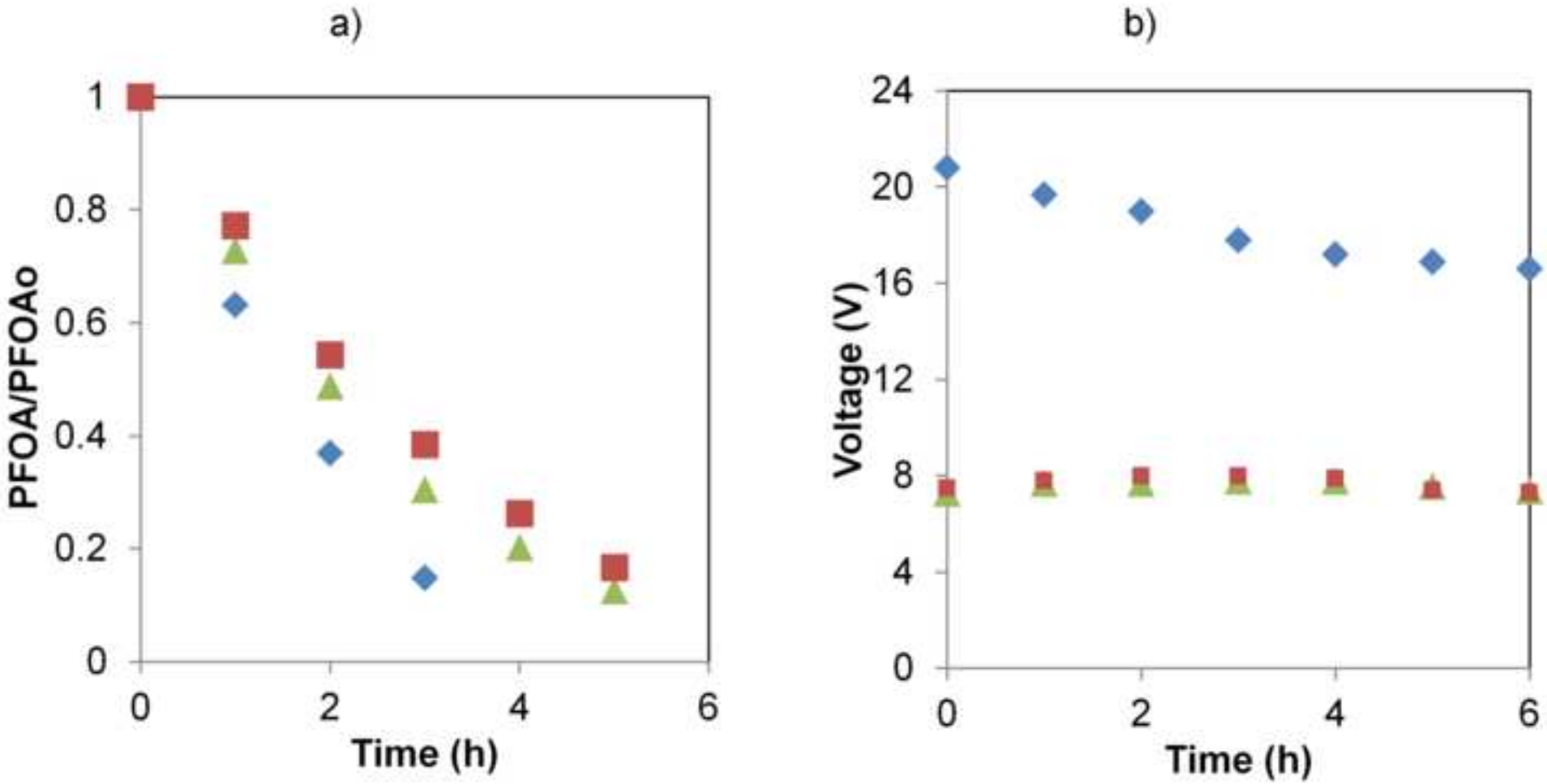
a)
PFOA/PFOAo
1
0.8
0.6
0.4
0.2
0
0
2
4
6
Time (h)
b)
Voltage (V)
24
20
16
12
8
4
0
0
2
4
6
Time (h)

Figure 3

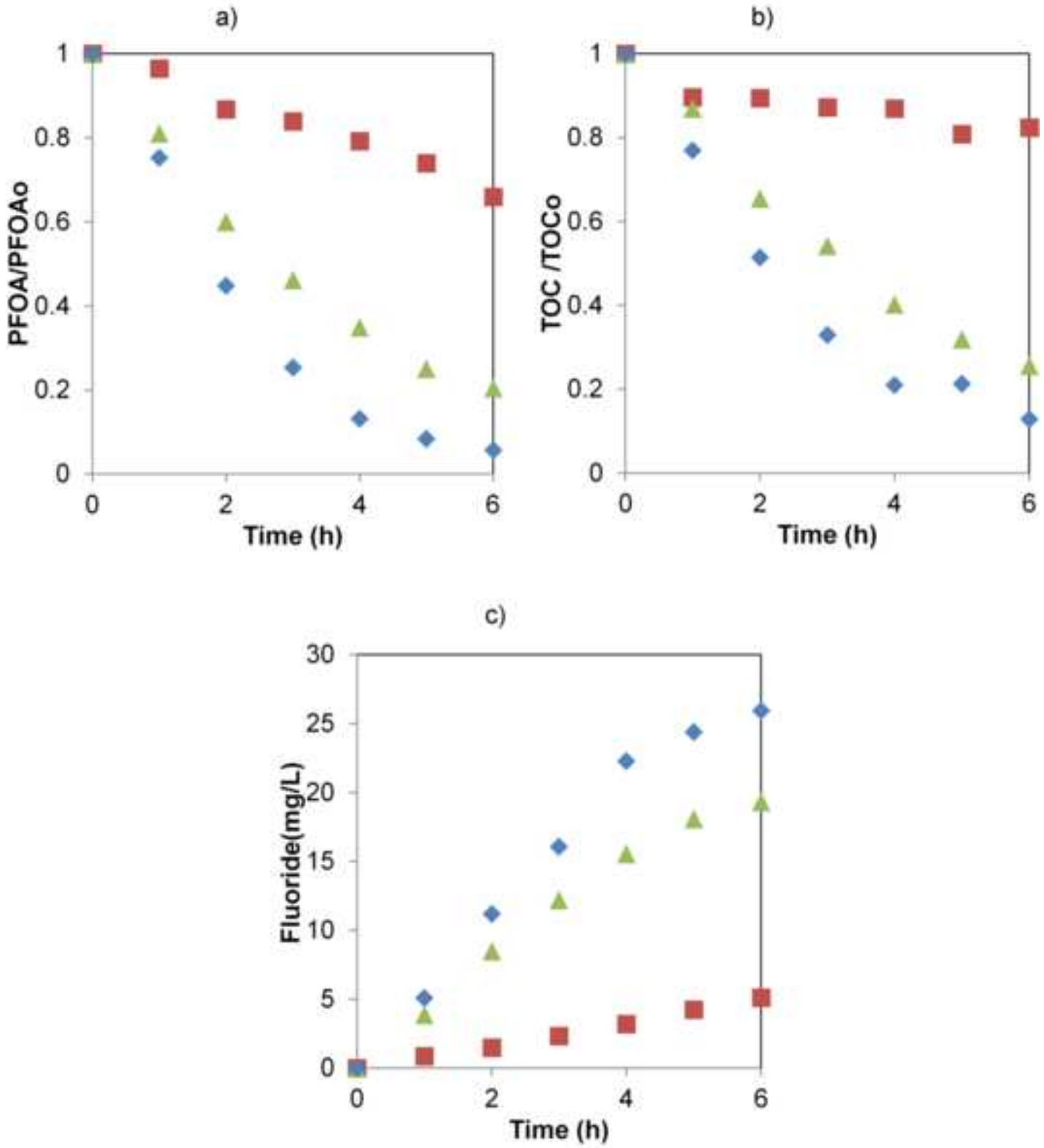

Figure 4

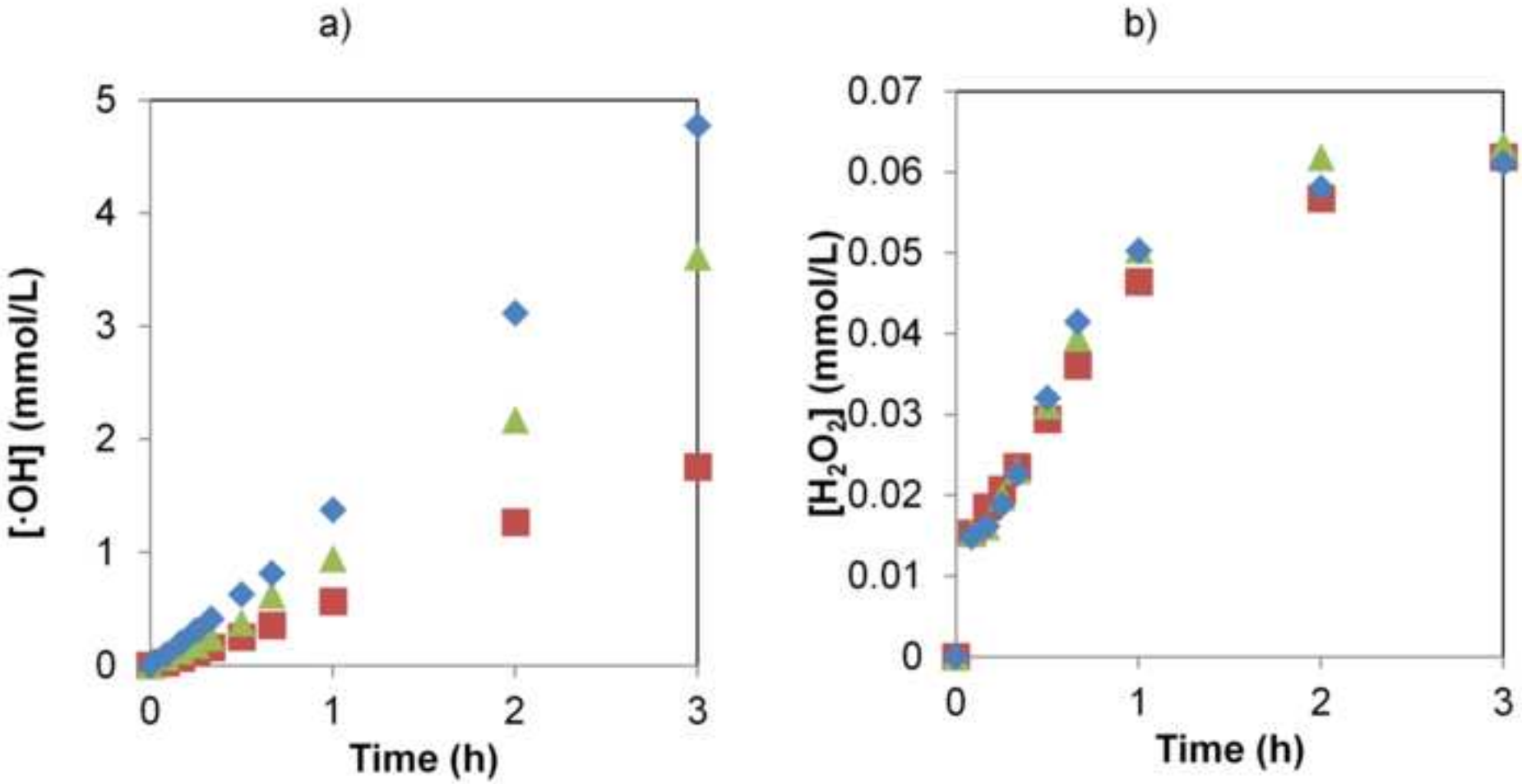
a)
[·OH] (mmol/L)
5
4
3
2
1
0
0
1
2
3
Time (h)
b)
[H2O2] (mmol/L)
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
0
1
2
3
Time (h)

Figure 5

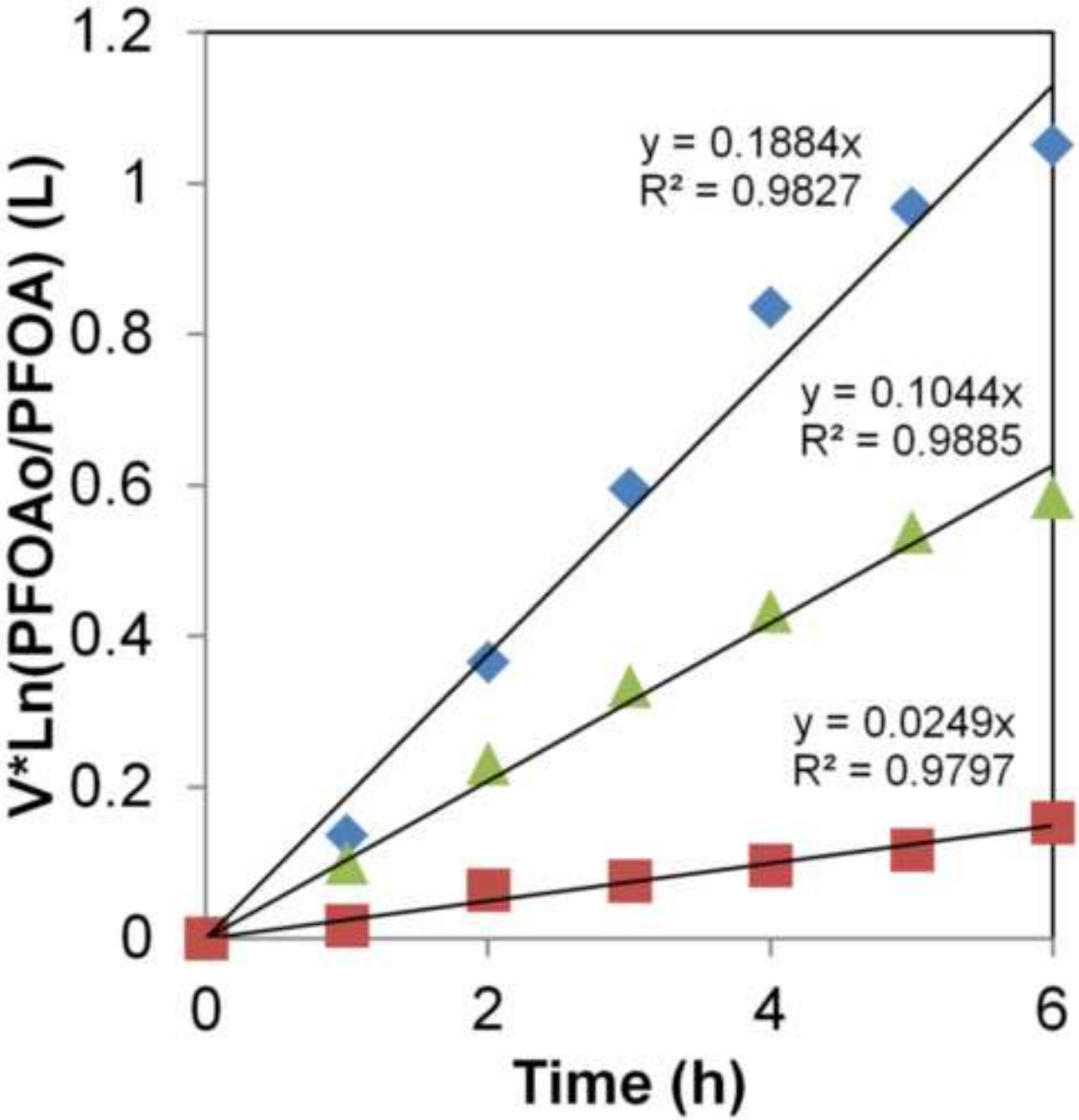
1.2
1
0.8
0.6
0.4
0.2
0
V*Ln(PFOAo/PFOA) (L)
y = 0.1884x
R² = 0.9827
y = 0.1044x
R² = 0.9885
y = 0.0249x
R² = 0.9797
0
2
4
6
Time (h)

Figure captions

Fig. 1. Flow sheet of the experimental system used for the electro-oxidation of PFOA and detail of the electrochemical cell geometry.

Fig. 2. Influence of the electrolyte (a) on PFOA degradation rate; (b) on the cell voltage. (♦) $NaClO_4$, 1.4 g/L; (▲) $NaClO_4$, 8.4 g/L and (■) Na_2SO_4, 5 g/L. T 293 K, j_{app} 200 A/m^2, $PFOA_0$ 100 mg/L.

Fig. 3. Effect of the applied current density on the evolution of (a) PFOA concentration, (b) TOC and (c) Fluoride concentration. (■) j_{app} = 50 A/m^2, (▲) j_{app} = 100 A/m^2, (♦) j_{app} = 200 A/m^2. $PFOA_0$ 100 mg/L, T 293 K, Na_2SO_4 5 g/L.

Fig. 4. Electrolysis on UNCD anodes of the electrolyte Na_2SO_4 5 g/L, DMSO 250 mol/m^3, T 293 K at different current densities: (■) j_{app} = 50 A/m^2, (▲) j_{app} = 100 A/m^2, (♦) j_{app} = 200 A/m^2. (a) Generation of hydroxyl radicals (b) Generation of hydrogen peroxide.

Fig. 5. Fitting of experimental data of PFOA degradation to the kinetic model, Eq. (11) (♦) j_{app} 200 A/m^2; (▲) j_{app} 100 A/m^2; (■) j_{app} 50 A/m^2

Fig. SM-1. Influence of the flowrate on the electrooxidation of PFOA: (♦) 0.4×10^{-4} m^3/s; (■) 1.11×10^{-4}; (▲) 1.7×10^{-4} m^3/s. $PFOA_0$ 100 mg/L, j_{app}=200 A/m^2, T 293 K, Na_2SO_4 5 g/L.

Fig. SM-2. Influence of the temperature on the electrooxidation of PFOA: (■) 293 K; (♦) 303 K; (▲) 313 K. Experimental conditions: j_{app} 200 A/m^2, Na_2SO_4 5 g/L.

SUPPLEMENTARY MATERIAL

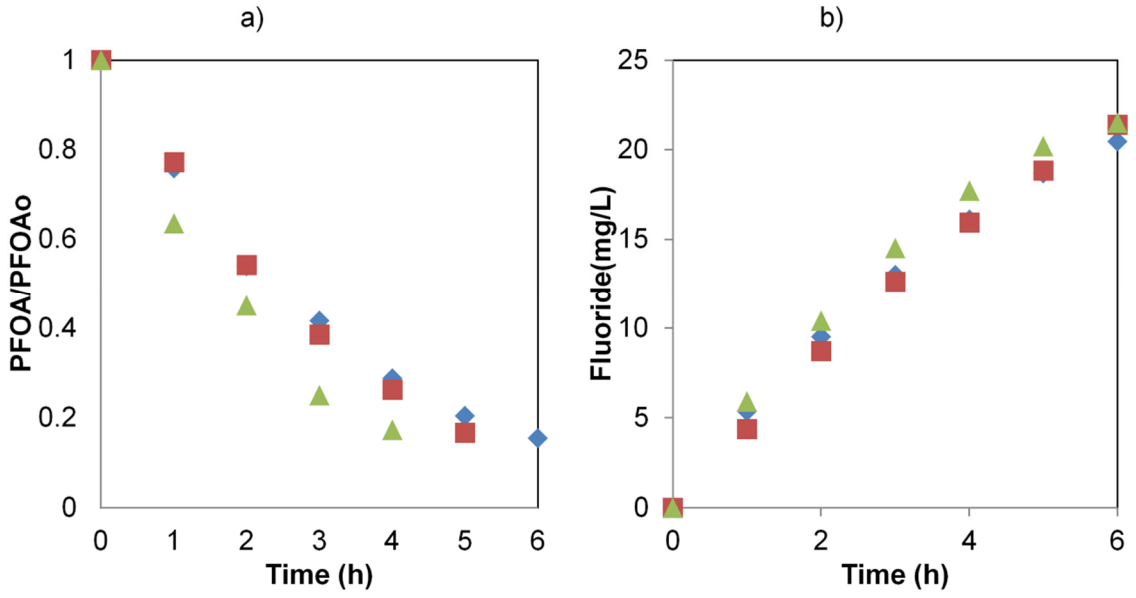

Fig. SM-1. Influence of the flowrate on the electro-oxidation of PFOA: (♦) 0.4×10^{-4} m^3/s; (■) 1.11×10^{-4}; (▲) 1.7×10^{-4} m^3/s. $PFOA_0$ 100 mg/L, j_{app}=200 A/m^2, T 293 K, Na_2SO_4 5 g/L.

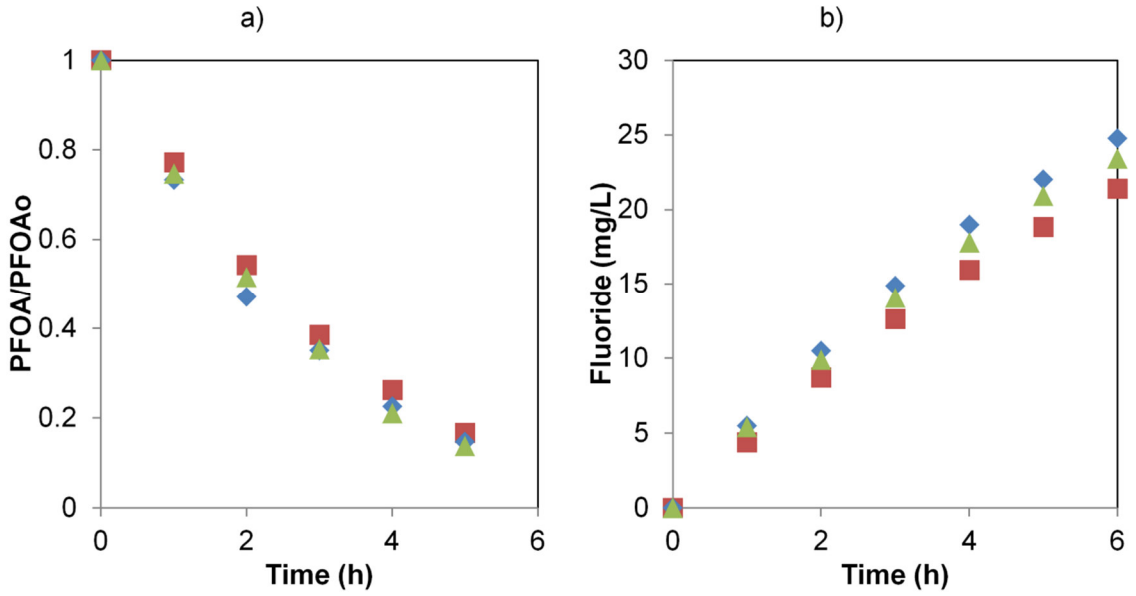

Fig. SM-2. Influence of the temperature on the electro-oxidation of PFOA: (■) 293 K; (♦) 303 K; (▲) 313 K. Experimental conditions: j_{app} 200 A/m^2, Na_2SO_4 5 g/L.