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**Efficient electrochemical degradation of poly- and perfluoroalkyl substances
(PFASs) from the effluents of an industrial wastewater treatment plant**

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ABSTRACT

This paper reports the electrochemical treatment of poly- and perfluoroalkyl substances (PFASs) in the effluent from an industrial wastewater treatment plant (WWTP). While most of the previous research focused on the electrochemical degradation of perfluorooctanoic acid and perfluorooctane sulfonate in model solutions, this work studies the simultaneous removal of 8 PFASs at environmentally relevant concentrations in real industrial emissions, which also contained organic matter and inorganic anions. The overall PFASs content in the WWTP effluent was 1652 $\mu\text{g/L}$, which emphasized the need to develop innovative technologies for the management of PFASs emissions. 6:2 fluorotelomer sulfonamide alkylbetaine (6:2 FTAB) and 6:2 fluorotelomer sulfonate (6:2 FTSA) were the major contributors (92% w/w) to the overall PFASs content, that also contained significant amounts of short-chain perfluorocarboxylic acids (PFCAs). Using a boron doped diamond (BDD) anode of 0.0070 m^2 , the effluent (2 L) was treated by applying a current density of 50 mA/cm^2 for 10 hours, that resulted in 99.7% PFASs removal. The operation at lower current densities (5 and 10 mA/cm^2) evidenced the initial degradation of 6:2 fluorotelomers into perfluoroheptanoic and perfluorohexanoic acids, that were later degraded into shorter chain PFCAs. The high TOC removal, >90%, and the fluoride release revealed that PFASs mineralization was effective. These results highlight the potential of the electrochemical technology for the treatment of PFASs contained in industrial wastewaters, which nowadays stands as the main source of this group of persistent pollutants into the environment.

Keywords: perfluoroalkyl substances (PFASs), 6:2 fluorotelomers, perfluorocarboxylates, electrochemical oxidation, boron doped diamond anode (BDD), industrial wastewater

1. INTRODUCTION

Poly- and perfluoroalkyl substances (PFASs) have been synthesized and widely used in industrial and commercial applications since the 1950s [1]. Releases of perfluoroalkyl carboxylic acids (PFCAs) into the environment during the period 1950-2004 were estimated to be 3200-7300 tons. The contribution of direct sources that result from the manufacture and use of PFCAs were estimated to be in the range 3200-6900 ton, most of them used as processing aids in the manufacture of fluoropolymers [2,3]. Therefore, historically PFASs emissions are dominated by industrial manufacturing processes.

Recently, perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) have been subjected to increasingly intense research due to their potential toxicity and the extent of their environmental distribution [4]. PFOS and its salts are included in the Annex B of the Stockholm Convention on Persistent Organic Pollutants (POPs) [5]. In addition, PFOS is part of the OSPAR List of Chemicals for Priority Action [6] and is also listed as a priority substance in the field of European water policy according to Directive 2013/39/EC [7]. U.S. EPA has also established the health advisory level at 70 parts per trillion of combined PFOA and PFOS in drinking water [8].

The scientific community is now facing the challenge of developing new technologies for the treatment at source of PFASs emissions, and where necessary, to abate the pollution already introduced in the environment. Many of the already published studies emphasize the low efficiency of the conventional water treatment technologies for the elimination of PFASs [9]. It is thought that PFASs removal takes place by adsorption onto sludge, although the biodegradation of some precursors might contribute to the observed increase of PFCAs concentrations in wastewater treatment processes [10], as it happens in AFFF (Aqueous Film Forming Foams) impacted soils and groundwaters

[11]. Several studies have reported that activated carbon adsorption and reverse osmosis remove significant amounts of PFASs [10, 12-16]. However, these are physical separation technologies that transfer the contaminants from the water phase to a second phase that still needs to be treated, and that work properly only for long-chain PFASs. Because of this reason, advanced oxidation processes [17] such as persulfate addition [18], photocatalysis [19-20], and particularly electrochemical oxidation are receiving growing attention [21]. Electrochemical oxidation has the advantages of mild temperature and pressure operating conditions, versatility and ease of operation [22-25]. Furthermore, the efficiency of this process has already been assessed for landfill leachates [26], recalcitrant compounds in industrial wastewater [27], pharmaceuticals in reverse osmosis concentrates [28], and other emerging contaminants contained in the secondary effluents of wastewater treatment plants (WWTP) [29-31].

The ability of electrochemical technologies for PFASs degradation is now under intensive research. Most of the previous studies were focused on the selection of the anodic material. “Non-active” anodes such as SnO_2 , PbO_2 and boron doped diamond (BDD), provided high mineralization of PFOA and some perfluoroalkane sulfonic acids [24,32-35]. The electrochemical efficiency of the anode material depends on its electron transfer ability, as well as on its hydroxyl radical ($\text{HO}\cdot$) generation capacity. To improve the treatment efficiency some studies paid attention to the optimization of the experimental conditions, such as cell potential, current density and pH, as it has been recently reviewed [34]. Even though previous studies of electrochemical degradation of PFASs have shown promising results, most of the studies were performed using model solutions of single PFASs upon addition of an electrolyte, and using initial concentrations in the range of ten to hundred milligrams per liter, which are much higher than the concentrations usually found in polluted groundwater or even in

industrial effluents. Very few studies dealt with real water samples under environmental conditions. Exceptions include the recent studies that demonstrated the electrochemical degradation of PFOA and PFOS in groundwaters impacted by the use of AFFFs [35, 36]. Particularly, the removal of PFASs from heavily contaminated industrial wastewaters has not been reported yet.

The present innovative work analyzes the electrooxidation of PFASs in real effluents from an industrial WWTP. This water treatment facility was selected based on the wide variety and the high amount of PFASs contained in the effluent, as it will be shown later on. BDD anodic material was selected due to its high stability, low adsorption capacity, high overpotential for oxygen generation and long life span, and moreover, because of its proven capacity to degrade non-biodegradable organic compounds [26]. Both the influent and the effluent streams of the industrial WWTP were physico-chemically characterized. The electrochemical degradation and mineralization of 8 PFASs were evaluated in the WWTP effluent, together with the reduction of major organic pollution parameters such as total organic carbon (TOC). The formation and degradation of intermediate PFCAs, which were generated as degradation products of the most abundant fluorotelomers, is also reported. In addition, the effect of the applied current density (j), on the rate of PFASs degradation is also reported.

2. MATERIALS AND METHODS

2.1. Materials and wastewater samples

Grab samples, 50 liters each, of the influent (I) and effluent (E) streams from an industrial WWTP located in France were obtained in one sampling campaign in 2015. It is worthy to note that both I and E samples were simultaneously collected, so the effluent sample did not come from the influent sample, as the residence time in the

treatment plant (nine days) was not taken into account. Four manufacturing plants discharge their wastewater into the WWTP, but only one of them produces side-chain-fluorinated polymers and fluorotelomer based products for fire-fighting foams. This chemicals manufacturer contributes with 3 to 17% to the overall flow treated in the industrial WWTP. More details on the WWTP facility, including the description of the conventional treatment stages, were recently described elsewhere [37]. The same study estimated the PFASs release from this WWTP facility in the range of 21-247 g/day of PFCAs and 1,622-6,963 g/day of fluorotelomers, taking into account the variations observed in several sampling campaigns.

Table 1 summarizes the characteristics of I and E samples, including the concentration of the PFAS (ng/L) that were found over the limits of quantification (LOQ) of the analytical procedure. The chemical structure of these compounds is provided in Table 2. The analytical method included perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSAs), n:2 fluorotelomer carboxylic acids (n:2 FTCAs), n:2 unsaturated fluorotelomer carboxylic acids (n:2 FTUCAs), n:2 fluorotelomer sulfonic acids (n:2 FTSA), perfluorooctane sulfonamide (FOSA), 6:2 FTAB and 6:2 fluorotelomer sulfonamide propyl N,N dimethylamine. The latter compound, which has been identified in several previous works [38,39] will be named M4, following the simplified nomenclature reported by Moe et al. (2012) [40]. It can be observed that the concentration of Σ PFASs included in the analytical survey was 1402 $\mu\text{g/L}$ in the influent and 1652 $\mu\text{g/L}$ in the WWTP effluent. Moreover, the conventional water treatment technologies applied at this WWTP resulted in a considerable increase in the concentration of 6:2 FTSA, as well as all PFCAs.

The most abundant PFASs in the influent was 6:2 FTAB (6:2 Fluorotelomer

sulphonamide alkybetaine) followed by 6:2 FTSA (6:2 Fluorotelomer sulphonic acid), and M4. As it can be seen in Table 2 the bio-oxidative breakdown of 6:2 FTAB and M4 at the S-NH position can give rise to both 6:2 FTSA and PFHxA (Perfluorohexanoic acid) [41-43]. An explanation for the observed increase in the PFHpA (Perfluoroheptanoic acid) concentration is not readily available, although it could be due to the bio-degradation of unknown 8:2 fluorotelomer compounds not included as target analytes in the current research [17,44]. It is also worthy to mention that a recent study by Dauchy et al. [37] on the characterization of PFASs mass flow rates in the same WWTP recognized the presence of PFHpA precursors by means of an oxidative conversion analytical method [44]. These results emphasize the low efficiency of the conventional water treatment technologies for the removal of PFASs, and the need to develop advanced treatments specially designed for PFASs degradation.

2.2. Electrochemical experiments

Electro-oxidation treatment was applied to the effluent sample. Experiments were performed at laboratory scale in an undivided flow-by cell (Diacell 106, Adamant Technologies, Switzerland) formed by two circular parallel electrodes: a BDD anode and a stainless steel cathode, each one with a surface area of 70 cm² and an electrode gap of 5 mm. The cell was connected to a power supply (Agilent 6654 A) and experiments were performed under galvanostatic conditions. Figure S1 shows a diagram of the experimental set-up, and further details can be found in previous works [26, 28]. Aliquots (volume=2 L) of the E sample were introduced in the feed jacketed glass tank (temperature = 20 °C), and the fluid was circulated at a flowrate of 3 L/min, from the feed tank to the electrooxidation cell and back to the tank. Most of the experiments were performed at a current density of 50 mA/cm². In these conditions, the voltage developed by the cell varied in the range 13.9 – 15.3 V. In addition, different current densities (2, 5

and 10 mA/cm²) were applied to assess their effect on the removal rate of PFASs and TOC from the WWTP effluent. The salts content of the effluent sample was enough to provide the adequate conductivity for the electrochemical treatment. Treated liquid samples were collected in polypropylene containers, and stored in the refrigerator at 4 °C until they were delivered for analysis. Gas phase sampling was not considered, even though it could contain small amount of short-chain volatile PFCAs as final products of the electrochemical treatment. Each point of the kinetic experiments shown in Figures 3 and 4 was obtained as a single electrochemical experiment. This way of operation allowed to keep constant the feed volume along the electrochemical treatment time. Preliminary experiments using a model solution of PFOA (100 mg/L) were conducted in the absence of current, to check that the concentration of PFOA was maintained within $\pm 5\%$ of the initial value, thus showing that adsorption of PFASs in the experimental system could be minimized.

2.3. Analytical methods

TOC analyses were performed using a TOC-V CPH (Shimadzu). Chemical oxygen demand (COD) was determined by the closed reflux and colorimetric method following the procedure 5220D from Standard Methods [45]. Anions were determined by ion chromatography (Dionex 120 IC) provided with an IonPac As-HC column, using a solution of 9 mM of Na₂CO₃ as eluent, with a flowrate of 1 mL/min and a pressure of 2000 psi, based on Standard Methods 4110B. Free chlorine was determined following the N,N-Diethyl-p-phenylene diamine (DPD) Ferrous Titrimetric Method according to Standard Methods 4500-Cl. pH was measured using a portable pH-meter.

The detailed protocol of the PFASs analysis has been recently published [46]. Briefly, non-filtered water samples were diluted prior to extraction, purification and pre-

concentration by a solid-phase extraction (SPE) procedure (Strata X-AW[®] (200 mg, 6 mL) cartridge (Phenomenex, Torrance, CA)). Recovery rates of the SPE procedure were reported elsewhere [46]. An ultra-high performance liquid chromatograph coupled to tandem mass spectrometer (UHPLC-MS/MS) in negative electrospray ionisation (ESI) mode was employed to separate and detect targeted compounds (Waters Xevo TQ-MS tandem mass spectrometer (Waters Corporation, Milford, MA, USA)). Table S2 lists the MS/MS transitions, cone voltages and collision energies applied for the different target analytes and isotope labelled standards. Twelve labelled internal standards (IS) were used to provide an adequate correction compensating for matrix effects. Due to initial dilutions, LOQs were between 2 to 5 µg/L in water samples depending on the analytes (see Table S1 of supporting information).

3. RESULTS AND DISCUSSION

3.1. Evolution of chloride and TOC

The unknown nature of the industrial wastewaters under study and the complexity of their matrix components suggested to study the evolution with time of the major pollutants. TOC acts as an indicator of mineralization of the overall organic pollutants load. Particular attention was paid to chlorine species, in order to identify the operating conditions that would prevent the formation of undesirable perchlorate.

Figure 1 reports the evolution of the concentration of chlorine species with time. Firstly, the depletion of chloride (Figure 1, a) as a result of its anodic oxidation generated the increase of free chlorine (Figure 1, b). During the formation of free chlorine, that occurred in the initial 4 hours, the sample slightly reduced its bulk pH from 7.36 to 6.47. Therefore, hypochlorous acid was the most abundant chlorine species in solution. Free chlorine is not expected to promote the degradation of PFASs, e.g.: Schaefer et al.

[47] showed that the presence of chloride had a minimal effect on the observed rate constants for PFOA removal from groundwaters, by BDD electrochemical treatment, compared to the absence of chloride. After 4 hours of treatment, free chloride started to decrease (Figure 1, b), in coincidence with the depletion of its chloride precursor and the formation of more oxidized chlorine species, such as chlorate (Figure 1, c) and perchlorate (Figure 1, d). Nevertheless, it is also observed that the formation of hazardous perchlorate was avoided in a period up to 4 hours of electrochemical treatment when most of the PFASs were degraded, as it will be shown below. The total concentration of all chlorine species at 10 hours (42.4 ± 0.9 mM) was quite similar to the value at the beginning of the experiment (38.2 ± 1.6 mM), and the small increase could be assigned both to the experimental error or to the release of chloride upon oxidation of organochlorinated compounds [22].

The TOC removal of the industrial WWTP effluent is given in Figure 2. A reduction of 91.1 ± 0.31 % was achieved when working at a current density of 50 mA/cm², showing the good performance of the BDD anodes for the mineralization of recalcitrant organic pollutants. If we look back to Table 1, the treatment applied in the WWTP achieved a significant removal of both COD and TOC, so the remaining TOC in the effluent was mostly assigned to non-identified soluble organic compounds that are refractory to traditional physico-chemical and biological treatments. The effect of the applied current density on the TOC removal was examined at 2, 5, 10 and 50 mA/cm². At the low current regime (2 mA/cm²) the TOC development was slow, and showed zero order kinetics, which is typically observed when electrolysis is under current control. By increasing the applied current density to 50 mA/cm² the observed kinetics changed to first order, which is usually found when the electrolysis is under mass transport control [48,49]. The use of intermediate current densities (5 and 10 mA/cm²) originated TOC

removal rates which fell in the middle, that in the case of 5 mA/cm^2 showed an initial zero order trend followed by a first order trend after 3 hours of treatment. The complex reaction scheme involved in the BDD electrooxidation of chloride-rich waters requires a detailed analysis of the operating conditions that enable the removal of TOC and at the same time the minimization of undesirable chlorinated species. Our previous studies using BDD electrodes to oxidize landfill leachates have documented that waters that initially contained high levels of dissolved organic carbon scavenged the chlorine produced from chloride oxidation and thus limited perchlorate formation [50]. In the present study, the formation of perchlorate was hindered at operation times before 4 h when working at 50 mA/cm^2 , which resulted in a TOC removal of 79%.

3.2. Electrochemical oxidation of PFASs

This section is focused on the degradation and transformation of the group of PFASs found in the effluent of the industrial WWTP. Figures 3 and 4 show the evolution with time of the concentration of those PFASs which were detected in higher amounts. The detail about the concentration of all the compounds included in the analytical procedure is provided in the supplementary material (Table S1 of supplementary material).

The development of the major fluorotelomers, 6:2 FTAB and 6:2 FTSA is depicted in Figure 3. Due to the use of a specific calibration method, which is costly and time-consuming (standard addition, details are described by Boiteux et al. [46]), 6:2 FTAB was determined only in three samples, which corresponded to the initial effluent and two samples that were electrooxidized for 2 and 10 hours. The $\text{CH}_2\text{-CH}_2$ unit between the perfluoroalkyl chain and the sulfonate end group makes fluorotelomers much more susceptible to oxidation than PFCAs. Looking at the chemical structures in Table 2, it is possible to foresee that 6:2 FTAB was partially degraded into 6:2 FTSA which in these

conditions would be simultaneously generated and broken. However, the kinetics of 6:2 FTSA elimination was faster than its formation kinetics, as 6:2 FTSA follows a decreasing trend all the time. The removal of both 6:2 FTAB and 6:2 FTSA followed first-order kinetic trends, typically observed in BDD electro-oxidation processes that are governed by mass transfer limitations. In a previous work, BDD electrodes were recognized as strong generators of HO· at the anode surface during the electrooxidation of PFOA [51], a process that was enhanced at higher values of the applied current density. The concentration data shown in Figure 3 were fitted to a first-order kinetic model, $C = C_0 e^{-kt}$, where C is the concentration of the compound at a given time t , C_0 is the initial concentration and k is the apparent kinetic constant. The values of k for 6:2 FTAB and 6:2 FTSA removal were 0.923 and 0.469 h⁻¹, respectively. The lower kinetic constant of 6:2 FTSA disappearance supports the assumption of simultaneous electrochemical formation and degradation of this compound. The electrochemical degradation of fluorotelomers has not been fully investigated in the literature yet. Among the very few studies, Zhuo et al. [52] reported the use of a Ti/SnO₂-Sb₂O₅-Bi₂O₃ anode for the degradation of 6:2 FTSA, that provided a rate constant of 0.074 h⁻¹. However, the comparison is not straightforward, as the applied current and systems dimensions were different. Furthermore, in the present study, PFASs were simultaneously treated with other major pollutants (the analyzed PFASs contributed only with 0.5 % to the initial TOC) that could have hindered the kinetics of fluorotelomers degradation.

The degradation of 6:2 FTAB and 6:2 FTSA gave rise to the formation of PFCAs, as it is shown in Figure 4. Initially, electrochemical experiments were performed at 5 and 10 mA/cm², and for shorter degradation times, up to 2 hours. After checking that PFASs degradation was incomplete, it was decided to work at a higher current density (50

mA/cm^2) and for longer times, in order to assure complete PFASs degradation. It should be reminded, that additionally to the PFASs content, electro-oxidation is also acting on other recalcitrant organic pollutants that are consuming most of the applied current for their degradation and mineralization.

Paying attention to Table 1, the most abundant PFCAs in the effluent sample were PFHpA ($C_0= 37.85 \mu\text{g/L}$), PFHxA ($C_0= 24.83 \mu\text{g/L}$), PFPeA (Perfluoropentanoic acid) ($C_0= 52.50 \mu\text{g/L}$) and PFBA (Perfluorobutanoic acid) ($C_0= 7.54 \mu\text{g/L}$). The low initial concentration of PFOA ($C_0= 2.06 \mu\text{g/L}$) could be related to the low concentration of 8:2 fluorotelomers and other PFOA precursors in the WWTP influent. The development of PFCAs during the electro-oxidation treatment (Figure 4) varied according to the applied current density. For the lowest values of the applied current, 5 mA/cm^2 , the progress of all PFCAs showed increasing concentrations with time, indicating that these compounds were formed at a faster rate than they were degraded. Based on the very few previous studies dealing with the degradation of 6:2 FTSA, which include the use of $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_5\text{-Bi}_2\text{O}_3$ anode [52], heat activated persulfate oxidation [53] and with hydrogen peroxide activated by UV light [54], 6:2 FTSA was transformed into a mixture of PFHpA and PFHxA, where the proportions of each PFCA coming from 6:2 FTSA degradation seem to strongly depend on the oxidation technique implemented [44]. 6:2 FTSA degradation would start with the attack of hydroxyl radical at the positions of the two unfluorinated carbons. Further reaction with hydroxyl radical caused the desulfonation, cleaving the bond between the end group of the sulfonate and the polyfluorinated tail. After that, the polyfluorinated tail could be carboxylized at the end to form PFHpA and PFHxA [54]. Furthermore, these PFCAs obtained after breakdown of the main 6:2 fluorotelomers was broken into shorter-chain perfluorocarboxylates through a step by step mechanism that involved the loose of one electron to the anode to

form a perfluoroalkyl carboxyl radical, which was later decarboxylated and defluorinated by hydroxyl radical mediated reaction. In each step, the PFCA molecule loses a CF_2 unit, and generates CO_2 and fluoride ions [33, 34]. This proposal of degradation pathway, which includes the above mentioned previous literature contributions, is described in Figure S2 of the supplementary material [44,53,54].

Increasing the applied current density to 10 mA/cm^2 had the effect of reducing the maximum peak of PFCAs concentration. A further increase to 50 mA/cm^2 reinforced this effect and therefore, increasing trends were observed only for PFHxA and PFBA. According to these observations, it could be concluded that on the one hand PFHxA is the main initial degradation product of the major 6:2 fluorotelomers. On the other hand, PFBA is, among the measured compounds, at the end of the degradation pathway of longer chain PFCAs, and tends to accumulate at all the applied current conditions under study. Further degradation of PFBA into shorter PFCAs or transfer to the gas phase of volatile PFPrA and trifluoroacetic acid are expected to have occurred too.

Figure 5 depicts the evolution of the total concentration of PFASs. Solid bars represent the sum of 6:2 FTAB and M4 that were measured only at times 0, 2 and 10 hours. Dotted bars gather the sum of 6:2 FTSA, PFCAs, and other minor PFASs. The remaining concentration of all the detected PFASs at $t=10$ hours was $4.22 \mu\text{g/L}$, that represents a reduction of 99.74% of the initial total PFASs content. The energy consumption required for the 99.74 % PFASs removal was estimated as 256 kWh/m^3 , which is significantly reduced to 153 kWh/m^3 when the target PFASs removal rate is set at 98% (treatment time 6 h). Therefore, energy consumption, that is strongly dependent on the target PFASs removal rate [55], and the potential formation of disinfection by-product could be considered the main drawbacks of the electrochemical treatment. In this way it is demonstrated that the electrochemical treatment of the industrial WWTP

effluent with BDD anodes allows the effective removal of PFASs at the same time that the general TOC content is nearly completely eliminated. Moreover, the Si/BDD anodic material offered a robust stability. The electrochemical cell used in the present study had been in operation at laboratory scale for more than 10 years. Its degradation efficiency was periodically checked using a phenol degradation test, that proved its stability after more than 4000 hours of discontinuous operation and acid/caustic cleaning in a wide range of applied current densities, and under a variety of wastewaters and contaminants [22,27,30,56], a factor that proves the robustness of BDD electrooxidation technology.

The data about the release of fluoride anions is given in Figure 6. The fluoride content in solution, given by the black dots, increased progressively, in coincidence with the disappearance of the analyzed PFASs. The total fluorine in solution, calculated as the sum of fluorine contained in the analyzed PFASs plus fluoride in solution, is also shown in Figure 6 as open circles. After 10 hours of electrochemical treatment, the fluoride concentration in solution was 0.053 mM. The defluorination factor at $t=10$ h was calculated according to equation 1, where C_{F^-} is the final concentration of fluoride ions in the solution (mM), $C_{0,i}$ is the initial concentration of each PFASs and $n_{F,i}$ is the stoichiometry factor of the fluoride anion for each PFAS.

$$D_{F^-}(\%) = \frac{C_{F^-}}{\sum C_{0,i} \cdot n_{F,i}} \cdot 100 \quad (\text{Equation 1})$$

The calculated defluorination factor was 126 %. This value, higher than 100%, supports the assumption that other unknown fluorotelomers were also degraded during electrochemical oxidation of the effluent. Similarly, previous works highlighted the presence of unidentified perfluorinated compounds in various types of samples by the determination of total fluorine and total oxidizable precursors [37,44,57,58].

4. CONCLUSIONS

Results herein reported highlight the potential of electrochemical technology for the treatment of poly and perfluoroalkyl substances (PFASs) contained in industrial wastewaters coming from the manufacturing of fluorotelomer-based products and side-chain-fluorinated polymers. In this work, the use of a commercial BDD anode reduced the PFASs contained in the effluent from an industrial WWTP by 99.7%, as the concentrations decreased from 1652 $\mu\text{g/L}$ in the feed water (effluent of the WWTP) to 4.2 $\mu\text{g/L}$ in the electrochemically treated water. The only compound, among a group of 29 analyzed PFASs, that was detected in the final sample of the electrooxidation treatment was 6:2 FTSA, since all the other perfluorinated compounds were found below the LOQ of the analytical method. It was evidenced that the degradation of fluorotelomers induced the formation of PFCAs, that nevertheless were further degraded into shorter chain PFCAs and finally mineralized, as it was also supported by the increase of the fluoride content and the TOC decay.

However, further research will be focused on the optimization of the electrochemical process considering that variation of the PFASs concentration in the feed water will likely act as a source of uncertainty. Moreover, one of the key points for the economic viability of electrochemical technologies lies in the reduction of their energy demands.

In the present study, the energy consumption for 99.74 % PFASs removal was estimated at 256 kWh/m^3 . Therefore, the large scale implementation of the electrochemical process will require of new strategies to reduce its high energy consumption and operation costs. PFASs treatment at source before mixing with other diluting water streams and PFASs pre-concentration by means of membrane separation are envisaged as possible strategies.

APPENDIX A. SUPPLEMENTARY DATA

Additional information regarding the analytical procedure, evolution with time of PFASs during electrochemical experiments, PFASs degradation pathways and names, acronyms and optimised UHPLC-MS/MS.

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Table captions

Table 1. Main characteristics and initial concentration of PFASs ($\mu\text{g/L}$) in the influent (I) and effluent (E) samples of the industrial WWTP.

Table 2. Chemical structure by compound class, of PFASs included in the analytical method.

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Table 1

	Influent	Effluent
Physico-chemical Parameters		
Suspended Solids (mg/L)	125	55
Conductivity (mS/cm)	6.7	6.9
pH	8.4	7.6
Organic Pollutants		
COD (mg/L)	2,944	227
TOC (mg/L)	722	99
Inorganic Compounds		
Sulfate (mM)	9	11.3
Chloride (mM)	28.4	38
Fluoride (mM)	<LOQ	<LOQ
PFASs		
PFBA (ng/L)	496	7544
PFPeA (ng/L)	3154	52500
PFHxA (ng/L)	5291	24827
PFHpA (ng/L)	2793	37847
PFOA (ng/L)	449	2063
6:2 FTSA (ng/L)	242,496	382,200
8:2 FTSA (ng/L)	874	<LOQ
6:2 FTCA (ng/L)	328	<LOQ
6:2 FTAB (ng/L)	1,111,000	1,143,000
M4 (ng/L)	34361	2414

LOQ: limit of quantification. The LOQ for fluoride was 0.002 mM. The LOQs for 8:2 FTSA and 6:2 FTCA were 2000 and 5000 ng/L, respectively.

Table 2

Compound Name	Chemical structure	n
Perfluoroalkyl carboxylic acids (PFCAs)		3-13
Perfluoroalkane sulfonic acids (PFSAs)		4, 6-8, 10
Fluorotelomer carboxylic acids (n:2 FTCAs)		6, 8, 10
5:3 Polyfluorinated acid (5:3 Acid)		
Unsaturated fluorotelomer carboxylic acids (n:2 FTUCAs)		6,8,10
Fluorotelomer sulfonic acids (n:2 FTSA)		4,6,8
Perfluorooctane sulfonamide (FOSA)		
6:2 Fluorotelomer sulfonamide alkylbetaine (6:2 FTAB)		
6:2 Fluorotelomer sulfonamide propyl N,N dimethylamine (M4)		

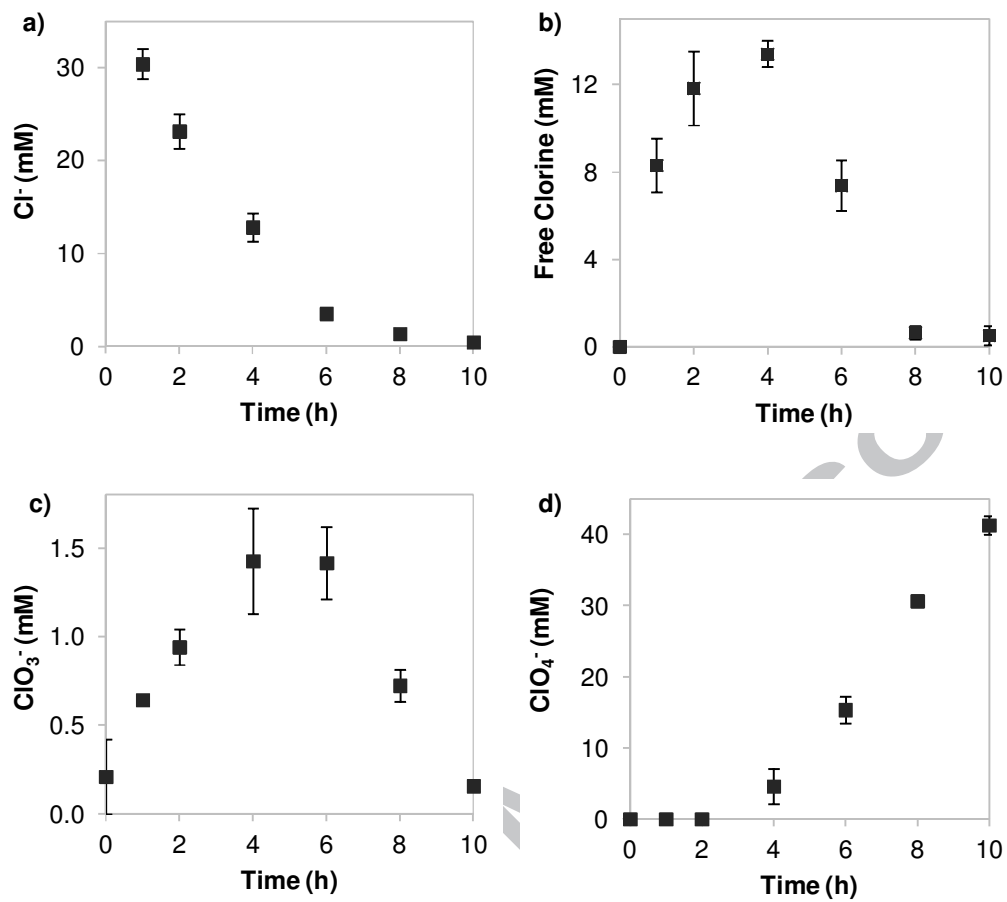


Figure 1

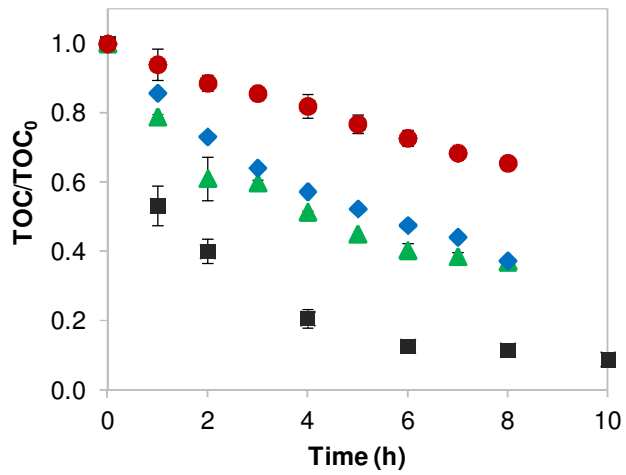


Figure 2

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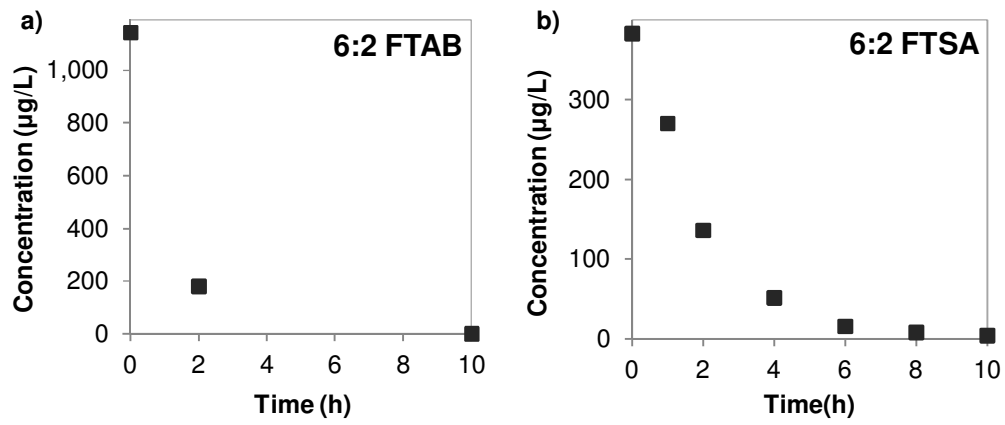


Figure 3

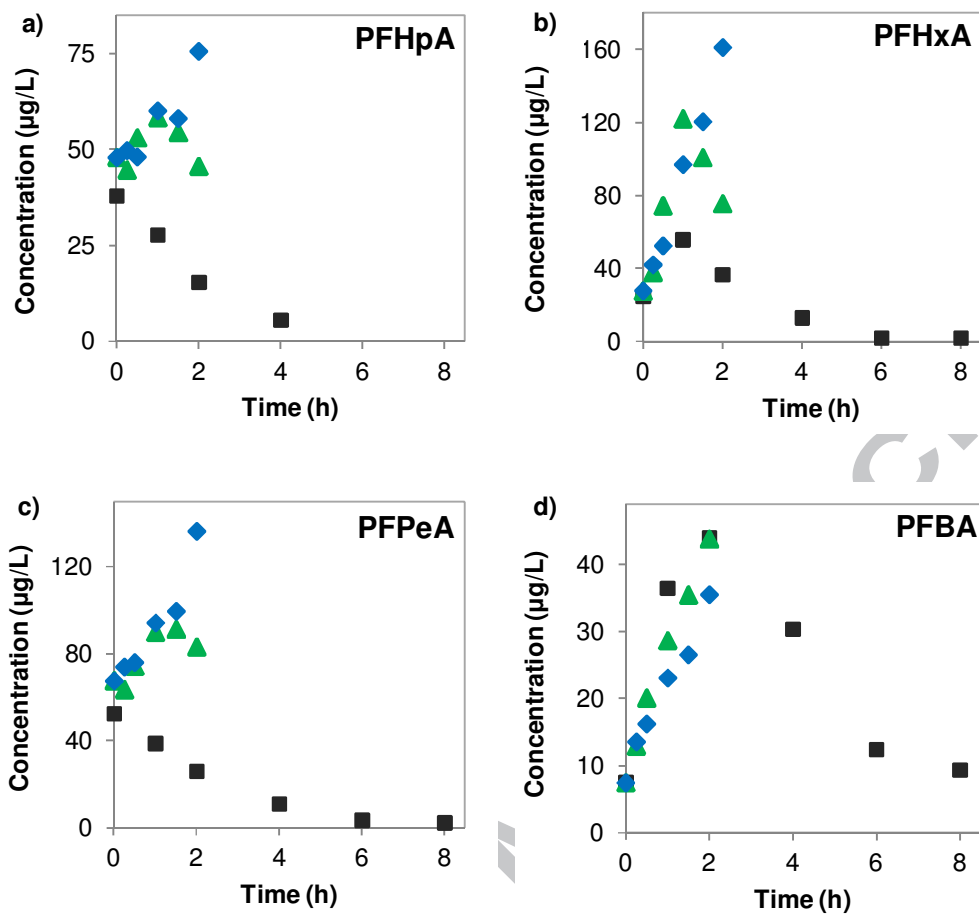


Figure 4

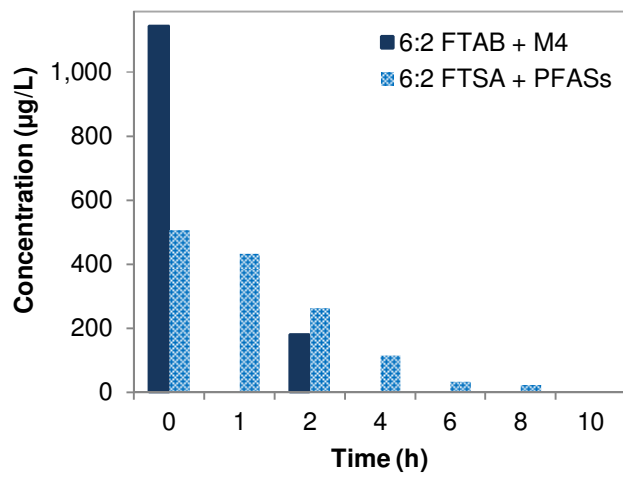


Figure 5

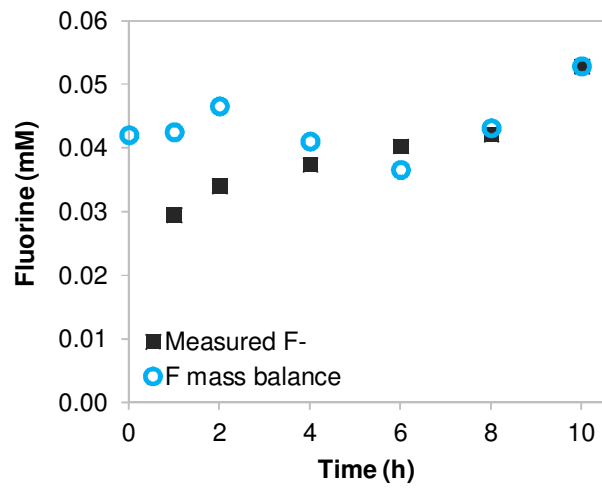


Figure 6

Figure captions

Figure 1. Evolution of inorganic chlorine species a) chloride, b) free chlorine, c) chlorate and d) perchlorate, with electro-oxidation time, under $j = 50 \text{ mA/cm}^2$ of applied current density to the effluent (E) sample. Average values of duplicate experiments are shown.

Figure 2. Evolution of TOC/TOC₀ ratios during electrooxidation of the effluent sample, where TOC₀ is the initial TOC concentration in the E sample (99 mg/L). (■) $j = 50 \text{ mA/cm}^2$, (▲) $j = 10 \text{ mA/cm}^2$, (◆) $j = 5 \text{ mA/cm}^2$, (●) $j = 2 \text{ mA/cm}^2$.

Figure 3. Evolution of the main fluorotelomers a) 6:2 FTAB and b) 6:2 FTSA with electro-oxidation time, $j = 50 \text{ mA/cm}^2$, of effluent (E) sample.

Figure 4. Influence of the applied current density on the concentration of a) PFHpA, b) PFHxA, c) PFPeA and d) PFBA with electro-oxidation time, in effluent (E) sample. (■) $j = 50 \text{ mA/cm}^2$ (cell voltage = $14.6 \pm 0.5 \text{ V}$), (▲) $j = 10 \text{ mA/cm}^2$ (cell voltage = $5.4 \pm 0.02 \text{ V}$), (◆) $j = 5 \text{ mA/cm}^2$ (cell voltage = $4.5 \pm 0.07 \text{ V}$).

Figure 5. Evolution of total concentration of PFASs with electro-oxidation time under $j = 50 \text{ mA/cm}^2$, in effluent (E) sample.

Figure 6. Evolution of fluoride concentration in solution and total fluorine mass balance with electro-oxidation time, under $j = 50 \text{ mA/cm}^2$, in effluent (E) sample.

Highlights

- Industrial wastewaters with a high PFASs content, Σ PFASs = 1642 $\mu\text{g/L}$, were treated
- The most abundant PFASs were fluorotelomers 6:2 FTAB and 6:2 FTSA
- Boron doped diamond anode allowed 99.7 % PFASs removal
- TOC decay and fluoride release revealed PFASs mineralization
- Fluorotelomer sulfonamides decomposed into PFCAs via FTSA formation

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Graphical Abstract

