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Boron doped diamond electrooxidation of 6:2 fluorotelomers and perfluorocarboxylic acids. Application to industrial wastewaters treatment.

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ABSTRACT

The aim of this study was to determine the viability of electrochemical oxidation to degrade and mineralize poly- and perfluoroalkyl substances (PFASs) in wastewaters from an industrial facility dedicated to the production of side-chain-fluorinated polymers and fluorotelomer-based products for fire-fighting foams. 6:2 fluorotelomer sulfonamide alkylbetaine (6:2 FTAB, 1111 µg/L), 6:2 fluorotelomer sulfonic acid (6:2 FTSA, 242.5 µg/L) and 6:2 fluorotelomer sulfonamide propyl N.N dimethylamine (M4, 34.4 µg/L) were the most abundant PFASs in the industrial wastewater, that also contained perfluorocarboxylic acids (ΣPFCAs, 12.2 µg/L), high TOC and chloride as main anion. 2 L samples were treated in bench scale experiments performed at a current density of 50 mA/cm^2, in a commercial cell equipped with a boron doped diamond (BDD) anode (70 cm^2). 97.1% of the initial PFASs content was removed after 8 hours of electrochemical treatment. Furthermore, the TOC removal (82.5%) and the fluoride release confirmed the PFASs mineralization. Based on the evolution of the different PFASs, electrochemical degradation pathways were proposed. Fluorotelomers sulfonamides 6:2 FTAB and M4 would be degraded into 6:2 FTSA, which conversely would give rise to PFHpA and preferentially PFHxA. The latter PFCAs were transformed into shorter-chain PFCAs, and eventually into CO_2 and fluoride. The reported results support the technical viability of BDD electrooxidation for the treatment of PFASs in industrial wastewater.

Keywords: poly- and perfluoroalkyl substances (PFASs), 6:2 FTSA and 6:2 FTAB, perfluorocarboxylic acids, electrochemical oxidation, boron doped diamond anode, industrial wastewater

1. INTRODUCTION

Poly- and perfluoroalkyl substances (PFASs) have been synthesized and widely used in different industrial and commercial applications since the 1950s, including oil and water repellent surface coatings for packing and textiles, surfactants and aqueous fire-fighting foams [1]. PFASs have been detected globally in wildlife and humans, and this group of substances is now recognized as a worldwide health threat. Recent studies reported that PFASs exceed recommended safety levels in public drinking water supplies for 6 million people in the United States [2] and that as many as 100 million people could be at risk from exposure to these chemicals. The United States Environmental Protection Agency established health advisory levels for PFOA and PFOS in drinking water at 0.07 µg/L, both individually and combined [3]. The European Water Directive (2013/39/EU) defined the environmental quality standard (EQS) for the annual average value of PFOS at 6.5×10^{-4} µg/L in inland surface waters [4].

PFASs are released into the environment during their industrial production and application, and as a result of leaching from the PFASs-containing consumer products [5]. Eventually, PFASs enter wastewater treatment plants (WWTP), which together with landfill sites have been suggested as the major point sources of PFASs to surface waters and to the atmosphere [6–8]. Groundwater contamination is often encountered at or near firefighting training areas where aqueous film-forming foams (AFFFs) have been used [9].

Monitoring of PFASs in WWTP utilities have shown the inefficiency of conventional water treatment technologies to remove PFASs [10,11]. Therefore, there is a need to develop innovative water treatment technologies that enable the removal of this group of persistent and hazardous substances. Electrochemical oxidation is among the most promising technologies for PFASs degradation. It is a versatile option that benefits from working at mild operation conditions and provides high removal efficiency [12–16].

Most of the previous research on PFASs electrochemical treatment was focused on testing different anodic materials, and was conducted with model solutions of a single compound, usually PFOA. In this way, “non-active” anodes such as SnO_2, PbO_2 and boron doped diamond (BDD) provided high mineralization ratios of some perfluorocarboxylic (PFCAs) and perfluoroalkane sulfonic acids (PFSAs) [13–15,17–20]. In contrast, a poor performance for PFOA degradation was obtained when using “active” anodes, such as Pt, Ti/Ru-IrO_2, and Ti/SnO_2-Sb/MnO_2 [14,21]. In order to enhance the treatment efficiency, some studies paid attention to the influence of the operating conditions, such as cell potential, current density and pH, as it has been recently reviewed [22]. However, very few studies have reported the treatment of PFASs in real water samples under environmental conditions. Within this group of pioneering studies, Schaefer et al. [9,23] and Trautmann et al. [24] demonstrated the ability of electrochemical oxidation to remove PFOA, PFOS and other shorter-chain PFCAs and PFSAs from groundwaters impacted by the use of AFFFs. Zhang et al. [25] studied the electrochemical treatment of municipal WWTP effluents and reported the efficient removal of PFAS traces. A recently reported study has contributed to a significant scientific progress on the technology for the treatment of industrial wastewaters by obtaining excellent results in the removal of perfluorohexanoic acid (PFHxA) using a hybrid process that combined nanofiltration and electrochemical oxidation using commercial BDD cells [26].

However, the treatment of industrial wastewaters polluted by elevated concentrations of fluorotelomers is still unexplored. More studies need to be conducted to focus on the feasibility and effectiveness of the electrochemical process to remediate PFASs mixtures present over a wider concentration range and under the effect of complex matrix composition with higher organic load background. The lack of studies about the treatment of industrial effluents with a high PFASs load is remarkable, particularly when production of PFASs is recognized as one of the main PFASs emission sources to the environment [1].

The aim of the present study was to investigate the efficiency of electrochemical oxidation to degrade and mineralize a mixture of PFASs of a highly polluted raw industrial wastewater that was generated in a chemical production facility. For this purpose, a bench scale commercial cell provided with a BDD anode was selected. A group of ten PFASs, that included 6:2 fluorotelomer sulfonamide alkylbetaine (6:2 FTAB) and 6:2 fluorotelomer sulfonic acids (6:2 FTSA) as major contributor to the load of PFASs, was monitored along the electrochemical treatment. At the same time, the formation and disappearance of five perfluorocarboxylic acids was analyzed in order to elucidate the degradation pathway followed by fluorotelomers and PFCAs. In addition, the electrochemical treatment allowed the mineralization of the organic pollutant load, using total organic carbon (TOC) as global indicator and the release of fluoride as individual indicator of PFASs mineralization.

2. MATERIALS AND METHODS

2.1. Materials and water sample

One raw industrial wastewater grab sample (50 L) was collected from the influent to an industrial wastewater treatment utility. The WWTP received the sewage of 4 different manufacturing plants, and only one of them produced side-chain-fluorinated polymers and fluorotelomer-based products, such as 6:2 FTAB and 6:2 FTSA for fire-fighting foams [27]. Its flow accounted for 3 to 17% of the overall WWTP influent flowrate.

The characteristics of the industrial wastewater are summarized in Table 1. The main anions, chloride and sulfate, provided the wastewater with the conductivity required for the electrochemical treatment. Ten individual PFASs were found over the limit of quantification (LOQ) of the analytical method, among the group of 29 PFASs that were included in the monitoring program. The chemical structure of these compounds is provided in Figure 1, in which the proposed degradation pathways were gathered and will be discussed later. The PFASs profile was dominated by the presence of 6:2 FTAB, 6:2 FTSA and 6:2 fluorotelomer sulfonamide propyl N.N dimethylamine. The latter compound was designated as M4, following the simplified nomenclature reported by Moe et al. [28]. Several PFCAs were also identified, such as PFHxA, perfluoropentanoic acid (PFPeA), perfluoroheptanoic acid (PFHpA), perfluorobutanoic acid (PFBA). On the other hand, perfluorobutane sulfanic acid (PFBS) was the only compound of the group of perfluorosulfonates that was detected in the industrial wastewater. The following list of PFASs were included in the analytical method but were not detected over the LOQ: perfluorohexane sulfonic acid, perfluoroheptane sulfonic acid, perfluorooctane sulfonic acid, perfluorodecanesulfonic acid, perflurononanoic acid, perfluorodecanoic acid, perfluoroundecanoic acid, perfluorododecanoic acid, perfluorotridecanoic acid, perfluorotetradecanoic acid, 4:2 fluorotelomer sulfonic acid, 6:2, 8:2 and 10:2 fluorotelomer carboxylic acids, 5:3 polyfluorinated acid, 6:2, 8:2 and 10:2 unsaturated fluorotelomer carboxylic acids and perfluorooctane sulfonamide.

2.2. Electrochemical experiments

Bench scale electro-oxidation experiments were performed in an undivided cell (Diacell 106, Adamant Technologies, Switzerland) consisting of two circular parallel electrodes: a BDD anode and a stainless steel cathode, each one with a surface area of 70 cm^2 and an electrode gap of 5 mm (Figure 2). The cell was connected to a power supply (Agilent 6654 A) and experiments were conducted in galvanostatic conditions at a current density of 50 mA/cm^2. The average cell potential was 11.7 V. The industrial wastewater was filtered using 0.45 µm nitrocellulose filters (Millipore). 2 L samples were used as feed in the experiments that were conducted in batch mode at constant temperature of 20 ºC.

Treated samples were collected in polypropylene containers, and preserved at 4 ºC until delivery for analysis. Each point of the kinetic data was obtained as a single electrochemical experiment, a procedure that allowed to keep the volume constant along the experimental time.

2.3. Analytical methods

Detailed protocol of the PFASs analysis has been previously published [29] . 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 [29]. An ultra-high performance liquid chromatography coupled to tandem mass spectrometry (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)). Twelve labelled internal standards (IS) were used to provide an adequate correction compensating for matrix effects. Considering the initial dilutions, the LOQ in wastewater samples were 0.05 µg/L for 6:2 FTAB and M4, and 0.4 and 1 µg/L for the other PFASs depending on the analytes.

TOC was determined using a TOC-V CPH (Shimadzu) analyzer. Chemical oxygen demand (COD) was measured following the Standard Method 5220D [30]. Ion chromatography was used for anion analysis following the procedure that was detailed elsewhere [26]. Total ammonium nitrogen (TAN) was determined according to Standard Method 4500-NH_3. Finally, free chlorine and total chlorine were determined by DPD Ferrous Titrimetric Method. pH was measured using a portable pH-meter.

3. RESULTS AND DISCUSSION

The principal objective of this work was to study the viability and efficiency of the electrochemical oxidation to remediate industrial wastewaters heavily polluted by PFASs. As a whole, the BDD electrochemical treatment achieved 97.1% elimination of the overall ΣPFASs, that was reduced from 1400 μg/L to a final content of 41 μg/L.

Figure 3 depicts the electrochemical oxidation of the predominant fluorotelomers (6:2 FTAB, 6:2 FTSA and M4). The three compounds include an alkyl chain formed by 8 carbon atoms, 6 of which are fully substituted by fluorine atoms (see Figure 1). 6:2 FTAB was the most abundant PFASs in the wastewater sample, with an initial content higher than 1000 μg/L. The electrochemical treatment allowed a fast decrease of 6:2 FTAB that was reduced to 302 μg/L in only 2 hours, and a concentration lower than 0.05 μg/L after 8 hours of treatment. 6:2 FTAB and 6:2 FTSA removal data were fitted to a first-order kinetic model, as shown in the logarithm plot of Figure 3c. The resulting pseudo first-order kinetic constant for 6:2 FTAB removal was 1.22 h^{-1}, which is significantly faster than the kinetic constant for 6:2 FTSA removal, 0.35 h^{-1}. By inspection of the chemical structures depicted in the Figure 1, the cleavage of the S-N bond by the electrogenerated oxidants would promote the partial conversion of 6:2 FTAB and M4 into 6:2 FTSA, which in these conditions would be simultaneously generated and broken. The formation of 6:2 FTSA as a degradation product of 6:2 FTAB in abiotic conditions has been recently reported. D'Agostino et al. [31] postulated a degradation pathway that involved the activation of molecular oxygen by Fe(II) ions contained in the aqueous solutions to form reactive oxygen species. Formation of 6:2 FTSA through reaction of hydroxyl radicals (·OH) with the sulfur center of the sulfonamide, as was observed for gas phase N-methyl perfluorobutane sulfonamide ethanol, has also been described [32].

Figure 4 shows the change with the treatment time of the PFCAs that were detected in the wastewater sample: PFOA, PFHpA, PFHxA, PFPeA and PFBA. PFOA was initially at low concentration (0.44 μg/L) which passed to 0.96 μg/L at the end of the experiment. This increase was assigned to the decomposition of 8:2 FTSA, that was present in the feed sample at a concentration of 0.87 μg/L. Fang et al. [33] reported the chemical oxidation of 8:2 FTSA into PFOA using hydrogen peroxide and potassium permanganate. These findings support the increase of PFOA observed in the present study during the electrochemical treatment of the industrial wastewaters. PFHxA was the compound with the highest increase in concentration, changing from the initial 5.3 μg/L to a maximum of 28 μg/L after 6 hours of treatment. The peak of PFHxA concentration coincided with the complete depletion of 6:2 FTSA and 6:2 FTAB. In contrast, PFHpA increased only during the initial 2 hours, and the variation was not as marked as for PFHxA. The progress of PFHpA and PFHxA revealed that PFHxA is the main product obtained in the degradation of 6:2 fluorotelomers. Our experimental analysis in real industrial wastewaters seems to be in accordance with the mechanisms for 6:2 FTSA splitting reported by Park et al. [34], who found a 25/75 formation ratio of PFHpA/PFHxA upon 6:2 FTSA degradation using heat activated persulfate oxidation. Similarly, the UV-activated hydrogen peroxide oxidation of 6:2 FTSA resulted in a 2-fold formation of PFHxA over PFHpA generation, as reported by Yang et al. [35]. Regarding PFPeA and PFBA (Figures 4d and 4e), both compounds followed increasing trends up to 6 hours of treatment, in coincidence with the time at which PFHxA started to decrease. This behavior points to the simultaneous formation and consumption of the shorter chain PFCAs.

The evolution of the PFASs analyzed in this work can be described by the degradation pathways gathered in Figure 1. 6:2 fluorotelomers degradation [35,36] would start with the attack of electrogenerated ·OH radicals to the C-C and C-H bonds of the two unfluorinated carbons, causing the desulfonation and forming $C_6F_{13}COO^-$ and $C_5F_{11}COO^-$. The degradation of 8:2 FTSA was expected to follow a similar pathway to form PFOA as main secondary product. Once the PFCAs have been formed, the following degradation steps would start with the electron transfer from the carboxyl group to the anode to generate the $C_nF_{2n+1}COO\cdot$ radical (Eq. 1). Next, this highly unstable radical would undergo Kolbe decarboxylation to form a perfluoroalkyl radical ($C_nF_{2n+1}\cdot$) (Eq. 2). Then, the electrogenerated hydroxyl radical reacts with the perfluoroalkyl radical to form a perfluoroalcohol $C_nF_{2n+1}OH$ (Eq. 3), which is a thermally unstable species that would undergo intramolecular rearrangement to form the perfluoro carbonyl fluoride and release fluoride anion (Eq. 4). Finally, the latter species hydrolyses to give the one-carbon-shorter-chain perfluorocarboxylic acid, $C_{n-1}F_{2n-1}COO^-$ (Eq. 5) [14,19,21,36].

$$C_nF_{2n+1}COO^- \rightarrow C_nF_{2n+1}COO^\bullet + e^- \quad (1)$$

$$C_nF_{2n+1}COO^\bullet \rightarrow C_nF_{2n+1}{}^\bullet + CO_2 + H^+ \quad (2)$$

$$C_nF_{2n+1}{}^\bullet + \bullet OH \rightarrow C_nF_{2n+1}OH \quad (3)$$

$$C_nF_{2n+1}OH \rightarrow C_{n-1}F_{2n-1}COF + F^- + H^+ \quad (4)$$

$$C_{n-1}F_{2n-1}COF + H_2O \rightarrow C_{n-1}F_{2n-1}COO^- + F^- + H^+ \quad (5)$$

The $C_{n-1}F_{2n-1}COO^-$ repeats the above steps and decomposes into shorter-chain PFCAs by gradually losing a CF_2 unit. Nevertheless, more studies using model solutions of single fluorinated compounds would be needed to completely assess the proposed degradation pathway.

The change of TOC and the fluoride release with time, shown in Figure 5, were indicators of mineralization of the overall organic pollutants load. The high TOC content of the industrial wastewaters (see Table 1) revealed that the analyzed PFASs contributed with less than 0.1% to the total organic load. Nevertheless, the electrochemical treatment successfully removed more than 80% of TOC after 8 hours (Figure 5), a demonstration of the effectiveness of BDD anodic oxidation for the removal of recalcitrant organic compounds in a variety of chemical compositions. Figure 5 also shows the evolution of fluoride concentration. Initially, F^- concentrations were below the LOQ of the analytical method. Then, the appearance of fluoride was due to PFASs degradation. After 8 hours of electrochemical treatment, fluoride increased to 0.012 mM, a value that is significantly below the initial fluoride contained in the analyzed PFASs, 0.034 mM. This difference could be explained by the formation of other shorter-chain PFASs not included as target species or due to the possible fluoride adsorption on the BDD electrode during the mineralization of PFASs, as it has been previously reported when PFOA was electrochemically degraded on BDD [17,37].

The transformation of chloride into other inorganic chlorine species was also evaluated. Figure 6 shows the evolution of chloride, free chlorine, chlorate and perchlorate. The experimental data show that chloride was transformed into free chloride that was simultaneously oxidized to chlorate. However, the findings recently reported by Schafer et al. [23] demonstrated that chloride in solution had a negligible effect on the kinetics of PFOA and PFOS electrochemical treatment using BDD anodes. On the other hand, the operating conditions must be carefully selected in order to avoid the formation of undesirable perchlorate [38,39]. It is important to note that in the present study the oxidation of chlorate to perchlorate was significantly delayed and started after 6 hours of electrochemical treatment, a behaviour that can be explained by the preferential consumption of the electrogenerated hydroxyl radicals for the oxidation of organic compounds. It is not only after most of the organic load and chloride have been oxidized, that hydroxyl radicals are available for perchlorate formation [40,41]. As a result, the formation of undesirable perchlorate was avoided in the period in which more than 91% of the initial PFASs content had been degraded.

Nitrate formation was observed during the first two hours to reach a plateau at 2.8 mM, a value that is lower than the initial 5 mM ammonium concentration of the industrial wastewater. This result is showing that ammonium was partially converted into gaseous nitrogen, as it typically occurs in the BDD electrochemical removal of ammonium from wastewaters that also contain organic pollutants and chloride [41–43]. The oxidation of nitrogen in 6:2 FTAB and M4 cannot explain itself the change of nitrate concentration, as it would only contribute to 0.15% of the observed nitrate increase. Similarly, there was a net formation of sulfate that was attributed to the oxidation of unknown sulfur compounds contained in the industrial wastewater. Nevertheless, the sulfur content of 6:2 FTSA, 6:2 FTAB and M4 could contribute to a maximum of 0.1% of the change in sulfate concentration. Therefore, nitrate and sulfate formation due to the degradation of fluorotelomers contained in the industrial wastewater was observed to be negligible.

One of the key points for the practical feasibility of electrochemical water treatment lies in the reduction of their energy demands. In the present study, the energy consumption for 97% PFASs removal was estimated at 164 kWh/m^3 . In contrast, the extraordinary technical efficiency of BDD electrochemical oxidation has not been reported by any other technique.

4. CONCLUSIONS

The present study demonstrated the electrochemical degradation of PFASs contained in the wastewaters generated in an industrial facility dedicated to the production of side-chain-fluorinated polymers and fluorotelomer-based products for fire-fighting foams. The effectiveness of a commercial BDD anode was assessed by studying the evolution of ten PFASs. The most abundant PFASs were 6:2 FTAB, 6:2 FTSA and M4. The BDD anode was able to reduce the PFASs content by 97.1% after 8 hours of electrochemical degradation conducted at a current density of 50 mA/cm^2. While fluorotelomers were completely removed, the degradation of these fluorotelomer compounds gave rise to the formation of PFCAs, being PFHxA the most abundant. However, PFHxA was also converted into shorter chain PFCAs, and eventually mineralized, as it was confirmed by the TOC removal and the release of fluoride. This research contributes to get insight about the electrochemical degradation pathways of fluorotelomers contained in real industrial wastewaters. Future studies should be carried out to verify the suggested mechanisms and determine the presence and the role of possible unknown PFASs.

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Figure captions

Figure 1. Proposal for the electrochemical degradation pathway of the group of PFASs observed in the industrial wastewater case of study. Solid lines represent the main degradation pathways, whereas dotted lines show alternative pathways that may also take place.

Figure 2. Electro-oxidation system (1: Electro-oxidation Cell, 2: Power Supply, 3: Feed Tank, 4: Pump, 5: Cooling System).

Figure 3. Change with the treatment time of the main fluorotelomers: a) 6:2 FTAB and 6:2 FTSA, b) M4 and c) Fitting of 6:2 FTAB and 6:2 FTSA removal data to a first-order kinetic model. j = 50 mA/cm^2.

Figure 4. Change with the treatment time of the main PFCAs: a) PFOA, b) PFHpA, c) PFHxA, d) PFPeA and e) PFBA. j = 50 mA/cm^2.

Figure 5. Reduction of TOC and fluoride release during electrochemical oxidation of the industrial wastewater. j = 50 mA/cm^2. The LOQ of fluoride analysis was 0.002 mM. Data shown as the average of duplicate experiments.

Figure 6. Change with the treatment time of inorganic chlorine species (chloride, free chlorine, chlorate and perchlorate) during electrochemical oxidation of the industrial wastewater. j = 50 mA/cm^2.

Figure 7. Change with the treatment time of nitrate and sulfate concentration during electrochemical oxidation of the industrial wastewater. j = 50 mA/cm^2.

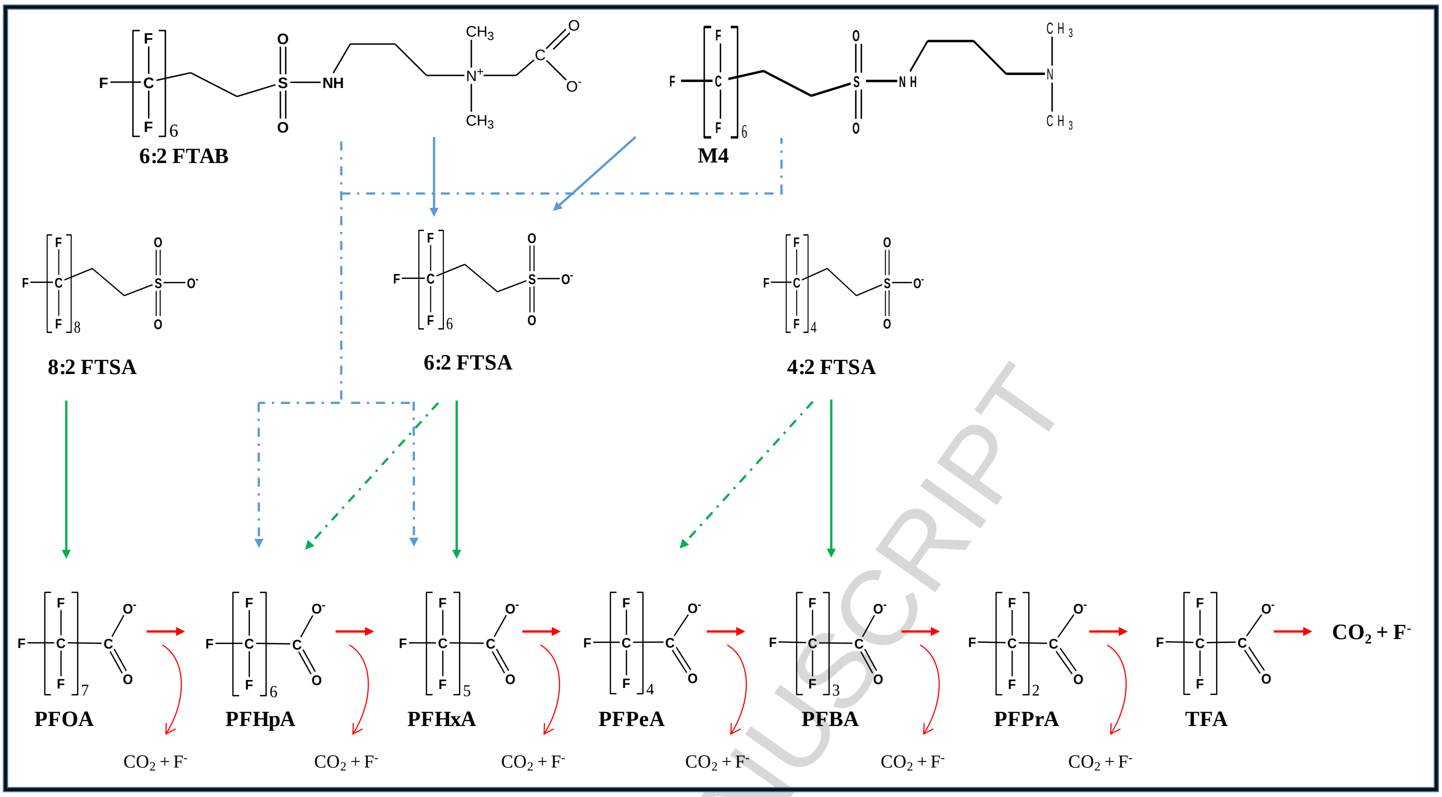

Figure 1

(2-column fitting image)

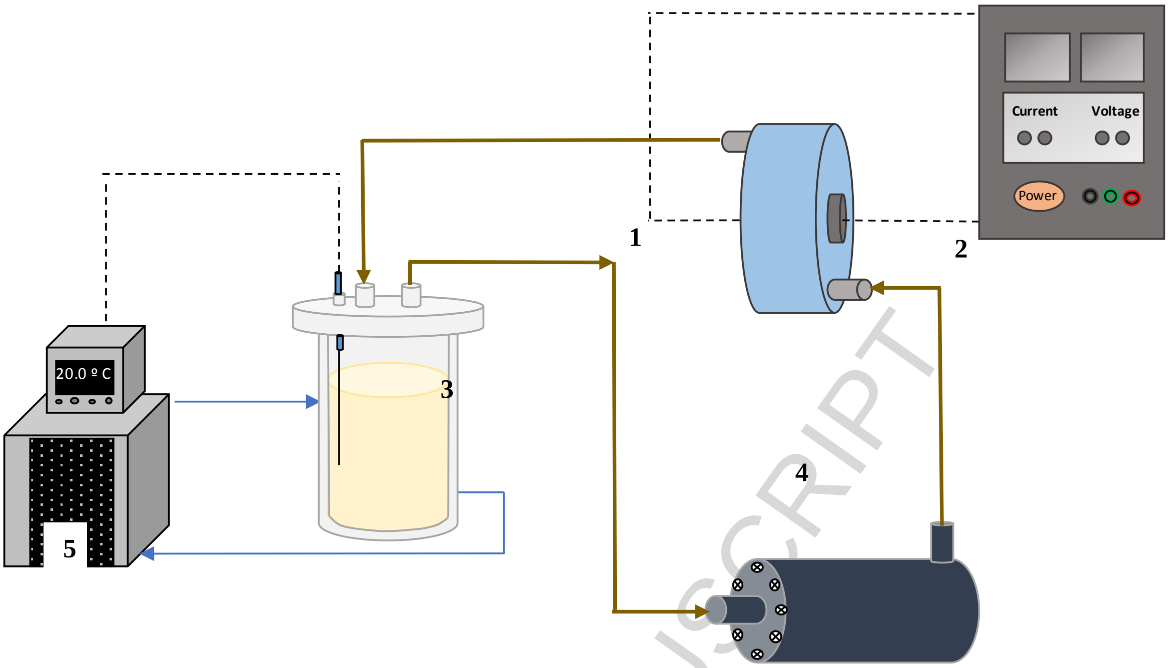

Figure 2

(1.5-column fitting image)

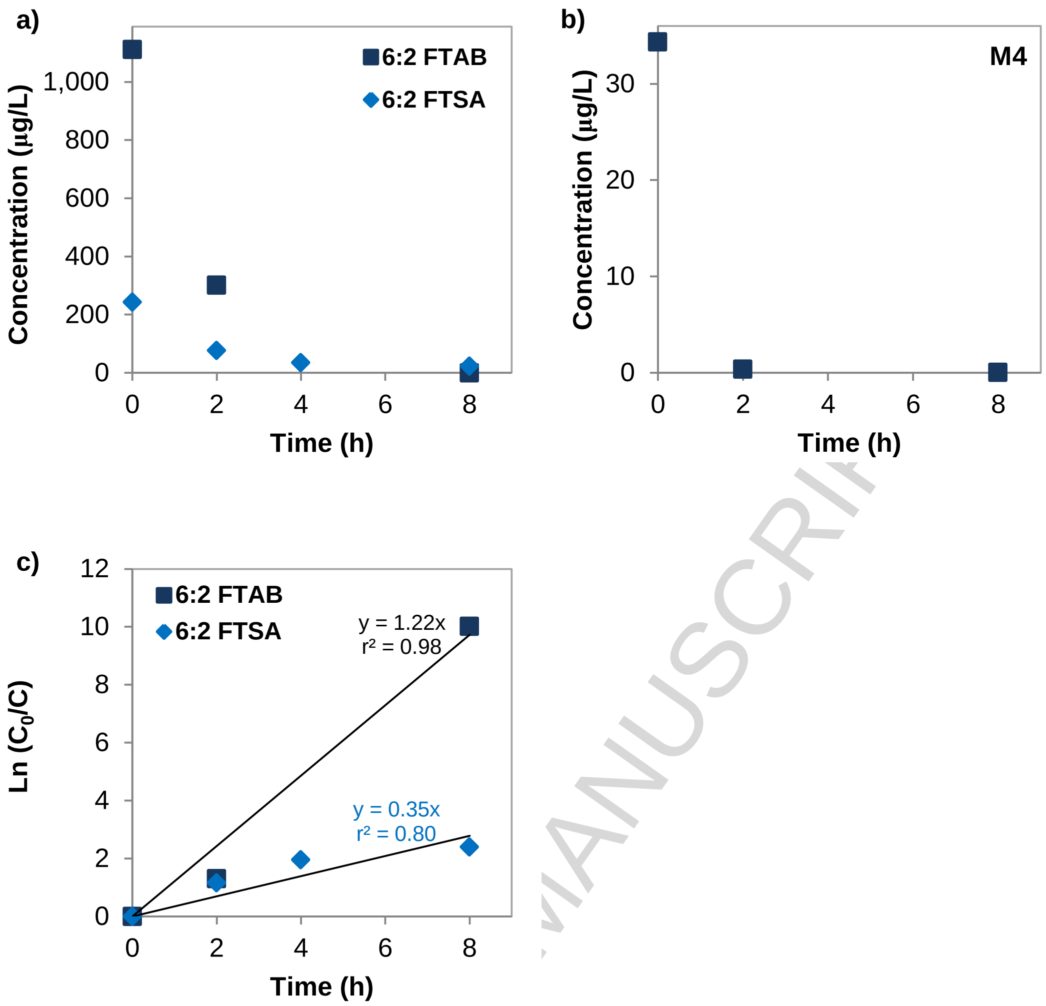

Figure 3

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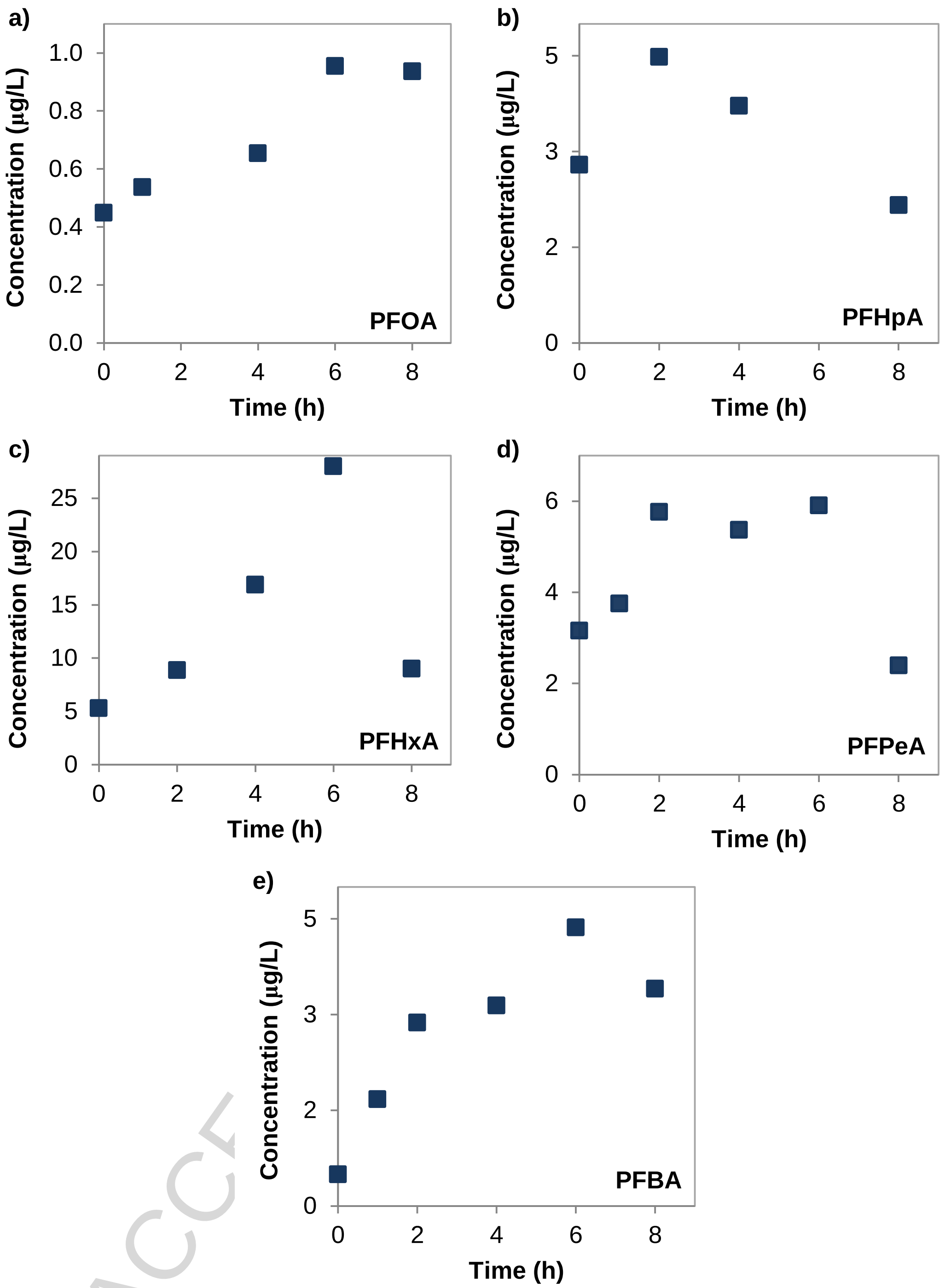

Figure 4

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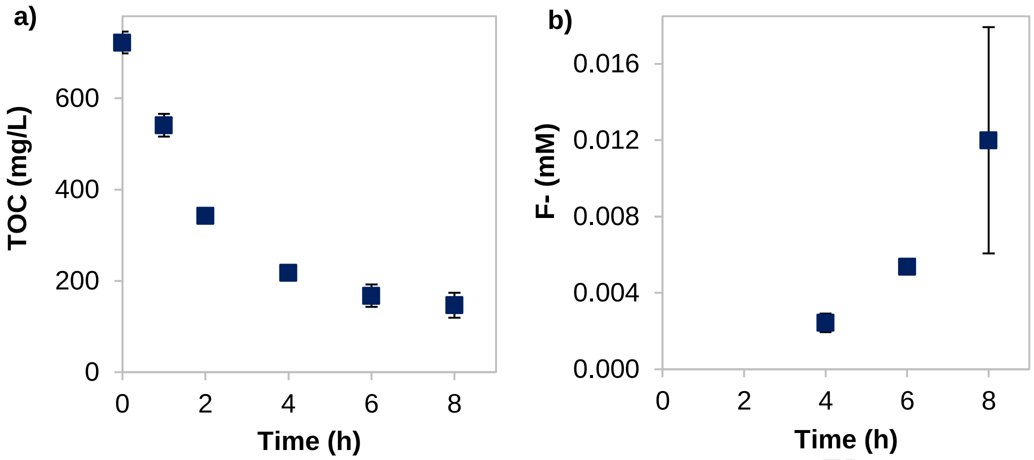

Figure 5

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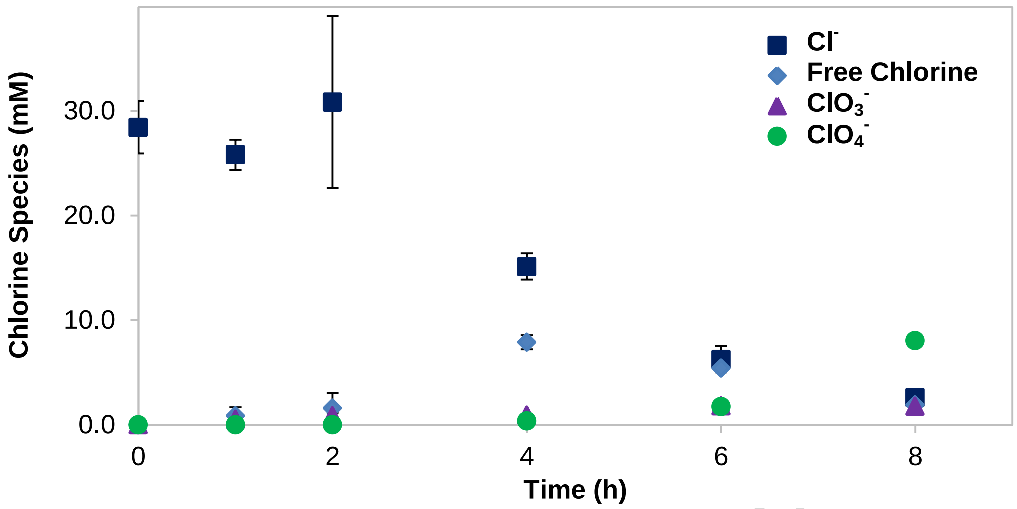

Figure 6

(1.5-column fitting image)

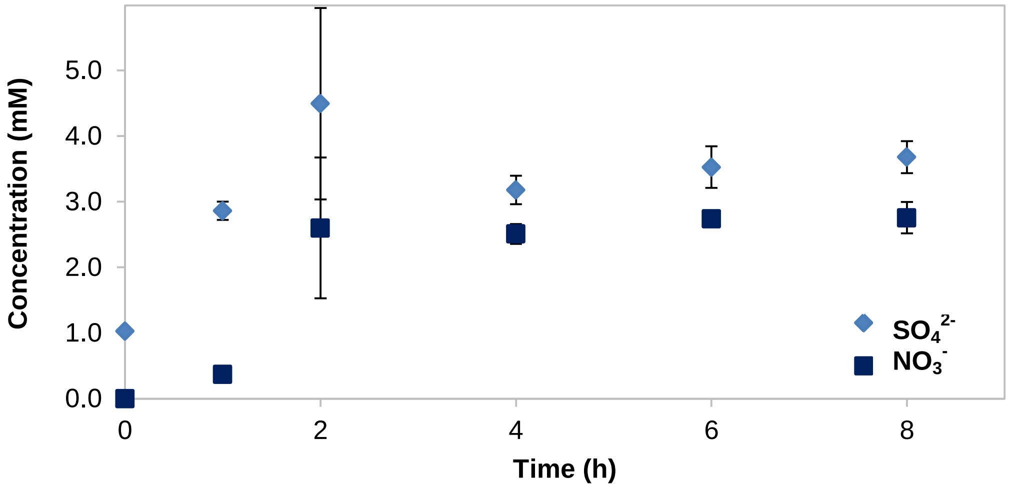

Figure 7

(1.5-column fitting image)

Table captions

Table 1. Characteristics of the raw industrial wastewater and initial PFASs concentration (µg/L).

Table 1

Physico-Chemical Parameters	
Suspended Solids (mg/L)	125
Conductivity (mS/cm)	6.7
pH	8.4
Organic Pollutants	
COD (mg/L)	2,944
TOC (mg/L)	722
Inorganic Compounds	
Sulfate (mM)	1.03
Chloride (mM)	28.4
Ammonium (mM)	5
Fluoride (mM)	<0.002
Perfluorinated Compounds	
PFBS (µg/L)	0.974
PFBA (µg/L)	0.496
PFPeA (µg/L)	3.154
PFHxA (µg/L)	5.291
PFHpA (µg/L)	2.793
PFOA (µg/L)	0.449
6:2 FTSA (µg/L)	242.496
8:2 FTSA (µg/L)	0.874
M4 (µg/L)	34.361
6:2 FTAB (µg/L)	1111

(One column fitting table)

Highlights

- Effluents from production of fluorotelomers and fluorinated polymers were treated
- Electrooxidation of 6:2 FTAB, 6:2 FTSA and perfluorocarboxylic acids is reported
- Boron doped diamond anode achieved 97.1% PFASs removal at 50 mA/cm^2
- The fluorotelomer sulfonamide 6:2 FTAB decomposed into PFCAs via intermediate 6:2 FTSA formation
- TOC decay and fluoride release revealed the mineralization of PFASs