



Research article

Electrochemical degradation of per- and poly-fluoroalkyl substances using boron-doped diamond electrodes

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ABSTRACT

Electrochemical degradation using boron-doped diamond (BDD) electrodes has been proven to be a promising technique for the treatment of water contaminated with per- and poly-fluoroalkyl substances (PFAS). Various studies have demonstrated that the extent of PFAS degradation is influenced by the composition of samples and electrochemical conditions. This study evaluated the significance of several factors, such as the current density, initial concentration of PFAS, concentration of electrolyte, treatment time, and their interactions on the degradation of PFAS. A 2⁴ factorial design was applied to determine the effects of the investigated factors on the degradation of perfluorooctanoic acid (PFOA) and generation of fluoride in spiked water. The best-performing conditions were then applied to the degradation of PFAS in wastewater samples. The results revealed that current density and time were the most important factors for PFOA degradation. In contrast, a high initial concentration of electrolyte had no significant impact on the degradation of PFOA, whereas it decreased the generation of F⁻. The experimental design model indicated that the treatment of spiked water under a current density higher than 14 mA cm⁻² for 3–4 h could degrade PFOA with an efficiency of up to 100% and generate an F⁻ fraction of approximately 40–50%. The observed high PFOA degradation and a low concentration of PFAS degradation products indicated that the mineralization of PFOA was effective. Under the obtained best conditions, the degradation of PFOA in wastewater samples was 44–70%. The degradation efficiency for other PFAS in these samples was 65–80% for perfluorooctane sulfonic acid (PFOS) and 42–52% for 6–2 fluorotelomer sulfonate (6-2 FTSA). The presence of high total organic carbon (TOC) and chloride contents was found to be an important factor affecting the efficiency of PFAS electrochemical degradation in wastewater samples. The current study indicates that the tested method can effectively degrade PFAS in both water and wastewater and suggests that increasing the treatment time is needed to account for the presence of other oxidizable matrices.

1. Introduction

Per- and poly-fluoroalkyl substances (PFAS) are fluorinated anthropogenic organic compounds that have been in use since the 1950s (Kissa 2001) as surfactants, coatings, water repellents for leather and textiles, impregnating agents, firefighting foams, metal plating materials and aqueous film forming foams (Busch et al., 2010; Yan et al., 2015; Favreau et al., 2017). Today, approximately 4730 compounds related to PFAS have been registered (OECD 2018). Due to high PFAS production for commercial purposes, their wide range of applications and their

persistent properties, these compounds are ubiquitously distributed in the environment (Paul et al., 2009; Krafft and Riess 2015). PFAS can also be widespread in aquatic systems from landfill leachate receiving municipal solid waste and industrial effluents (Dauchy et al., 2017; Fuertes et al., 2017; Gomez-Ruiz et al., 2017). When released to the environment, conditions that cannot be met naturally are required to break down the C–F bonds and mineralize PFAS compounds (Ochoa-Herrera et al., 2008; Park et al., 2009; Zhang et al., 2013). A high concentration of PFAS in soils and industrial waste may pose risks for the contamination of ground and surface water, which would subsequently

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limit the use of these water sources as a source of drinking water (Banzhaf et al., 2017). Consequently, more studies about feasible and effective techniques leading to the removal and complete degradation of PFAS should be explored to fully decrease the amount of pollution already present in the environment.

Recently, various oxidative methods, such as electrochemical, photochemical and sonochemical techniques, have been proven to be promising for PFAS degradation with varying degrees of treatment efficiency and costs (Merino et al., 2016; Xu et al., 2017; He et al., 2019; Nzeribe et al., 2019; Cao et al., 2020). Electrochemical methods have shown a high potential considering both the treatment efficiency and its costs (Nzeribe et al., 2019). The choice of the right electrodes impacts the treatment efficiency. The use of boron-doped diamond (BDD) electrodes would be preferable over other electrode materials due to their wide potential window, non-corrosiveness and generation of hydroxyl radicals rather than favouring the oxygen evolution reaction (Panizza et al., 2008; He et al., 2019; Nidheesh et al., 2019). In addition, BDD electrodes do not require a catalyst to favour electrochemical conversion, and they do not contain other toxic chemicals (Lin et al., 2013; Shestakova and Sillanpää 2017). The use of BDD has been widely explored for organic pollutant treatment in landfill leachates (Cabeza et al., 2007) and in other daily wastewaters (Peralta-Hernández et al., 2012). Gomez-Ruiz et al. (2017) demonstrated efficient PFAS degradation, with efficiencies reaching up to 99.7%, even in the presence of other organic and inorganic substances in industrial wastewater (Gomez-Ruiz et al., 2017).

Although it is acknowledged that the experimental conditions (e.g., time, current density, plate distance, and electrolyte concentration) and solution properties (e.g., pH and PFAS concentration) impact the treatment efficiency, the extent of their effects on PFAS degradation is ambiguous (Carter and Farrell 2008; Ochiai et al., 2011; Zhuo et al., 2012; Trautmann et al., 2015; Urriaga et al., 2015; Schaefer et al., 2017; Gomez-Ruiz et al. 2017, 2019). As emphasized in the recent literature (Ahmed et al., 2020; Radjenovic et al., 2020), most of the available studies were conducted on synthetic PFAS solutions, which may differ significantly from groundwater or wastewater samples to be treated. Therefore, prior to suggesting an electrochemical degradation method for the treatment of specific solutions (leachates, wastewaters, industrial effluents, etc.), method development and method validation for a specific matrix are needed.

The aim of this study was to optimise electrochemical degradation of PFAS in aqueous solutions i) by evaluating the importance and effect of several factors, namely, the electrical current density, initial concentration of perfluorooctanoic acid (PFOA), electrolyte concentration and time, on the degradation of PFOA in spiked solutions and ii) by evaluating the effect of the best-performing conditions on PFAS degradation in contaminated wastewater samples.

2. Materials and methods

2.1. Materials

The chemicals used to prepare the synthetic solutions were PFOA (96%) and sodium sulfate (Na_2SO_4 , 99%). Sodium fluoride (NaF, 99%) was used to prepare calibration standards. Ultrapure water was used to prepare all electrolyte solutions. Chemicals such as sodium chloride (NaCl, ≥ 99.5), sodium hydroxide (NaOH, $>99\%$), 1,2-diamino cyclohexane N,N,N,N-tetra acetic acid (CDTA, pro analysis) and glacial acetic acid (100%) were used to prepare a total ionic strength adjustment buffer (TISAB). All reagents were purchased from Merck except PFOA, which was obtained from Sigma Aldrich.

Three types of PFAS-containing industrial wastewater samples from a Swedish waste management company were used to test the studied degradation method. Table 1 summarizes the characteristics of the three wastewater samples including the concentration of 11 PFAS compounds.

Table 1
Characteristics of wastewater samples.

Parameter	Sample I	Sample II	Sample III
pH	7.59	8.53	6.27
F^- ($\mu\text{g L}^{-1}$)	3.87	3.82	0.84
Cl^- (mg L^{-1})	272.7	261.2	245.0
Electrical conductivity (mS cm^{-1})	11.7	11.1	10.4
TOC (mg L^{-1})	3570	2860	10678
PFBA	<3.00	5.67	<10.0
PFPeA	1.69	1.03	1.02
PFHxA	2.35	1.19	2.72
PFHpA	0.34	0.32	0.65
PFOA	0.57	0.45	0.80
PFNA	<0.01	<0.01	<0.01
PFDA	<0.01	<0.01	<0.01
PFBS	0.96	1.13	2.74
PFHxS	3.65	4.29	11.50
PFOS	7.82	3.23	19.10
6:2 FTSA	23.20	24.30	14.70
$\Sigma 11$ PFAS	40.57	41.61	53.23

2.2. Electrochemical degradation and factorial design of the experiment

2.2.1. PFOA degradation in synthetic water

Experiments were conducted on a laboratory scale using a simple batch mode. Briefly, the electrochemical system consisted of a 300 mL beaker containing 200 mL of solution spiked with PFOA and Na_2SO_4 , in which electrodes were immersed. BDD coated on grade 2 niobium was used as both the anode and cathode. The surface area of the cathode was 21.57 cm^2 , and that of the anode was 35.05 cm^2 , with an electrode spacing of approximately 2 cm. The electrodes were connected to a power supply system (PLH120 DC Power Supply). Current densities of 2.3, 11.85 and 21.4 mA cm^{-2} were applied to assess their effects on PFOA degradation in spiked water. The supplied voltage was varied between 5.2 and 22.5 V depending on the current density and electrolyte concentration. Before and during the experiment, the electrolytic solution was homogenized by re-circulating the solution at a flow rate of 1.13 mL min^{-1} from the beaker through a polymer tube using a peristaltic pump. A control experiment in a solution containing a known amount of PFOA and Na_2SO_4 was performed without a power supply to account for any loss of PFOA that might occur during the time of the experiment. After the time assigned for each run had passed, the experiment was stopped. The samples were then collected and stored in polypropylene containers at 4°C until further analysis.

A randomized duplicate full factorial design of four factors at two levels (2^4) with two central points (Carlson 1992; Antony 2014) (Table 2) was applied to study the impact of the selected factors on the degradation of PFOA in batch mode. The factors were chosen based on their importance and effect on electrochemical treatment processes and

Table 2
Experimental design matrix of factors and their levels applied in PFOA electrochemical degradation experiments.

Factors	Levels			References
	Low (-)	Central point (0)	High (+)	
Current density (mA cm^{-2}) (X_1)	2.3	11.85	21.4	(Urriaga et al., 2015; Schaefer et al., 2017; Gomez-Ruiz et al., 2019)
Initial PFOA concentration (mg L^{-1}) (X_2)	1	5.5	10	(Trautmann et al., 2015; Schaefer et al., 2017)
Electrolyte concentration Na_2SO_4 (g L^{-1}) (X_3)	1.5	7.85	14.2	(Trautmann et al., 2015; Urriaga et al., 2015; Schaefer et al., 2017)
Time (h) (X_4)	1	2.5	4	(Urriaga et al., 2015; Schaefer et al., 2017; Gomez-Ruiz et al., 2019)

costs (Chatfield and Owen 2003; García-Gómez et al., 2014; Gomez-Ruiz et al., 2017; Nzeribe et al., 2019). The selected electrolyte (Na_2SO_4) is commonly applied in electrochemical methods and is not considered a contaminant itself (Urutiaga et al., 2015). The factor levels were selected based on ranges reported in the literature: a current density of 2–23.24 mA cm^{-2} ; a time of 0–6 h; a Na_2SO_4 concentration of 1.5–14.2 g L^{-1} ; and PFAS concentrations found in polluted water and wastewater (Zhuo et al., 2012a; Trautmann et al., 2015; Urutiaga et al., 2015; Yan et al., 2015; Schaefer et al., 2017; Gomez-Ruiz et al., 2019).

2.2.2. PFAS degradation in wastewater

The degradation of PFAS in wastewater samples was performed by applying the experimental conditions that showed the highest PFOA degradation in spiked water, i.e., a time of 4 h and a current density higher than 14 mA cm^{-2} . The current density value of 14.61 mA cm^{-2} was used based on larger size of new electrodes and the capacity of the power supply unit (PLH120 DC Power Supply). The electrodes initially used for the treatment of synthetic water were not suitable after the first stage of the experiments, and new BDD electrodes were produced using the same materials. A test comparing old and new BDD electrodes was performed, and no deviation in current density from the intended values was observed. The supplied voltage varied in the range of 9.2–15.9 V depending on the type of sample and whether the electrolyte was added or not. Although the electrolyte concentration was sufficient for providing electrical conductivity, paired experiments were run for each sample with and without the addition of 1.5 g L^{-1} Na_2SO_4 to assess the impact of Na_2SO_4 on sample treatment.

2.3. Analytical methods

The extent of PFAS degradation in treated samples was analytically measured with liquid chromatography-tandem mass spectrometry (LC-MS/MS) by following available standard methods (DIN 38407–42, UNEP Chemicals Branch, 2015 mod; W-PFCLMS02). Eleven PFAS compounds (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFBS, PFHxS, PFOS, and 6:2 FTS) were analysed in spiked water and wastewater samples; the sum of linear and branched PFOS, PFHxS and PFOA is reported (Nomenclature and list of abbreviation of analysed PFAS is given in Table S1). The F^- generated from the degradation of PFAS was measured using an F^- ion-selective electrode (ISE). Prior to F^- measurement, calibration standards were prepared by diluting a stock solution of 0.1 M NaF to desired concentrations. The calibration curve was linear in all analytical ranges, and the lowest standard (10^{-6} mol L^{-1}) was chosen based on the detection limit of the ISE assigned by the manufacturer (Metrohm). Before each F^- analysis, 10 mL of TISAB III was added to 10 mL of calibration solution to adjust the pH to 5.4–5.5, which is the optimal pH range for F^- determination using an ISE. The total organic carbon (TOC) was analysed using a TOC-V CSH total organic carbon analyser (SHIMAZOU) (LOD = 4 $\mu\text{g L}^{-1}$), and chloride ions were analysed using a calorimetric analyser (QUAATRO BRAN + LUEBBE).

2.4. Data analysis and statistical computation

The target experimental responses were PFOA degradation (%) and the fraction of generated F^- (%). Fluoride production upon treatment is an indirect measurement of complete degradation (mineralization), whereas the measured PFOA degradation indicates both the partial and complete degradation of PFOA. To evaluate the response output, the ratios were calculated using equations (1) and (2):

$$\% \text{ generated fluoride} = \frac{C_{\text{F}_i} * Mm_{\text{PFOA}}}{(\text{PFOA})_i * n_{\text{PFOA}}} * 100 \quad (1)$$

$$\% \text{PFOA degradation} = \frac{(\text{PFOA})_i * - (\text{PFOA})_t}{(\text{PFOA})_i} * 100 \quad (2)$$

where C_{F_i} is the molar concentration (mol L^{-1}) of fluoride measured with the ISE, and $(\text{PFOA})_i$ and $(\text{PFOA})_t$ are mass concentrations (g L^{-1}) of the initial and remaining PFOA, respectively. Mm is the molar mass of PFOA, whereas n_{PFOA} is the number of fluorine atoms comprising PFOA. A mass balance approach was applied to determine the speciation of fluorine in treated and untreated samples. To estimate the organic, inorganic and undetected fluorine, mathematical equations (3)–(5) were used.

$$m\text{F}_{\text{inorganic}} = C_{\text{F}_i} * Mm_{\text{F}} * V \quad (3)$$

$$m\text{F}_{\text{organic}} = \sum \frac{C_{\text{PFAS}_i} \times V \times n_{\text{F}_i} \times Mm_{\text{F}}}{Mm_{\text{PFAS}_i}} \quad (4)$$

$$m\text{F}_{\text{undetected}} = m\text{F}_{\text{PFOA}_i} - m\text{F}_{\text{organic}} - m\text{F}_{\text{inorganic}} \quad (5)$$

where V is the volume of sample (L) used in the experiment, C_{PFAS_i} is the mass concentration (g L^{-1}) of each detected PFAS molecule at time (t), and n_{F_i} is the number of fluorine atoms in each PFAS molecule.

It was assumed that fluoride ($m\text{F}_{\text{inorganic}}$) represented the F^- measured using the ISE, organic fluorine ($m\text{F}_{\text{organic}}$) was the mass of fluorine atoms constituting all detected PFAS after a certain degradation time, and undetected fluorine ($m\text{F}_{\text{undetected}}$) was the mass of all unknown fluorinated compounds.

Modde 12.1 software (Umetrics, Sartorius Stedim Biotech, Sweden) was used for the design of the experiment and data analysis, as well as to compute the importance of regression coefficients and the significance of each factor and their interactions with respect to the responses. The parameters of basic model statistics, such as R^2 , Q^2 and reproducibility, were also evaluated. The model was applied to predict the degradability of PFAS in wastewater samples.

3. Results and discussion

3.1. Factor and interaction effects on the degradation of PFOA in spiked water

The results of PFOA degradation (Y_1), the generation of F^- (Y_2) and the levels of degradation products obtained with the studied factors are presented in Table 3. The results show that the responses varied when the factors changed. The influence of each factor and their interactions on the degradation of PFOA and generated F^- is displayed in the regression coefficient plot (Fig. 1).

The regression coefficients represent the weight of each factor or their interactions on the responses. A positive coefficient indicates that increasing the factor level had a positive effect on the response, whereas a negative coefficient indicates that when the factor level increased, the response decreased and *vice versa*. As presented in table of significance of model terms (Table S2), the small standard errors and low p-values to each factors and interactions demonstrate that those factors are statistically significant to the degradation of PFOA and fluoride generation.

The factors that were important for PFOA degradation and for the formation of fluoride ions were different. These two responses measure different outcomes since the degradation of PFOA is a measurement of how many PFOA molecules undergo transformation upon treatment, whereas F^- generation is an indirect measurement of the complete degradation of PFOA.

The data analysis showed that current density (X_1) and time (X_4) were both the most important factors in the degradation of PFOA and F^- generation. A PFOA degradation efficiency of 99.5% was achieved after using a 10 mg L^{-1} initial PFOA concentration, 21.4 mA cm^{-2} and 4 h (Table 3). However, the current density was more important than time; their regression coefficients for PFOA degradation and F^- generation were $b_1 = +23.0$ and $+5.8$ and $b_4 = +11.3$ and $+5.3$, respectively. The impacts of time and applied current density were in agreement with those of several previous studies conducted using different BDD-coated

Table 3
Average (\pm standard deviation) PFOA degradation (%) at different levels of the four studied factors (n = 2).

Factors				Responses		
	Current density (mA cm ⁻²)	Initial PFOA (µg L ⁻¹)	Initial Na ₂ SO ₄ (g L ⁻¹)	Time (h)	% PFOA degradation	% F ⁻ generation
2.3	10 ³	1.5	1		2.9 ± 6.6	11.3 ± 0.7
21.4	10 ³	1.5	1		86.5 ± 6.4	26.1 ± 2.8
2.3	10 ⁴	1.5	1		17.9 ± 2.9	6.8 ± 0.2
21.4	10 ⁴	1.5	1		65.8 ± 0.7	28.4 ± 0.1
2.3	10 ³	14.2	1		19.2 ± 10.2	8.1 ± 0.5
21.4	10 ³	14.2	1		90.5 ± 5.5	15.7 ± 1.1
2.3	10 ⁴	14.2	1		17.3 ± 4.2	7.7 ± 2.0
21.4	10 ⁴	14.2	1		55.2 ± 14.1	17.8 ± 0.4
2.3	10 ³	1.5	4		57.6 ± 0.0	28.0 ± 1.7
21.4	10 ³	1.5	4		99.2 ± 0.3	47.4 ± 0.4
2.3	10 ⁴	1.5	4		54.3 ± 0.0	25.9 ± 0.3
21.4	10 ⁴	1.5	4		99.5 ± 0.3	50.0 ± 1.4
2.3	10 ³	14.2	4		67.4 ± 4.9	22.9 ± 1.7
21.4	10 ³	14.2	4		99.5 ± 0.1	17.7 ± 0.7
2.3	10 ⁴	14.2	4		53.5 ± 1.0	19.1 ± 0.4
21.4	10 ⁴	14.2	4		97.3 ± 2.5	26.2 ± 0.0
11.85	5.5·10 ³	7.85	2.5		91.1 ± 0.5	28.6 ± 0.6

materials (Carter and Farrell 2008; Liao and Farrell 2009; Urtiaga et al., 2015; Gomez-Ruiz et al., 2019).

The increasing electrolyte concentration (X₃) had a negative impact only on the generation of F⁻. For example, when 21.4 mA cm⁻² was applied for 4 h, the generation of F⁻ dropped from 50.0% to 26.2% after the concentration of Na₂SO₄ was changed from 1.5 to 14.2 g L⁻¹ (Table 3).

The degradation of PFOA was slightly decreased by increasing its initial concentration, unlike a prior study that reported a slight increase in PFOA degradation (on Si/BDD) when the PFOA concentration was increased from 20 to 50 mg L⁻¹ (Zhuo et al., 2012). However, the current behaviour was similar to the findings of Lin et al. (2012), where PFOA degradation over Ti/SnO₂-Sb increased when the initial PFOA concentration was increased from 5 to 500 mg L⁻¹ (Lin et al., 2012). The initial concentration of PFOA (X₂) was determined to be non-significant with respect to the generation of fluoride (p = 0.893), but its interaction with the current density (X₁*X₂) significantly impacted (p = 0.001) the generation of F⁻.

PFOA degradation and the generation of F⁻ were both significantly affected by factor interactions. The density*time interaction (X₁*X₄) had a negative impact on PFOA degradation, whereas three factor interactions, i.e., current density*PFOA (X₁*X₂), current density*electrolyte (X₁*X₃) and electrolyte*time (X₃*X₄), showed a significant impact on the generation of F⁻, with only the X₁*X₂ interaction having a synergistic effect. This implies that increasing electrolyte concentration may reduce the significance of time and current density for the complete degradation of PFOA, as their interaction coefficients had a negative effect on fluoride generation. Even if time and current density have a positive impact on PFOA degradation, their corresponding squared terms, X₁² and X₄², have negative coefficients. To improve the model, the addition of square terms was necessary; a similar approach was applied by (García-Gómez et al., 2014) in the electrochemical oxidation of carbamazepine using Ti/BDD electrodes. The current analysis yielded good models after including square terms; for example, for PFOA degradation, R² and Q² increased from 0.86 to 0.96 and 0.81 to 0.94, respectively, at the 95% confidence level. Likewise, for F⁻ generation, R² and Q² improved from 0.92 to 0.97 and 0.85 to 0.91, respectively. The calculated statistical model validity for both PFOA degradation and defluorination were low (i.e. -0.2 and 0.1 respectively), which is commonly observed for the small datasets generated by the experiments. However, the analysis displayed good R², Q² and an excellent reproducibility (>0.97), indicating that predictive accuracy of the model is very good.

By running multiple regression analyses on significant factors, two polynomial regression models (Eqs. (6) and (7)) describing a relationship between the degradation of PFOA or generation of F⁻ and important factors were generated:

$$Y_1 = 92.7 + 23.0X_1 - 4.0X_2 + 11.3X_4 - 11.9X_1^2 - 13.1X_4^2 - 4.6X_1*X_4 \quad (6)$$

$$Y_2 = 30.3 + 5.8X_1 - 5.3X_3 + 5.3X_4 - 5.9X_1^2 + 1.6X_1*X_2 - 3.3X_1*X_3 - 2.3X_3*X_4 \quad (7)$$

where Y₁ is the percentage of PFOA degradation and Y₂ is the percentage of generated F⁻ predicted by the two models. The factors X₁, X₂, X₃, and X₄ stand for current density, initial concentration of PFOA, initial concentration of electrolyte and time respectively. The high values of the regression model parameters (R² and Q²) indicated that the models were significant and that future predictions had good precision. Thus,

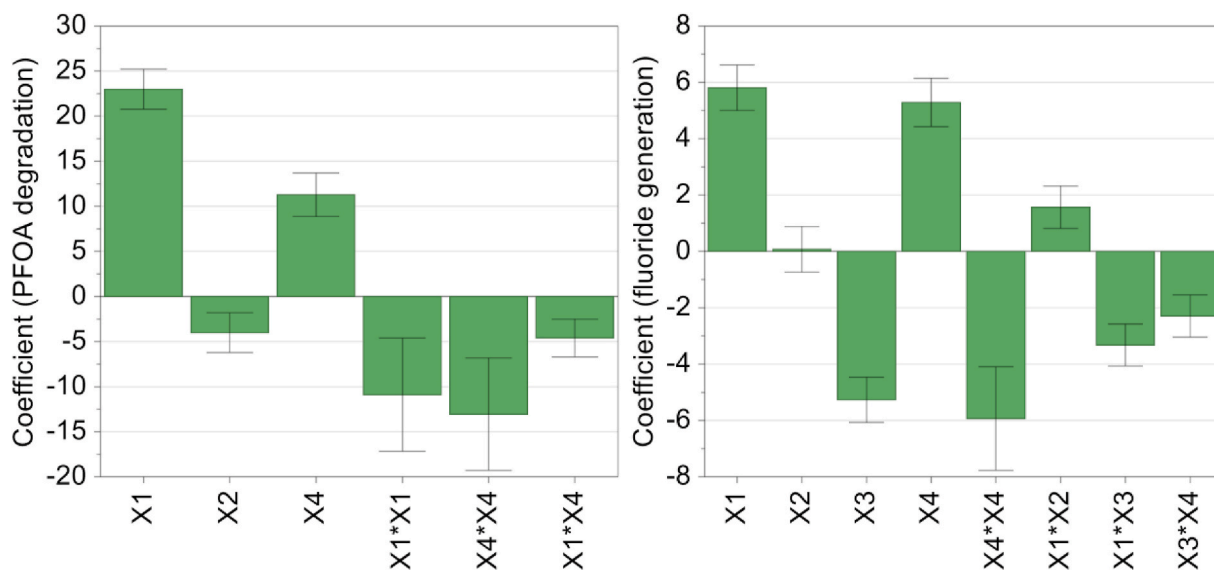


Fig. 1. Scaled and centred coefficients for PFOA degradation (left) and the generation of F⁻ (right); a description of each variable symbol is presented in Table 2. Error bars represent the 95% confidence interval, and the initial PFOA concentration (X₂) is included because its interaction with the current density is a significant factor for the generation of fluoride (X₁*X₂).

assuming that there were no other factors that had an influence on the response, PFOA degradation (Y_1) and the generation of F^- (Y_2) could be predicted with 94% and 91% accuracy, respectively, within the experimentally investigated ranges.

3.2. Electrochemical degradation of PFOA in spiked water

The experimental results revealed that the highest PFOA degradation and generation of F^- were 99.5% and 50%, respectively (Table 3). These responses were found after combining the following factors: a current density of 21.4 mA cm^{-2} , time of 4 h, initial PFOA concentration of 10 mg L^{-1} and initial Na_2SO_4 concentration of 1.5 g L^{-1} .

Indeed, PFOA degradation of up to 91% and F^- generation of 29% in 150 min were observed by running central points, which indicates that complete PFOA transformation could be achieved at the factor levels below the maxima applied in the current study. These results were in reasonable agreement with the findings by Schaefer et al. (2017), although the previous study reported higher fluoride recovery (approx. 60%), which was probably due to the higher current density utilized in their experiment (50 mA cm^{-2}).

Extrapolation/interpolation was used to find variations in the responses as a function of electrical charge. As illustrated in Fig. 2, the degradation of PFOA and generation of F^- quickly increased as the cumulative charge increased. The degradation of PFOA and generation of F^- reached approximately 100% and 41%, respectively, when the cumulative charge increased to 1.5 Ah. Further increasing the charge slightly increased F^- generation.

In general, PFOA degradation was consistently greater than F^- generation. A small part of PFOA is degraded into shorter-chain PFAS (Table S3), which ultimately undergo slower mineralization (Lin et al. 2012, 2013; Zhuo et al., 2012a; Trautmann et al., 2015; Li et al., 2020; Wang et al., 2020). The impacts of various factors on PFAS degradation and F^- generation differed (Fig. 1), which indicates that the mechanisms driving these processes are different. This in turn led to the observed differences between the degraded concentration of PFOA and the amount of generated F^- .

Response contour plots obtained from the 2^4 full factorial design were used to illustrate the role of time and current density at a constant electrolyte concentration ($1.5 \text{ g L}^{-1} \text{ Na}_2\text{SO}_4$) and an initial concentration of PFOA of 5.5 mg L^{-1} (Fig. 3). The contours are curved because the models contain significant squared terms. Both plots indicate that to maximize PFOA degradation as well as the generation of F^- , time and current density should be increased. The contour plots were not

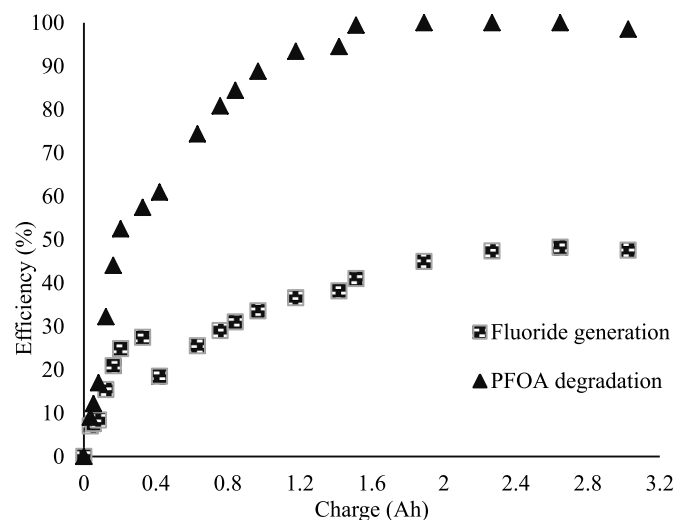


Fig. 2. Effect of electric charge on PFOA degradation (triangles) and the generation of F^- (squares). Conditions: $1.5 \text{ g L}^{-1} \text{ Na}_2\text{SO}_4$ and 5.5 mg L^{-1} PFOA.

identical, once again indicating that the degradation of PFOA and release of fluoride ions in solution are not exactly proportional in the studied region. The calculated results demonstrate that by increasing the current density (X_1) and time (X_4) from the lowest levels to the centre points (from 2.30 to 11.85 mA cm^{-2} and 1 – 2.5 h), the degradation of PFOA increased 5.3-fold, and the amount of generated F^- increased 4.1-fold. When the two factors were fixed to their highest levels (21.3 mA cm^{-2} and 4 h), the degradation of PFOA increased 5.8-fold, and the amount of generated F^- increased 5.7-fold.

The model showed that the increase in degradation rate over time at a fixed current density was not linear. According to Panizza et al., (2001), this is an indication that PFOA degradation was most likely limited by mass transfer towards the electrode surface. The best regions for the responses were a time of 3–4 h and a current density higher than 14 mA cm^{-2} ; under these conditions, approximately 100% PFOA degradation and 40–50% generation of F^- could be achieved.

3.3. Effect of electrochemical factors on degradation products

The complete disappearance of PFOA from solution after treatment does not necessarily mean that PFOA underwent complete degradation, leading to the production of carbon dioxide and fluoride. PFOA degradation is a stepwise reaction that removes each carbon group until the smallest and not easily degradable molecule is formed (Lin et al., 2013; Li et al., 2020; Wang et al., 2020).

A high PFOA degradation efficiency (99.5%) in $1.5 \text{ g L}^{-1} \text{ Na}_2\text{SO}_4$ solution resulted in the generation of approximately 49% undetected fluorinated compounds and 50% F^- (Fig. 4). As presented in Table S3, only low concentrations of short-carbon-chain PFAS (PFBA, PFPeA, PFHxA and PFHpA) and PFOA were detected (a fraction of organic fluoride).

Regarding the influence of electrochemical conditions on fluorine speciation, the current results indicate that the fraction of undetected fluorinated compounds increased when the level of one of three factors (i.e., time, electrolyte or current density) was increased. For example, the percentage of undetected fluorine increased from 61% to 75% when the level of Na_2SO_4 changed from 1.5 to 14.2 g L^{-1} under the same levels of the other factors (i.e., 1 mg L^{-1} PFOA, 1 h and 21.4 mA cm^{-2}). The undetected fluorine fraction increased again from 20% to 49% when the applied current density was changed from 2.3 to 21.4 mA cm^{-2} with the same long time, high PFOA concentration and low electrolyte concentration. In addition, the undetected fluorine fraction increased from 29% to 72% when the time was changed from 1 to 4 h in combination with high levels of the other three factors. Prior studies reported a similar behaviour for PFOA degradation, released fluoride and undetected fluorine when the time or current density was varied (Urriaga et al., 2015; Schaefer et al., 2017). In contrast, the fraction of undetected fluorinated compounds decreased as the initial concentration of PFOA increased. For example, when the initial PFOA concentration increased from 1 to 10 mg L^{-1} , $\text{mF}_{\text{undetected}}$ decreased from 61% to 32% when the time and current density were 1 h and 21.4 mA cm^{-2} , respectively.

3.4. Application of experimental factors to wastewater samples

Wastewater samples containing PFAS were treated by applying the best-performing factor levels (current density of 14.6 mA cm^{-2} , time of 4 h and with/without the addition of $1.5 \text{ g L}^{-1} \text{ Na}_2\text{SO}_4$) to estimate whether the complexity of the samples would interfere with PFAS treatment. Table 4 summarizes the concentrations of 11 PFAS compounds of treated samples.

Three categories of PFAS substances, including perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFASs) and 6–2 fluorotelomer sulfonic acid (6-2 FTSA), were detected in untreated samples. Among the 11 analysed PFAS, the most abundant PFAS were 6-2FTSA (14.7 – $24.3 \text{ } \mu\text{g L}^{-1}$), PFOS (3.23 – $19.10 \text{ } \mu\text{g L}^{-1}$), PFHxS (3.65 – $11.5 \text{ } \mu\text{g L}^{-1}$), PFHxA (1.19 – $2.72 \text{ } \mu\text{g L}^{-1}$) and PFPeA (1.02 – $1.69 \text{ } \mu\text{g}$

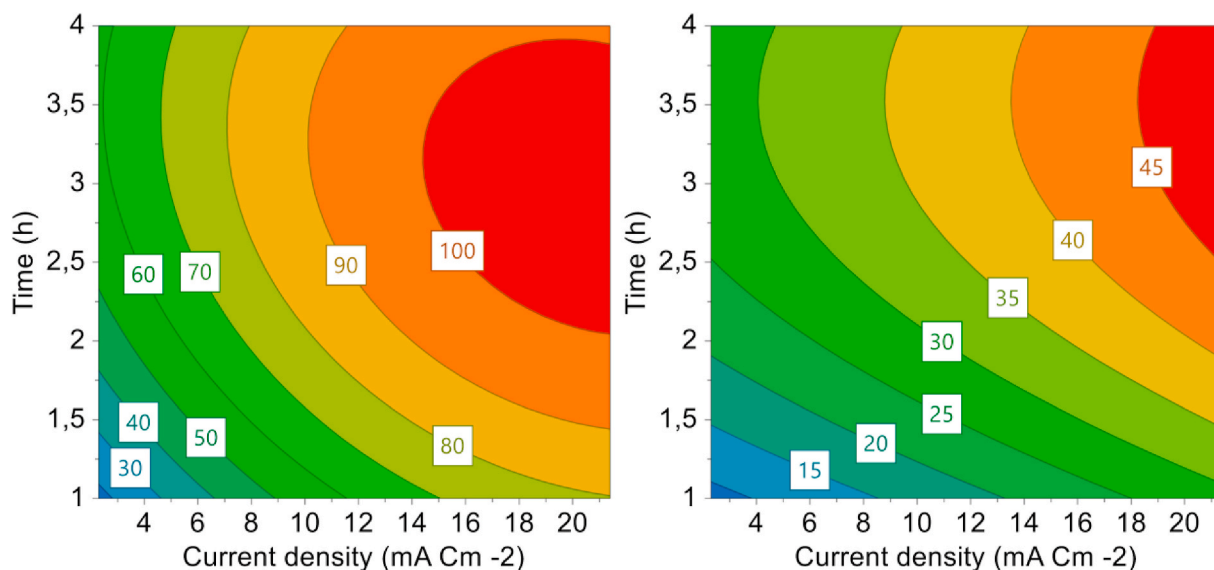


Fig. 3. Combined effect of current density and time on the degradation of PFOA (left) and measured F⁻ generation (right) under constant electrolyte (1.5 g L⁻¹ Na₂SO₄) and initial PFOA concentrations (5.5 mg L⁻¹).

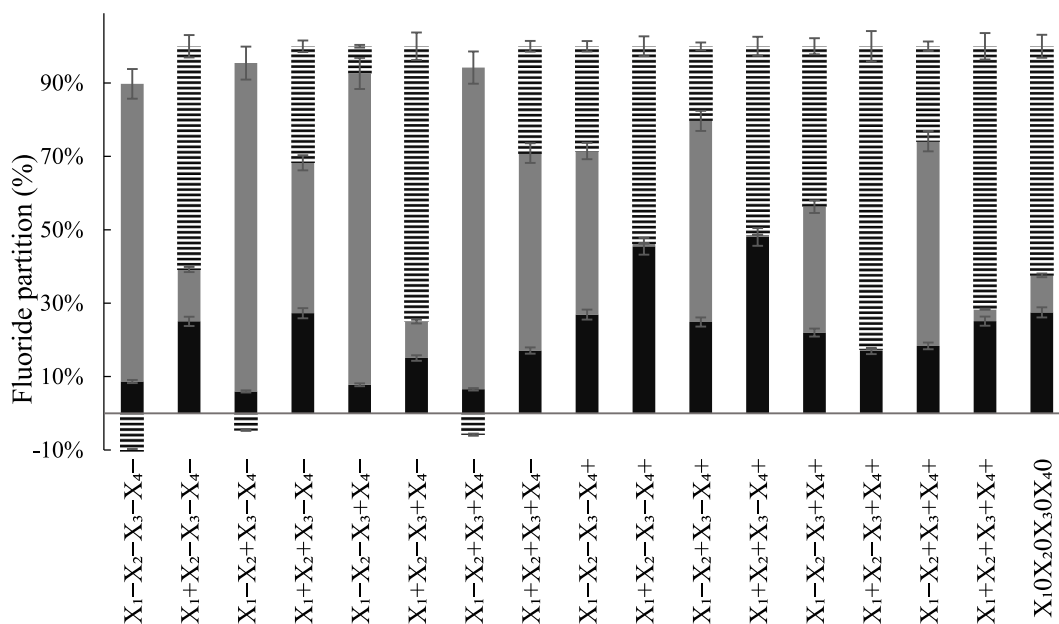


Fig. 4. Fluorine distribution among fluoride (dark bars), organofluorine (grey bars) and undetected fluoride species (horizontal lines). The X-axis represents the average results (n = 2) of successive experiment runs, and the four plus/minus/zero codes are the levels of the four factors. Details regarding the factor levels are presented in Table 1.

L⁻¹). The concentrations of the other PFAS ranged from below the detection limit (<0.01) to 1.00 µg L⁻¹. In general, the total concentrations of the 11 PFAS were 40.6, 41.6 and 53.2 µg L⁻¹ for sample I, sample II and sample III, respectively.

Electrochemical treatment reduced the concentrations of long-chain compounds (Fig. 5 a, b and c). However, due to the complexity of the samples, the applied current density and degradation time did not help to achieve maximum PFAS degradation.

The results showed that PFSA, PFCA and FTSA compounds were degraded with different efficiencies, and the order of degradation efficiency in the presence of Na₂SO₄ was PFSA > PFCA > FTSA (i.e., 65–80% PFOS, 44–70% PFOA and 42–52% 6-2 FTSA degradation). The observed degradation tendency was not similar to that of previous

studies, which showed that PFCAs (i.e., PFOA) degrade more easier than PFASs (i.e., PFOS) (Zhuo et al., 2012; Trautmann et al., 2015; Schaefer et al., 2017; Pierpaoli et al., 2021, Gomez et al., 2019). The probable reason for the observed low PFOA removal in wastewater could be that the samples contained PFOA precursors (not included in the target analytes), which increased the concentration of PFOA. Previous studies showed that 8:2 FTCA is transformed into PFOA during the oxidation process (Houtz and Sedlak 2012; Anumol et al., 2016). Short-carbon-chain PFCA, PFBA, PFPeA, PFHxA and PFBS were generated after wastewater treatment which are the degradation products. These molecules could have originated from decomposed PFSA and 6-2 FTSA, as previously reported (Zhuo et al., 2012; Yang et al., 2014; Li et al., 2020).

Table 4
PFAS concentrations of treated samples.

Parameters	Sample I		Sample II		Sample III	
	Treated (without SO ₄ ²⁻)	Treated (with SO ₄ ²⁻)	Treated (without SO ₄ ²⁻)	Treated (with SO ₄ ²⁻)	Treated (without SO ₄ ²⁻)	Treated (with SO ₄ ²⁻)
PFBA	1.40	1.40	1.40	1.60	4.46	3.79
PFPeA	0.81	0.65	0.76	0.96	1.57	1.89
PFHxA	1.90	1.90	2.00	2.10	2.74	3.40
PFHpA	0.40	0.34	0.42	0.52	0.51	0.51
PFOA	0.40	0.32	0.20	0.13	0.54	0.29
PFNA	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
PFDA	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
PFBS	2.00	2.30	1.80	1.80	3.39	3.35
PFHxS	2.00	1.60	1.20	0.98	5.18	4.42
PFOS	2.70	2.50	0.93	1.20	6.09	3.86
6:2 FTSA	16.00	11.00	11.00	14.00	10.30	8.43
Σ11 PFAS	27.61	22.01	19.71	23.29	34.78	29.94

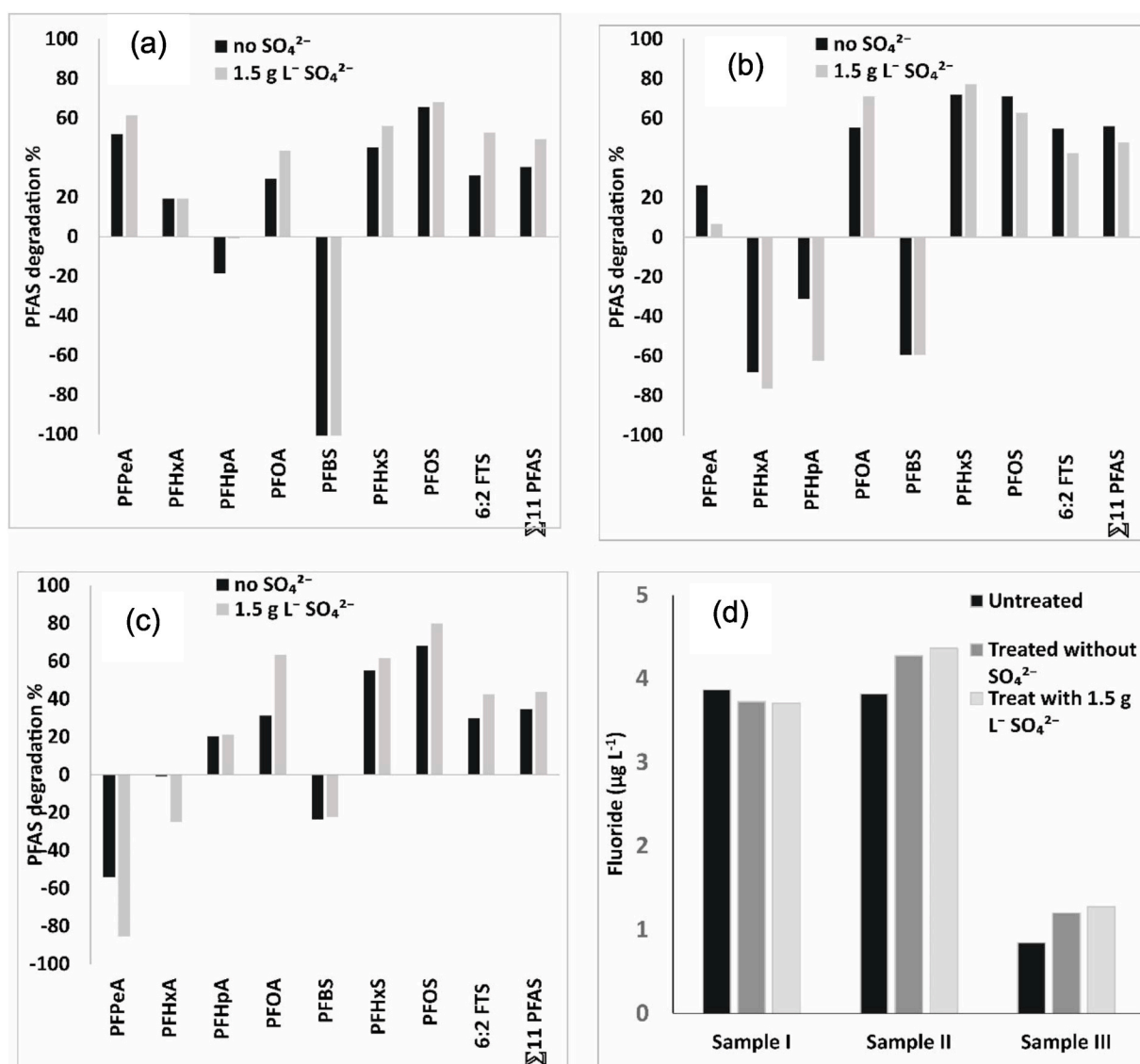


Fig. 5. Electrochemical degradation of PFAS in sample I (a), sample II (b) and sample III (c) and the evolution of fluoride (d); experimental conditions: CD = 14.6 mA cm⁻² and time = 4 h. Experiments were run with and without the addition of 1.5 g L⁻¹ Na₂SO₄. The percentage of PFBA degradation is not presented as its concentration in untreated samples was below the limit of detection even though it was detected in treated samples.

All samples initially contained a high concentration of TOC; sample III had a higher TOC content (10678 mg L⁻¹) than sample I (3570 mg L⁻¹) and sample II (2860 mg L⁻¹) (Table 1). The measured TOC shows the amount of organic compounds present in wastewater samples rather

than the mineralization of PFAS, which are not easily oxidized by the TOC analyser. Moreover, the high TOC in the samples allowed the contribution of any fraction of oxidized PFAS to be neglected.

The TOC measurement performed on the treated samples showed

that the electrochemical degradation of organic matter occurred while treating PFAS compounds. TOC degradation of 26%–36% (sample I), 50%–52% (sample II) and 20%–39% (sample III) was found after treating the three samples in the presence and absence of Na_2SO_4 (Fig. 6 a). Less TOC was removed when the electrolyte was added. The used electrolyte (SO_4^{2-}) might have reacted with generated hydroxyl radicals (Davis et al., 2014), which degrade organic compounds.

The presence of TOC may have competed with PFAS for degradation on the BDD electrode, as demonstrated in other studies (Schaefer et al., 2017; Gomez-Ruiz et al., 2017; Pierpaoli et al., 2021). Nevertheless, the degradation of PFAS was not proportionally affected by the concentration of TOC in the samples. For example, when Na_2SO_4 was added, the order of $\Sigma 11$ PFAS degradation in the three samples was sample I (49%) > sample II (48%) > sample III (44%), while the order of the TOC content in the untreated samples was sample III > sample I > sample II. The $\Sigma 11$ PFAS degradation efficiency was higher in the presence of Na_2SO_4 , except for sample II (the $\Sigma 11$ PFAS degradation efficiency reached 56% in the absence of Na_2SO_4).

Similar to the TOC, the removal of Cl^- was observed in electrochemically treated wastewater samples, although the trend was not the same as it was for the degradation of PFAS. Studies show that electrochemical treatment transforms chloride ions into other oxidized chlorine species (chlorine gas, ClO_2^- , ClO_3^- or ClO_4^-) (Bergmann et al., 2009; Song et al., 2010; Azizi et al., 2011; Radjenovic et al., 2020; Yang 2020), which was the likely reason for the decreased chloride concentration (45–60% removal) in the three samples (Fig. 6 b).

3.5. Overall efficiency of the electrochemical treatment of solutions contaminated with PFAS

The degradation of PFAS by using the electrochemical method was previously shown to be affected by different conditions, including current density, time, electrolyte, initial concentration, pH, temperature, and sample matrices (Zhuo et al., 2012; Trautmann et al., 2015; Urutiaga et al., 2015; Gomez-Ruiz et al., 2017; Schaefer et al., 2018). The current study showed that the current density (X_1) and time (X_4) were both the most important factors for the degradation of PFOA and generation of F^- in synthetic water. High current density and degradation time create a high accumulative charge on the BDD anode, which enhances the breakdown of organic compounds (Martínez-Huitle and Ferro 2006). Prior researchers have shown that the degradation of PFOA occurs due to the direct transfer of electrons from carboxyl groups to the BDD

surface anode (Carter and Farrell 2008; Ochiai et al., 2011; Zhuo et al., 2012). The slight increase in PFOA degradation and F^- generation at electrical charges higher than 1.5 Ah (Fig. 2) observed in our study could be due to the discharge of water at the anode, which may reduce the efficiency of the current density. Although generated hydroxyl radicals (OH^\cdot) could degrade organic contaminants (Michaud et al., 2003; Martínez-Huitle and Ferro 2006; Martínez-Huitle and Panizza 2018), several studies have demonstrated that these radicals have no potential to degrade PFOA (Carter and Farrell 2008; Vecitis et al., 2008; Ochiai et al., 2011; Zhuo et al., 2012).

In contrast to other oxidative methods (e.g., the photochemical method) that require supporting chemicals to achieve good efficiencies, the electrochemical method may be favoured due to the addition of small amounts of electrolyte, which can make it feasible due to the low cost of chemicals. Our study showed that the generation of F^- was negatively impacted by the high concentration of Na_2SO_4 (Fig. 1). The main reason might be that sulfate is electrochemically transformed into persulfate, which can decrease the electrical current efficiency (Panizza et al., 2001; Serrano et al., 2002; Samet et al., 2010; García-Gómez et al., 2014; Davis et al., 2014), while the formed persulfate itself has no effect on PFOA degradation (Urutiaga et al., 2015). The greater fraction of fluoride generated at the low electrolyte concentration might be attributed to the high cell voltage created by a high solution resistance, which is the driving force in electrochemical degradation reactions (Xiong and Karlsson 2002; Urutiaga et al., 2015). However, electrolyte concentration is critical when considering energy consumption, as lower electrolyte concentrations create higher electrical resistance, which increases the energy use, as well as the temperature of the solution. E.g., the energy consumption decreased twofold when the Na_2SO_4 concentration was increased from 1.5 to 14.2 mg L^{-1} (Table S4). Likewise, solution temperature decreased from 38.0 to 28.0 °C when the same change of Na_2SO_4 concentration was made under 21.4 mA cm^{-2} .

The results of PFOA degradation in synthetic water indicate that the method can effectively destroy PFAS from contaminated groundwater, which contains a small amount of other oxidizable substances. An effective treatment of PFOS and PFOA in contaminated groundwater was performed by Schaefer et al. (2017; 2018) in the presence of a low concentration of oxidizable substances, which did not have any significant impact on the degradation efficiency.

The degradation of PFOA is accompanied by the formation of short-chain PFAS that are persistent and very mobile in water and soil environments, but less bioaccumulative and less toxic (Zhuo et al., 2012;

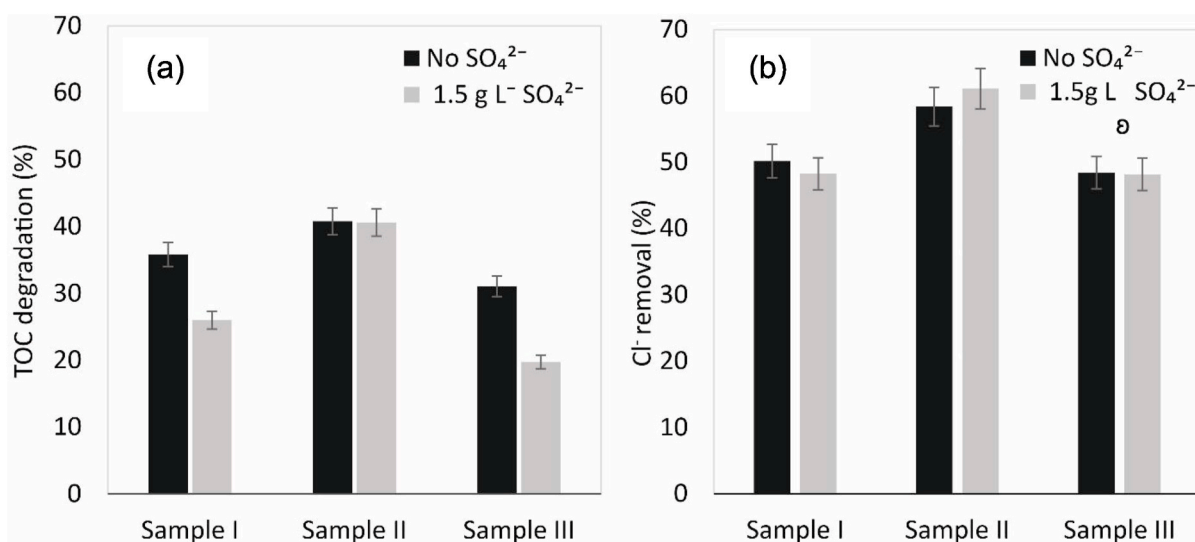


Fig. 6. Effect of electrochemical treatment (14.61 mA cm^{-2} and 4 h) on TOC (a) and chloride (b) in wastewater samples in the presence and absence of 1.5 g L^{-1} Na_2SO_4 electrolyte.

Wang et al., 2015; Brendel et al., 2018; Li et al., 2020). The current results indicate that the degradation of PFOA resulted in the formation of a small fraction of short-chain PFAS (C₄–C₇). Interestingly, no or a very small fraction of short-chain PFAS was detected in 4 h at 21.4 mA cm⁻². On the other hand, another fraction of fluorinated compounds disappeared, as demonstrated by the fluorine mass balance (Fig. 4). Prior studies showed that undetected fluorine may occur due to two main reasons: the adsorption of fluorinated radicals on the anode surface or the formation of volatile fluorinated products, such as CHF₃, CF₄ and C₂F₆ (Krusic and Roe 2004; Yamamoto et al., 2007; Guan et al., 2007; Ochiai et al., 2011). In addition, it is speculated that further degradation into ultrashort-chain PFAS (PFPeA or TFA) or the formation of fluorinated by-products is possible (Gomez-Ruiz et al., 2017), but these compounds were not detected here by the used analytical method. Our study suggests that a high current density and increased degradation time may enhance the adsorption of fluorinated compounds to BDD electrodes and the release of volatiles products.

The experimental results obtained for the treated wastewater samples did not match those calculated using the model for PFOA degradation (Eq. (6)). The model predicted approximately 100% PFOA degradation efficiencies in the three samples, whereas their observed degradation results were 44%, 71% and 64% for samples I, II and III, respectively. The difference in the expected and actual results might have originated from the sample matrix that incorporated other factors relevant for the electrochemical oxidation of PFAS. A large amount of oxidizable substances in samples decreases the extent of PFAS degradation (Gomez-Ruiz et al., 2017; Pierpaoli et al., 2021). Even though organic substances in the wastewater samples are degraded by generated oxidant species, such as OH[•] or OCl⁻ (Zhi et al., 2003; Ochiai et al., 2011; Martínez-Huitle and Panizza 2018; He et al., 2019), they are simultaneously oxidized through the direct transfer of electrons to the BDD anode, which may have competed with the degradation of PFAS.

Overall, the removal of up to 56% Σ11PFAS was achieved in wastewater samples. As observed in spiked water, the treatment of wastewater also resulted in the formation of short-chain PFAS, as represented by the negative degradation values in Fig. 5. However, different wastewater samples reacted differently to the treatment in terms of which short-chain molecules were created. Thus, further studies are needed to fully understand the reasons.

The current study suggests that the degradation time and applied current density might need to be increased for PFAS degradation to account for all oxidizable compounds (e.g., TOC and chlorides) in wastewater samples.

4. Conclusions

This study demonstrated that electrochemical degradation using BDD electrodes could be effectively applied for the degradation of PFAS in contaminated water and wastewater.

In this study, the highest PFOA degradation efficiency (up to 99.5%) was achieved by combining a high current density (21.4 mA cm⁻²) and long-time (4 h). The same efficiency was achieved both at high (10 mg L⁻¹) and low (1 mg L⁻¹) initial PFOA concentrations. A slightly lower PFOA degradation efficiency (91%) was achieved in a shorter time (2.5 h), so if the resulting final PFOA concentration is acceptable, the treatment duration can be significantly reduced. A shorter treatment time would be beneficial from the energy consumption point of view.

At the highest PFOA degradation efficiency, only half of fluoride was recovered, partly due to the formation of small amounts of shorter-chain molecules, such as PFBA, PFPeA, PFHxA and PFHpA, and partly due to the unaccounted loss of fluorine.

The presence of other oxidizable compounds (e.g., TOC and chloride) in the studied three industrial wastewater samples decreased the efficiency of PFAS degradation, while short-chain PFAS (mainly PFBS) were formed during the treatment. Nevertheless, the environmental impact of the incomplete degradation of PFAS might be smaller than that of the

initial PFAS compounds, as shorter-chain PFAS are expected to be less toxic. Furthermore, the complete removal of short-chain PFAS could be achieved in wastewater samples by further increasing the treatment time.

Electrochemical degradation is a non-selective method that degrades all oxidizable substances, including other organic pollutants and chloride. In this study, substances containing organic carbon were degraded and chloride were removed while targeting PFAS. This could be considered an added value of the treatment, since the removal of TOC and chloride from wastewater samples is usually also required. Further studies focusing on ecotoxicity of short chain PFAS, as well as upscaling the experiments, would help to decide on the optimal conditions required for PFAS treatment in various samples.

Credit author statement

Jean Noel Uwayezu: Conceptualization, Investigation, Methodology, writing – manuscript; Ivan Carabante: Conceptualization, planning, Methodology, manuscript editing & Supervision; Jurate Kumpiene: Conceptualization, planning, Methodology, manuscript editing & Supervision; Tore Lejon: Planning & Methodology; Patrick van Hees: Investigation & Methodology; Patrik Karlsson: Investigation & Methodology; Patrik Hollman: Funding acquisition & Methodology.

Declaration of competing interest

Authors declare that they have no conflict of interest related to this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jenvman.2021.112573>.

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