



Electrochemical treatment of municipal landfill leachates and implications for poly- and perfluoroalkyl substances (PFAS) removal

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ARTICLE INFO

Editor: Despo Kassinos

Keywords:

PFAS
PFOA
BDD
Electrooxidation
Landfill leachates

ABSTRACT

This work reports the electrochemical treatment of municipal solid waste landfill leachates in a parallel plate cell provided with boron doped diamond (BDD) anodes. Two types of samples were electrooxidized at three current densities between 200 and 800 A/m²: (i) raw leachates; and (ii) the leachate after treatment in a membrane bioreactor (MBR), characterized by its near-zero ammonia content. In absence of ammonia, the electrogenerated chlorine oxidants accelerated the removal of chemical oxygen demand but barely influenced the mineralization of persistent organic pollutants still retained in the MBR-treated leachate. Furthermore, we investigated the removal of 17 poly- and perfluoroalkyl substances (PFAS) contained in the real MBR-treated leachate ($\sum_{17} \text{PFAS} = 3456 \text{ ng/L}$). The operation at 200 A/m² increased perfluorocarboxylic acids (PFCAs) concentration, indicating the presence of unknown precursors in the MBR-treated leachate. Working at 800 A/m² successfully reduced the $\sum_{17} \text{PFAS}$ content by 95% in 6 h. $\sum_{17} \text{PFAS}$ showed decreasing trends, and only perfluoropentanoic and perfluorobutanoic acids showed temporal increases that later on went down as the long chain PFCAs were degraded into shorter chain homologs. 1-log (90%) $\sum_{17} \text{PFAS}$ reduction was achieved in 4.5 h, when the formation of undesirable perchlorate was still near undetectable. We estimate that the PFAS electrooxidation rate in the leachate matrix was one-sixth of the removal rate observed in a previous study treating a cocktail of PFAS in synthetic contaminated groundwater. Overall, this work provides useful data to guide the design of advanced onsite treatment of landfill leachates, one of the main secondary PFAS entry to the environment.

1. Introduction

Poly- and perfluoroalkyl substances (PFAS) are synthetic chemicals introduced in the environment through anthropogenic activities such as their use as surfactants, coatings, water repellents for leather and textiles, metal plating and aqueous film forming foam used in firefighting, among others [1–3]. Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) have been classified as PBT (persistent, bioaccumulative and toxic) chemicals and included in Annexes A and B, respectively, of the Stockholm Convention list of persistent organic pollutants [4]. The European Commission has recently adopted the Chemicals Strategy for Sustainability, which aims to increase the protection of human health and the environment from harmful chemicals and addresses the phase out of PFAS from consumer products [5].

Municipal solid waste (MSW) landfill leachates have been identified as one main secondary source of PFAS entry to the natural environment, together with the effluents of municipal wastewater treatment plants

(WWTP) [6,7]. Household wastes are comprised of goods containing, among others, specialty/functional textiles, non-stick fluoropolymer coatings and hydrophobic or stain-resistant coatings that can release PFAS into the MSW landfills leachates [3,8,9]. Other potential input of PFAS into MSW landfills are the sewage sludge of WWTP. Several studies on the characterization of PFAS occurrence in municipal landfill leachates have been carried out in different countries around the world. In Australia, the average PFAS concentration in landfill leachates from operating MSW landfills was 3466 ng/L, while closed MSW landfill leachates were still releasing PFAS at an average rate of 2219 ng/L (data given as sum of PFAS) [10]. In contrast, the reported PFAS content in landfill leachates in China was ranging between 7280 and 290,000 ng/L, one order of magnitude higher than the range 27–25,640 ng/L obtained in the USA and Canada [11–14]. In Europe, the PFAS concentration range reported so far was lower, the minimum was detected in Germany (146 ng/L) and maximum (6123 ng/L) in Norway [1,15–17]. Most investigations reported that perfluorocarboxylic acids (PFCAs) were the

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<https://doi.org/10.1016/j.jece.2022.107900>

Received 30 December 2021; Received in revised form 8 May 2022; Accepted 10 May 2022

Available online 13 May 2022

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most abundant group of PFAS in landfill leachates, followed by perfluorosulfonic acids (PFSAs). It is also worth noting that shorter-chain PFAS were predominant compared to longer alkyl chain lengths in the PFAS found in MSW landfills. Different authors estimated the PFAS mass discharged with landfill leachates, based on PFAS concentrations and leachate volume. Lang et al. estimated a national release in the USA ranging from 563 to 638 kg of PFAS per year in 2013 [18]. Busch et al. reported an average discharge rate of the sum of 43 PFAS ($\sum_{43} \text{PFAS}$) of 49 kg/year in Germany [1]. Fuertes et al. estimated a discharge rate of 1.21 kg/year for 16 PFAS in 2015 from MSW landfills located in northern regions of Spain serving a population of about 2 million inhabitants [16]. Furthermore, Liu et al. emphasized that many PFAS precursors (such as fluorotelomers) undergo transformation processes to form very persistent perfluoroalkyl acids (PFAAs) that are released to the environment [9]. Knutsen et al. warned that short chain PFAS released from a range of household and industrial wastes could dominate over long chain compounds in the leachates of historic landfill sites [17].

Electrochemical oxidation offers excellent properties for the treatment of MSW landfill leachate, a complex aqueous liquor that contains elevated concentrations of non-biodegradable organic compounds, ammonia and chloride anions. The excellent performance of mixed metal oxides anodes for chlorine electrogeneration is useful for ammonia removal, and to a certain extent for the reduction of the chemical oxygen demand (COD) [19,20]. Boron doped diamond (BDD) electrodes provided extensive elimination of the total organic carbon (TOC) of landfill leachates, indicating the high performance of these materials to degrade the most recalcitrant organic compounds [21–25]. However, very few studies focused on the electrochemical removal of micropollutants contained in landfill leachates. A few examples can be found in recent literature. Fernandes et al. reported the successful removal of methiocarb and bis-phenol A, although both compounds were intentionally added to the real landfill to increase their concentration to 20 mg/L, which is about 10^5 times higher than in real leachates [26]. Vallejo et al. [27] reported the elimination of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) by 73% compared to the initial concentration (3710–424411 pg/L) in landfill leachates by electrochemical oxidation with a BDD anode. Similarly, Ambauen et al. [28] demonstrated a 99% removal of bisphenol A (11 $\mu\text{g/L}$) by the same treatment technology in pretreated landfill leachates using two different anode materials, Ti/Pt and NB/BDD. Oturan et al. [29] investigated the removal of different refractory micropollutants present in MSW landfill leachates (polychlorobiphenyls, polycyclic aromatic compounds, and organochlorine pesticides) by anodic oxidation process with a BDD anode getting a removal of about 98%. Despite of these previous studies, Pisharody et al. [30] pointed out there are limited works focused on the removal of micropollutants in real landfill leachates by advanced oxidation processes and in particular, by anodic oxidation. So far, the study of PFAS electrochemical remediation in real wastewaters has been scarcely studied. Examples are the treatment of industrial effluents [31–33], fluoropolymer manufacturing process water [34], groundwater impacted by PFAS contaminated soils [35] and solutions used to regenerate ion exchange PFAS adsorbents [36]. However, none of these references were dealing with background electrolytes as complex as MSW landfill leachate in terms of ammonia and load of non-biodegradable organic pollutants. Only two previous studies have reported the treatment of PFAS in raw leachates. Pierpaoli et al. studied the influence of the boron doping level of BDD anodes on PFOA and PFOS degradation after fortifying the leachate samples with spikes of both compounds that increased the natural concentration of PFOA and PFOS from 1350 and 3280 ng/L to 0.1 mg/L [37]. The study concluded that the boron doping was not greatly affecting the removal of both compounds, that reached 80%, approximately. However, the scarcity of experimental data reported and the fact that the leachates had been doped, did not allow the kinetic analysis of the process. Maldonado et al. and Witt et al. studied the electrochemical oxidation of multiple PFAAs

in real landfill leachates using an innovative flow-through cell provided with perforated niobium anode plates coated with BDD [38,39]. While PFOA and PFOS degradation was demonstrated, the authors reported low degradation rates of short-chain PFAAs, in particular perfluorobutanoic acid (PFBA), perfluorobutane sulfonate (PFBS) and perfluoropentanoic acid (PFPeA). Importantly, Maldonado et al. highlighted that the percentage of PFAAs removal was negatively affected by the level of carbon containing compounds of the landfill leachate. It is important to note that these two preliminary studies dealt with the treatment of PFAS in raw landfill leachates, in which the load of ammonia and COD was much higher than in the leachates after the onsite membrane bioreactor (MBR) treatment that will be considered in the present study. In this regard, Fuertes et al. [16] reported nearly two-fold PFAS concentration increase after MBR treatment compared to the raw leachates, which may be explained by the biotransformation of the existing precursors in the raw leachates during treatment. Sharma et al. reported a review with the latest advances and limitations of the electrochemical treatment methods of PFAS [40]. However, regarding its application to landfill leachates, only the study by Pierpaoli et al. [37] was mentioned by this work. Therefore, this literature analysis concludes that more information is needed to evaluate the electrochemical oxidation of complex mixtures of PFAS, especially at the low concentration levels occurring in real landfill leachates and with different concentrations of co-existing organic matter and ions present in other types of landfill leachates such as treated leachates.

This work aims to gain insight in the electrochemical remediation of PFAS in MSW landfill leachates, using BDD anodic oxidation. The electrochemical treatment was applied on both the raw and MBR-treated leachates, characterizing the effect of the applied current to the degradation and mineralization of the global parameters such as COD, TOC, ammonia and inorganic chlorine species. Novel results are reported considering the significant composition differences between raw leachates previously reported and MBR-treated leachates herein studied. The MBR treatment introduced a substantial modification of the PFAS profile in the leachate, and was ineffective for PFAS removal. The kinetic evolution with time of the global PFAS load and of individual PFAS (10 PFCAs, 6 PFSAs and 6:2 FTSA) were analyzed in raw leachates, and after the onsite MBR treatment, providing valuable data to guide the discussion on the effect of the applied current density and the selection of operating conditions to get the effective PFAS removal in such complex matrix.

2. Experimental

2.1. Landfill site and leachate characterization

Leachate samples were collected in a MSW landfill located in Cantabria, northern Spain. The studied landfill site is used for treatment and disposal of non-hazardous municipal solid waste from residential urban areas. It is an active old site, from which 219,000 m^3/year of leachate are collected and treated onsite. Raw leachate grab samples (5L) were collected before the leachate was transferred to the onsite MBR treatment facilities. Additionally, MBR-treated leachate grab samples (5L) were collected from the effluent of the treatment facilities. All samples were collected in polypropylene (PP) bottles pre-washed with methanol, and polytetrafluorethylene (PTFE) based materials were avoided throughout the sampling and analysis to prevent potential sample contamination. Leachate samples were collected during five consecutive days.

The onsite treatment consisted of a MBR that integrated a two-stage biological process with an external ultrafiltration (UF) unit. The biological process removed the ammonia content by its conversion into nitrogen gas and nitrate. At the same time, the organic matter content was notably reduced. Then, the biologically treated leachate entered an UF unit provided with tubular membranes to separate the biomass from the treated leachate liquid fraction. The biomass returned to the

bioreactor, and the clarified treated leachate went to the general sewage system connected with the centralized municipal wastewater treatment facility. Table 1 presents an overview of the leachate samples chemical characterization. The reasonably low standard deviation of the results obtained in the five samples evidences no significant intra-day sampling differences.

The initial ammonia concentration of 1380 mg/L in the raw leachate, was completely removed in the MBR-treated leachate. The high load of organic pollutants in the raw leachate was reduced by near four times in the treated leachate. Still, the treated leachate presented a COD of 454 mg/L, although the MBR treatment could not degrade the remaining non-biodegradable organic compounds, exemplified by the TOC of 192 mg/L. A significant part of the organic carbon contained in the raw leachate was transformed into inorganic carbon (IC) that was retained as carbonate in the treated leachate. Chlorides were barely affected by the leachate treatment, with similar concentration in the raw and treated leachate samples. Therefore, the MBR-treated leachate used in this study differs significantly from the raw leachates analysed in the recent work of Maldonado et al. [38], which contained higher organic load (COD: 1670–5820 mg/L and TOC: 910–1320 mg/L) and NH_4^+ (1124–2689) mg/L.

2.2. Electrochemical treatment

Electrooxidation experiments were performed at laboratory scale in an undivided cell (Diacell 106, Adamant Technologies) 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 BDD anode was fabricated by a chemical vapor deposition technique that resulted into a microcrystalline conductive diamond coating on a silicon substrate. The characterization of the BDD coating showed size crystal grains in the range of 1–3 μm, boron doping at 1676 ppb of B, and a ratio of sp²/sp³ carbon forms of 0.08. All three characteristics made this electrode very active for PFOA electrochemical degradation [41]. Experiments were performed in galvanostatic conditions using an Agilent 6654A DC power supply (60 V, 9 A). A diagram of the experimental setup that includes a detailed scheme of the electrooxidation cell can be seen in Fig. S1 (Supplementary material) and further details of the experimental set-up can be found in previous works [42]. 2 L of the landfill leachate were recirculated from the feed tank through the electrochemical cell and back to the feed tank, at a flowrate of 4.5 L/min. The feed temperature was kept at 20 °C. The effect of current density was studied in the range 200–800 A/m². The saline content of the leachate samples was enough to provide the adequate conductivity.

2.3. Chemical characterization of leachate samples

COD was determined by the closed reflux and colorimetric method. TOC and IC analyses were performed using a TOC-V CPH (Shimadzu). Chloride, chlorate, perchlorate, nitrate and sulfate were analyzed by ion

Table 1
Characteristics of landfill leachate samples. Average values of 5 grab samples collected in 5 consecutive days.

Parameter	Raw Leachate (n = 5)	MBR-Treated Leachate (n = 5)
pH	8.3 ± 0.1	7.74 ± 0.1
Conductivity (mS cm ⁻¹)	14.7 ± 0.3	8.5 ± 0.1
COD (mg/L)	1728 ± 130	454.4 ± 36
TOC (mg/L)	779.7 ± 16	191.6 ± 13
IC (mg/L)	147.7 ± 4	778.2 ± 12
NH_4^+ (mg/L)	1368 ± 115	<LOQ
TDS (mg/L)	8.2 ± 0.1	4.6 ± 0.1
Cl^- (mg/L)	1920.2 ± 40	1803.6 ± 35
NO_3^- (mg/L)	<LD	670.9 ± 26
SO_4^{2-} (mg/L)	35.4 ± 26	52.3 ± 12

TDS: total dissolved solids; LOQ: Limit of quantification

chromatography (Dionex 120 IC). Free chlorine was determined following the N,N-Diethyl-p-phenylene diamine (DPD) ferrous titrimetric method. Ammonia concentration was obtained by distillation and titration.

2.4. PFAS analysis

The analytical method allowed the quantification of 10 PFCAs, 6 PFASs and 6:2 FTSA. The full list of compounds is depicted in Table 2. PFC-MXA and PFS-MXA, containing PFCAs and PFASs, respectively at individual concentrations of 2 μg/mL were the certified standard solutions purchased from Wellington Laboratories (Guelph, Ontario, Canada). The analytical standard MPFAC-C-ES of 2 μg/mL, also from Wellington Laboratories, was used as internal standard (IS). Evolute WAX (6cc, 200 mg, 50 μm) solid phase extraction (SPE) cartridges were purchased from Biotage. Bulk ENVI-Carb sorbent (100 m²/g, 120/400 mesh) was purchased from Supelco (Bellefonte, MA, USA). All solvents were UPLC-MS quality and Milli-Q water was used throughout.

An aliquot of 70 mL of leachate sample was spiked in duplicate with IS MPFAC-C-ES prior to SPE to correct losses and matrix effect. Leachate samples were extracted and purified according to the procedure described by Fuertes et al. [16]. The purified sample extracts were analyzed using an Ultrahigh Performance Liquid Chromatography (UHPLC) system (H-Class, Waters) coupled to a Triple Quadrupole Detector (TQD) (MS/MS, Waters, Milford, MA, USA) with an electrospray ionization (ESI) interface operated in the negative ionization mode. A Waters BEH C18 column (50 mm × 2.1 mm × 1.7 μm) at 50 °C was used for the analytical separation. The mobile phase consisted of Milli-Q water containing 2 mmol/L ammonium acetate and 5% methanol (A), and methanol (B). The operating flow rate was 0.4 mL/min in gradient mode. The initial mobile phase composition was 75% of A during the first half a minute of the analysis, which continued to reach 15% A at minute 5% and 100% B at minute 5.1 (hold time 0.5 min). Initial conditions were regained at 8 min followed by equilibration until 10 min. The detection was done in a multiple reaction monitoring acquisition mode. Nitrogen was used as nebulizer and drying gas, and argon as the collision gas. Electrospray negative ionization was carried out. A nitrogen gas flow rate of 750 L/h and a drying gas temperature of 400 °C were employed. Fragmentor voltages and collision energy were optimized for the different target analytes [43].

Dilutions from the stock standard solutions were prepared in methanol/water (70:30 v/v) at seven concentration levels ranging from 1 ng/mL to 250 ng/mL and calibration curves were built in order to calculate the PFAS concentrations in real samples and to control the linear range of the instrumental response. Analyte confirmation criteria were defined as the ion ratio for each compound obtained from PFAS standards analyses. The ion ratio was calculated by the Masslynx software for the precursor ion related to the secondary ion trace of each PFAS as product ions. It was updated with every calibration curve. Furthermore, a tolerance criterion was given for the ion ratio of each compound and an ion retention window was set for the secondary ion trace. For the PFAS quantification, the primary ion trace was employed. Quality control and validation of the method were made using internal standards and recovery rates, method blanks and calibration linearity. Recovery rates of internal standards detected in real samples ranged from 53% (MPFHxA, n = 5, RSD = 7.5%) to 91% (MPFHxS, n = 5, RSD=11%). Reported concentrations were corrected with recoveries of IS.

3. Results and discussion

3.1. PFAS in landfill leachates

Table 2 presents the PFAS concentrations in the studied MSW landfill leachate samples. 8 of the 16 PFAS included in the analytical method were detected in raw and MBR-treated leachates. Total concentration of PFAS (ΣPFAS) was 2957.2 ng/L (n = 2, RSD = 18%) in the raw

Table 2

Concentration of individual PFAS, total PFAS, total PFCAs and total PFASAs in raw and MBR-treated landfill leachate samples.

Analytes	Raw Leachate (n = 2) (ng/L)	MBR-treated Leachate (n = 4) (ng/L)
Perfluorobutanoic acid PFBA	143.5 ± 17*	131.2 ± 18
Perfluoropentanoic acid PFPeA	574.6 ± 25	324.0 ± 9
Perfluorohexanoic acid PFHxA	529.3 ± 8	827.2 ± 11
Perfluoroheptanoic acid PFHpA	112.1 ± 16	201.5 ± 15
Perfluorooctanoic acid PFOA	542.8 ± 20	538.5 ± 24
Perfluorononanoic acid PFNA	<LOD	25.7 ± 20
Perfluorodecanoic acid PFDA	<LOD	28.2 ± 19
Perfluoroundecanoic acid PFUDA	<LOD	<LOD
Perfluorododecanoic acid PFDoA	<LOD	<LOD
Perfluorotridecanoic acid PFTrDA	<LOD	<LOD
Perfluorotetradecanoic acid PFTeDA	<LOD	<LOD
Perfluorobutanesulfonic acid L-PFBS	994.5 ± 21	1058.7 ± 7.1
Perfluorohexanesulfonic acid L-PFHxS	10.4 ± 7	38.5 ± 15
Perfluoroheptanesulfonic acid L-PFHpS	<LOD	<LOD
Perfluorooctanesulfonic acid L-PFOS	49.9 ± 25	282.8 ± 37
Perfluorodecanesulfonic acid L-PFDS	<LOD	<LOD
∑PFAS	2957.2 ± 18	3456.2 ± 13
∑PFCAs	1902.4 ± 16	2076.3 ± 13
∑PFASAs	1054.8 ± 22	1379.9 ± 13
6:2 fluorotelomersulfonic acid 6:2 FTSA	218.7 ± 23	303.8 ± 118

* R.S.D. (relative standard deviation); <LOD: below limit of detection; L-: linear

leachate, and 3456.2 ng/L (n = 4, RSD = 13%) in the MBR-treated leachate. In both cases, short chain PFCAs (except PFOA), PFBS and PFOS, formed the predominant PFAS group, in accordance with previous findings [16]. However, treated leachates presented significantly higher concentration of PFHxA compared to the raw leachate. This is consistent with previous studies, which concluded that the MBR treatment is able to degrade unknown PFAS into short chain PFCAs. These short chain PFCAs behave as very persistent compounds and the MBR treatment fails to remove them [1]. 6:2 FTSA was also characterized in both leachate samples, finding that its concentration was higher after the MBR treatment (303.8 ng/L) than in the raw leachate (218 ng/L) which could be an indicative of potential PFAS precursors degradation into 6:2 FTSA [31,44].

3.2. Electrochemical treatment of leachates

The MBR treatment substantially modified the properties of the leachate, although the chloride content did not substantially change. Next, we outline the main electrochemical reactions involved in the formation of the oxidizing species that participate in the electrochemical treatment of landfill leachates, both in organics and ammonia removal, as it has been extensively reviewed in literature [45,46]. The electron transfer reactions on the anode allow the electrogeneration of chlorine (Eq. 1) and hydroxyl radicals (Eq. 2),

– Electrogeneration of chlorine



– Hydroxyl radical formation



Chlorine is hydrolyzed in aqueous solution to form hypochlorous acid (Eq. 3), which at the alkaline pH typically found in landfill leachates, is mainly in the form of hypochlorite anion (Eq. 4),



Free chlorine and hydroxyl radical mediated oxidation of organic

compounds (R) may be represented by reactions (5) and (6),



where R is an organic compound and M is an active site on the anode surface. Eventually, reactions (5) and (6) can progress to the complete mineralization of organic compounds, where the final products are CO₂ and H₂O, although in this regard reaction (5) is typically more efficient than reaction (6), due to the higher oxidation potential of hydroxyl radicals ($\bullet OH$) compared to $HClO/OCl^-$. In the raw landfill leachate, where chloride and ammonia are present simultaneously, breakpoint chlorination reactions consume free chlorine oxidants as described next,



In absence of ammonia, the electrogenerated chlorine will add its oxidation potential to the hydroxyl radicals that are produced by the BDD anodes [47]. This fact is expected to influence the kinetics of COD and TOC removal, the evolution of inorganic chlorine species, and the performance of the electrochemical PFAS removal. In this line of reasoning, a recent study has shown the energy-efficient treatment of bio-treated landfill leachates in reactive electrochemical membranes [48]. Fig. 1 presents the evolution of COD, TOC, ammonia, active chlorine, and inorganic chlorine species during the electrochemical treatment of raw leachates, both as a function time and as a function of the specific electric charge passed (Q), at different current densities in the range 200 – 800 A/m². Similarly, Fig. 2 shows the results that were achieved working with MBR-treated leachates.

Fig. 1a shows that increasing the applied current density enhanced significantly the kinetics of COD removal, e.g.: working at $J = 800 \text{ A/m}^2$, more than 93% of the initial COD was removed after 8 h of treatment. The behavior of TOC was similar to that of COD, although TOC removal was slower, e.g.: working at 800 A/m^2 reduced the TOC by 74% in 8 h of electrochemical treatment. On the other hand, the behaviors of COD and TOC with the specific charge passed (Q) (Figs. 1b and 1d) show that working at 200 A/m^2 provided a better utilization of the applied energy for the removal and mineralization of organic contaminants.

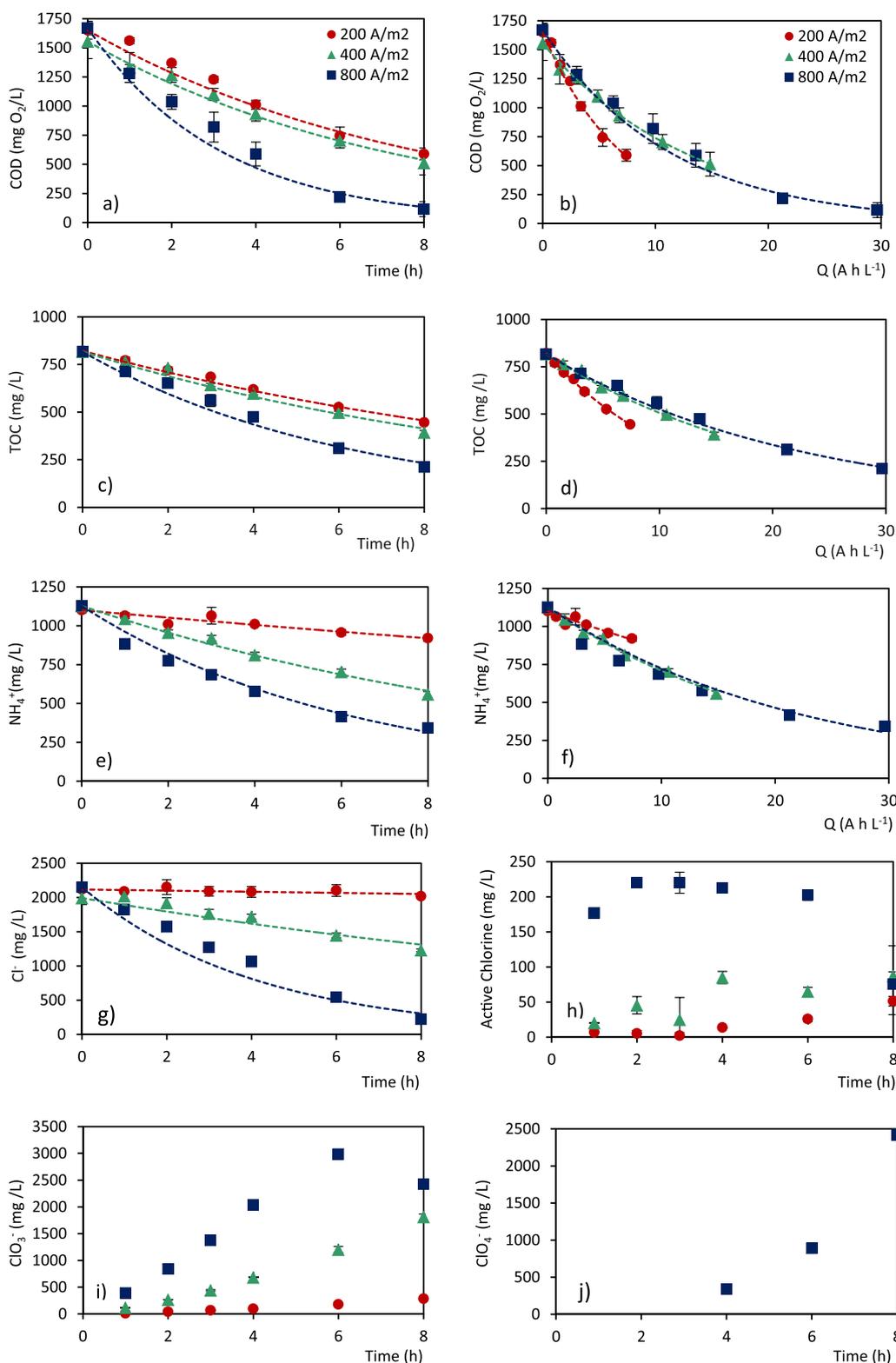


Fig. 1. Electrochemical treatment of raw leachate, at fx1200, fx2 400 and fx 3800 A/m². The progress of COD, TOC and ammonia with the treatment time and with the specific charge passed (Q) is presented in figures (a) to (f), in which the lines correspond to the fitting of experimental data to a first-order exponential model. The progress with time of chloride, active chlorine, chlorate and perchlorate is plotted in Figures g) to j).

However, it should be noted that working at 200 A/m² is penalized by the longer time needed to achieve equal removal rates than when using 400 and 800 A/m², or what is equivalent, to larger equipment size and higher capital costs. The best conditions for ammonia treatment of the raw leachate were at 800 A/m², in which the ammonia removal kinetics

became the fastest (Fig. 1e), and the energy utilization was also the most efficient one (Fig. 1f). However, data of ammonia and chlorine species should be discussed in parallel. Ammonia degradation takes place through an indirect mechanism, in which electrogenerated chlorine oxidizes ammonia, to give nitrogen and chlorine products, as depicted in

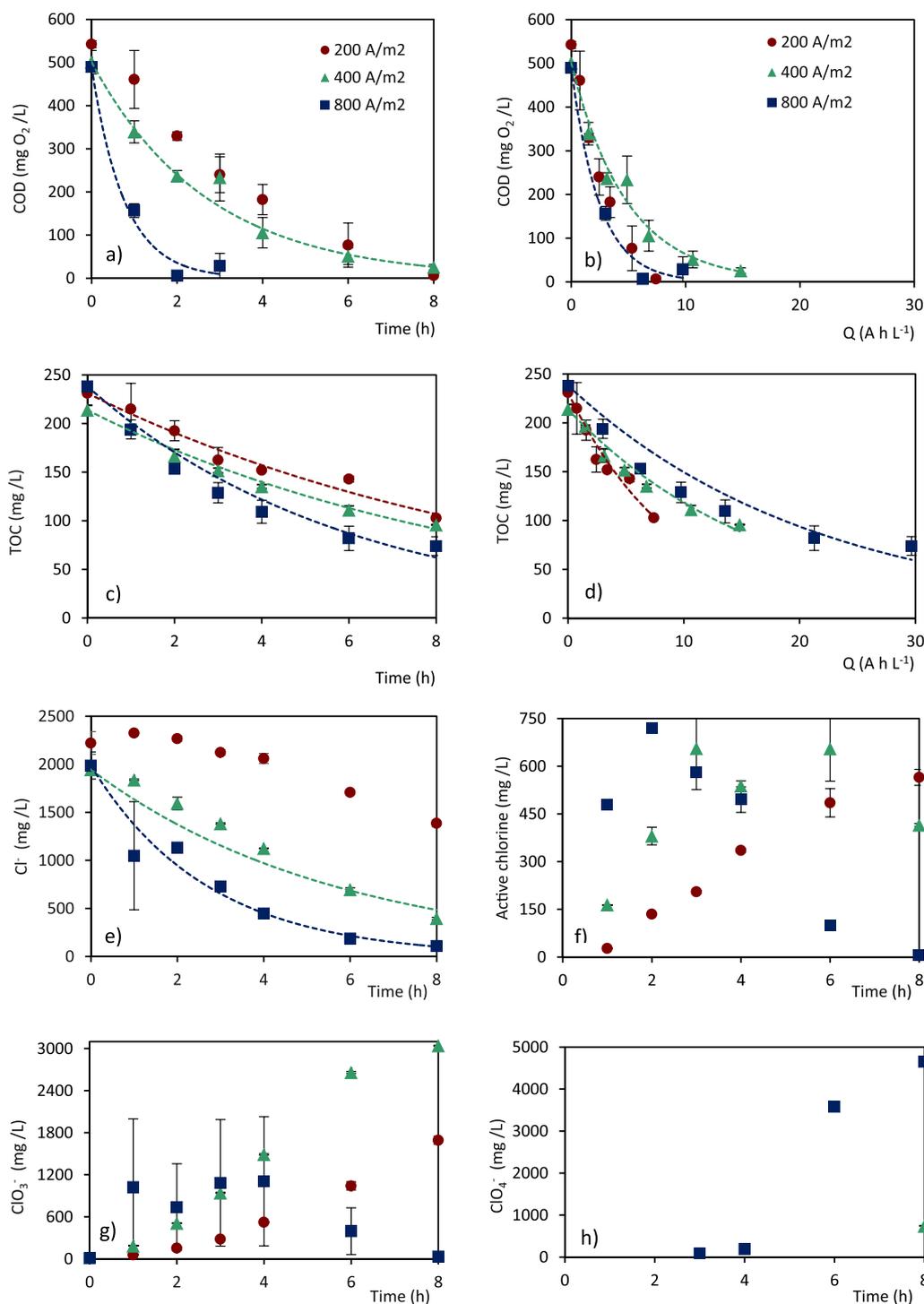


Fig. 2. Electrochemical treatment of MBR-treated leachate, at fx1200, fx2400 and fx3800 A/m². The progress of COD, TOC with the treatment time and with the specific charge passed (Q) is presented in figures a) to d), in which the lines correspond to the fitting of experimental data to a first-order exponential model. The progress with time of chloride, active chlorine, chlorate and perchlorate is plotted in Figures e) to h).

reactions (7)-(10) [49]. Working at 200 A/m², the active chlorine concentration (Fig. 1h) stayed at very low values and chloride concentration was nearly constant (Fig. 1g), meaning that the rate of chlorine production (reaction (1)) was low, and that electrogenerated chlorine was rapidly consumed by ammonia.

Fig. 2 presents the results of the electrochemical treatment of MBR-treated landfill leachate. COD removal took place with faster kinetics compared to the treatment of raw leachates. The differences were less pronounced in the case of TOC removal, which was only slightly faster

along the treatment of MBR-treated leachate. The absence of ammonia in the MBR-treated leachate may explain this distinctive behavior. When ammonia is not present, the electrogenerated chlorine is available to oxidize the organic pollutants (reaction (6)), accelerating the COD removal. However, it appears that the oxidation potential of hypochlorite, which is formed upon hydrolysis of the electrogenerated chlorine in water, was not strong enough to enhance the mineralization of the organic compounds that remained in the MBR-treated leachate. Overall, the electrogenerated chlorine may have contributed to the formation of

Table 3

Apparent kinetic constants of the BDD electrooxidation of raw leachate (RL) and MBR-treated leachate.

	200 A/m ² k_{app} (h ⁻¹)	$k_{app-RL}/k_{app-MBR}$	400 A/m ² k_{app} (h ⁻¹)	$k_{app-RL}/k_{app-MBR}$	800 A/m ² k_{app} (h ⁻¹)	$k_{app-RL}/k_{app-MBR}$	800 A/m ² k'_n (L A ⁻¹ h ⁻¹)
COD vs t - RL	–		0.133		0.317		0.0566
COD vs t MBR-treated leachate	0.425		0.368	2.8	1.308	4.1	0.2371
TOC vs t - RL	0.074		0.085		0.158		
TOC vs t MBR-treated leachate	0.097	1.3	0.106	1.2	0.168	1.06	
NH ₄ ⁺ vs t - RL	0.022		0.083		0.159		

more oxidized organic compounds, such as small carboxylic acids, which are highly recalcitrant to hypochlorite-mediated oxidation. Therefore, the TOC removal was taking place mainly through a hydroxyl radical mediated oxidation, that occurred at similar kinetic rates in the raw and MBR-treated leachates. A side consequence of chloride oxidation is its partial conversion into more oxidized forms of inorganic chlorine, that is, chlorate and perchlorate (Figs. 1i and 1j and Figs. 2g and 2h). Nevertheless, formation of undesirable perchlorate was only observed when working at the highest applied current, and it started after 4 h of electrochemical treatment.

Table 3 gathers the apparent kinetic constants (k_{app}) that result from the fitting of COD and TOC experimental data to a first order exponential model. $k_{app-COD}$ was near three times higher working at 800 A/m², compared to the kinetic rate observed at 200 and 400 A/m². Considering the electrochemical treatment of MBR-treated leachates, the COD removal rate is 2.8–4.1 times higher than in the case of treating the raw leachate. The enhancement of COD removal is particularly stronger working at 800 A/m². On the contrary, $k_{app-TOC}$ for the MBR-treated leachate at 800 A/m² is only 6% higher than for the raw leachate. We have calculated the limiting current density ($J_{lim} = 4Fk_mCOD_0$) [50] of the hydroxyl radical mediated oxidation for the initial COD, resulting in ~ 70 A/m² for the MBR-treated leachate and close to 300 A/m² for the raw leachate. Therefore, in the range of current densities applied in this study (200–800 A/m²), most experiments were performed over the limiting current, meaning that the hydroxyl radical mediated electro-oxidation of organic compounds should occur at similar rates [51]. Exception was the treatment of the raw leachate at 200 A/m², in which the COD data initially showed a linear trend indicating that the process was performed in a current control kinetic regime. We assign the improvements of COD removal kinetics to electrogenerated secondary oxidants, most of them associated to the anodic conversion of chloride into chlorine. However, chlorine oxidants are generally more reactive on the original organic load that define the COD of the raw leachate than for oxidizing the persistent secondary organic products that are formed upon the MBR treatment.

Table 3 also includes the current-normalized first order kinetic constants k'_n of COD and TOC electrochemical oxidation ($k'_n = k_{app}V/JA_e$, where V is the volume treated and A_e is the anode area). The k'_n of COD removal working with the raw leachate at 800 A/m² is close to previously reported kinetic data of BDD electrochemical treatment of raw MSW landfill leachates with similar initial COD and ammonia content, showing the reproducibility of the results [52]. Still, this work reports for the first time the great enhancement of the electrochemical COD removal rate in the zero ammonia MBR-treated leachates, characterized by an unprecedented high k'_n of 0.2371 L A⁻¹ h⁻¹. Overall, the application of electrooxidation as final polishing step of the MSW landfill leachate could be a viable approach for the removal of micro-contaminants and priority pollutants from this kind of complex and difficult to treat hazardous waste.

The energy consumption W (kWh m⁻³) of the electrochemical treatment of MBR-treated leachates was estimated. Energy consumption is directly proportional to the specific electrical charge passed (Q , kAh m⁻³)

and to the cell potential (v , V). If the disposal limit for COD to surface water bodies in Spain is considered ($COD_{limit} = 160$ mg/L), the time needed to treat the MBR-treated leachate ($COD_{initial} \sim 500$ mg/L) working at 800 A/m² is calculated as 0.89 h. The electrochemical cell voltage was 10.3 V. The specific energy consumption is estimated at 25.1 kWh m⁻³, which is less than half of the energy consumption previously reported for BDD electrooxidation of landfill leachates [53]. Therefore, the integration of electrooxidation with the MBR biological treatment encourages the sustainability of landfill leachates treatment.

3.3. PFAS removal

In this section we analyse the technical viability of BDD electro-oxidation to remove very persistent pollutants contained in MSW landfill leachates. Section 3.1 showed that the total concentration of the analysed 17 PFAS in the MBR-treated leachate was higher than in the raw leachate, indicating that the raw leachate contained unknown PFAS that were biodegraded into shorter chain PFCAs. Therefore, in this section we will focus on the effect of the electrochemical treatment on the removal of PFAS from the MBR-treated leachate.

Fig. 3 shows an overview of PFAS evolution with time during the electrolysis of MBR-treated MSW landfill leachate, at two applied current densities, 200 and 800 A/m². Concentration data are normalized to the initial value of each PFAS, as for the large variation in initial concentrations of the different compounds. The average R.S.D. of PFAS concentrations in duplicate experiments was 28%. Considering concentration data presented in Table 2, the group of PFCAs was predominant in the PFAS profile of the MBR-treated leachate sample.

On the one hand, the applied current plays a very significant influence on PFAS electrochemical removal, as observed in Figs. 3a and 3c. Both Figures present the sum of compounds concentration for each category, PFCAs (in red), PFASs (in purple), and total PFAS (in red), working at 200 and 800 A/m², respectively. At the lowest current density of 200 A/m², Fig. 3a shows that Σ PFCAs increased in the whole treatment period and Σ PFASs stayed at near steady concentration. Being Σ PFCAs \gg Σ PFASs, the evolution of Σ PFAS and Σ PFCAs followed similar trends. Increasing the applied current to 800 A/m² had a notorious effect on the PFAS degradation rate. Fig. 3c shows that Σ PFCAs and Σ PFAS were continuously decreasing along the treatment time, while Σ PFASs was moderately removed. Data in Fig. 3c demonstrate that working at sufficiently high applied current, BDD electrolysis is an effective treatment for degrading the PFAS retained in landfill leachates. In this work, the removal of Σ PFAS removal was higher than 95% after 6 h of treatment.

Given that the group of PFCAs was the major contributor to the PFAS load, Figs. 3b and 3d display the fate of each individual PFCA (PFOA, PFHpA, PFHxA, PFPeA and PFBA) during the electrochemical treatment of MBR-treated leachates. Working at 200 A/m², PFOA kept a steady concentration, while the concentration of other PFCAs increased with time. PFHxA and PFPeA observed the largest percentage increase, e.g., after 6 h of treatment, PFPeA content was six times the initial concentration of this compound in the MBR-treated leachate. The delay of PFBA to progress towards increasing values was due to the fact that it occupies

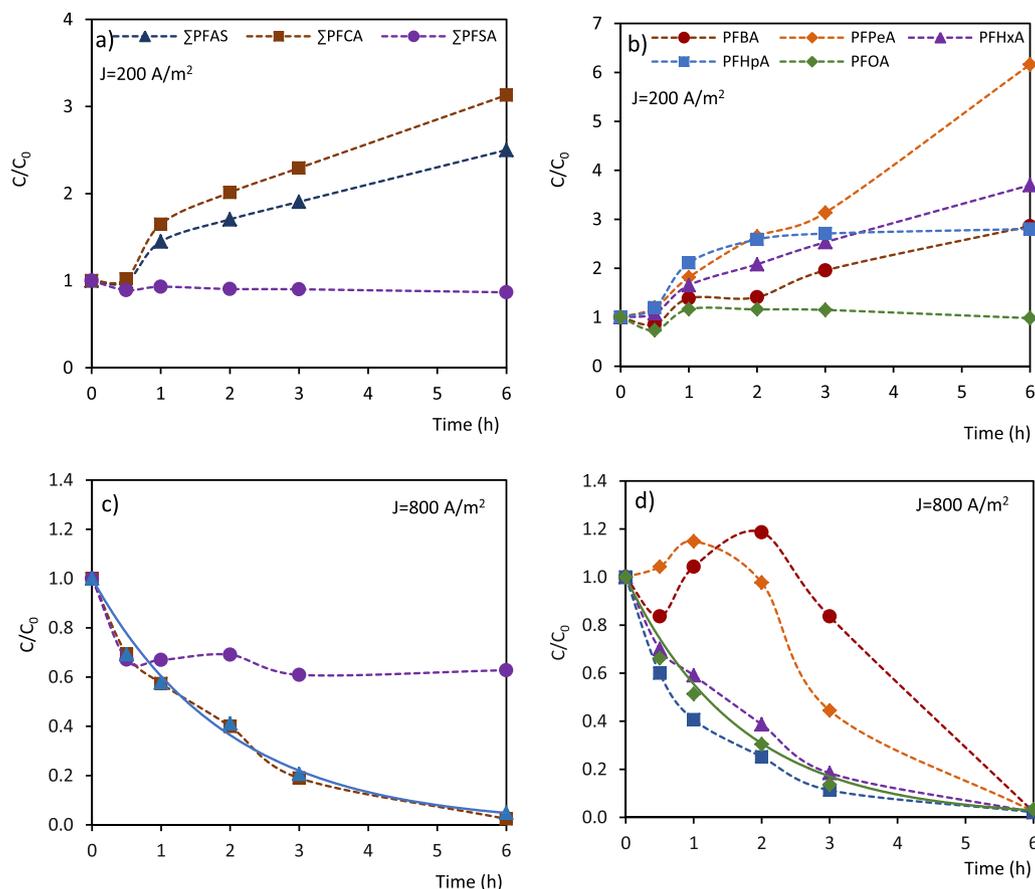


Fig. 3. Evolution of the normalized PFAS concentration in the electrochemical treatment of treated leachates. a) Sum of concentrations of PFAS, PFCAs and PFSAs, $J = 200 \text{ A/m}^2$; b) Evolution of main PFCAs, $J = 200 \text{ A/m}^2$; c) Sum of concentrations of PFAS, PFCAs and PFSAs, $J = 800 \text{ A/m}^2$; d) Evolution of main PFCAs, $J = 800 \text{ A/m}^2$. Dotted lines are included to guide the eye. Solid lines represent the exponential fitting of the experimental data.

Table 4

Comparison of apparent and current normalized kinetic constants and energy per order values for the electrochemical removal of Σ PFAS, PFOA, PFHpA and PFHxA among various studies. Most studies used a parallel-plate cell configuration, except for reference [38] that used a flow-through anode. Microcrystalline (MCD) and ultrananocrystalline (UNCD) BDD coatings are compared.

#	Anode	Matrix	Current density (A/m^2)	V/A_e (m)	Apparent kinetic constant PFOA (h^{-1})	Apparent kinetic constant Σ PFAS (h^{-1})	Normalized kinetic constant PFOA ($\text{h}^{-1} \text{ A}^{-1} \text{ L}$)	Normalized kinetic constant Σ PFAS ($\text{h}^{-1} \text{ A}^{-1} \text{ L}$)	Reference
1	MCD BDD	MBR-treated MSW landfill leachate (PFOA 0.54 $\mu\text{g/L}$, Σ PFAS 3.5 $\mu\text{g/L}$)	800	0.286	0.589	0.505	0.210	0.180	This study
2	MCD BDD	Simulated AFFF-impacted groundwater (PFOA 8.5 $\mu\text{g/L}$, Σ PFAS 60 $\mu\text{g/L}$, Na_2SO_4 0.011 M)	350	0.071	13.8	5.26	2.82	1.073	[35]
3	MCD BDD	Synthetic solution (PFOA 100 mg/L , Na_2SO_4 0.035 M)	50	0.143	2.17		6.2		[41]
4	UNCD BDD	Synthetic solution (PFOA 100 mg/L , Na_2SO_4 0.035 M)	200	0.119	0.403		0.24		[41]
6	UNCD BDD	Synthetic solution (PFOA 15 mg/L , Na_2SO_4 0.011 M)	500	0.066	1.4		0.184		[55]
7	BDD flow-through perforated plate	Synthetic solution (PFOA 70 $\mu\text{g/L}$, Na_2SO_4 0.010 M)	500	0.595	1.3		1.56		[38]
8	BDD flow-through perforated plate	Landfill leachate (Σ PFAS 18.4 $\mu\text{g/L}$)	1500	0.595	n.a.	n.a.	n.a.	n.a.	[38]

n.a.: Not available

the last position, among the compounds studied, in the degradation pathway of PFCAs. Conversely, when the applied current was 800 A/m², PFOA, PFHpA and PFHxA exhibited exponential decays with similar kinetics, and only PFPeA and PFHA, with the shortest perfluorinated alkyl chain among the group of PFCAs studied, initially increased their concentration, followed by a sharp decrease after a maximum peak.

The observed behavior can be explained by two factors. First, our analysis of PFAS in the landfill leachates considered 17 compounds: ten PFCAs, six L-PFSAs and one 6:2 fluorotelomer sulfonic acid. However, it has been reported that landfill leachates also contain other poly-fluorinated substances, many of them with 8:2 and 6:2 fluorotelomer structures [7,54] which are oxidized to PFCAs during the electrochemical treatment, e.g., 8:2 FTSA degrades to form PFOA, and 6:2 FTSA forms PFHxA, as main initial electrooxidation products. Secondly, it has been reported that the electrochemical oxidation of PFCAs follows a cyclic path in which PFOA loses one -CF₂ unit to form PFHpA, through the intervention of both direct electron-transfer reactions and hydroxyl radical mediated oxidation, to continue with the consecutive degradation and formation of shorter chain PFCAs [56–58]. On the other hand, several studies reported the minimal impact of electrogenerated chlorine on the rate of PFAS removal and defluorination [55,59]. The Supplementary information presents a summary of recent contributions to explain the electrochemical PFAS degradation route. Therefore, the undetermined presence of unknown PFAS in the leachate samples and the electrochemical degradation route explain the increase of short chain PFCAs in the first period of the electrochemical treatment. The differences between increasing trends in Fig. 3b and decreasing concentration trends in Fig. 3d are explained by the effect of increasing the applied current density that enhanced the degradation kinetics of PFCAs, in accordance with previous findings dealing with treatment of PFAS in real industrial wastewaters produced in fluoropolymer manufacturing [31] and in the treatment of mixed PFAS in simulated groundwater impacted by aqueous film forming foams (AFFF) contaminated soils [35].

Table 4 presents the apparent kinetic constants of the BDD electrochemical degradation of PFOA and mixed PFAS attained in various studies. The fitting of ΣPFAS data in Fig. 3c results in $C/C_0 = e^{-0.51 t}$. The normalization of the apparent kinetic constant, $k = 0.51 \text{ h}^{-1}$, with the volume treated (2 L), the anode area (70 cm²) and the applied current density (800 A/m²), results in $k'_{n,\Sigma PFAS} = 0.180 \text{ h}^{-1} \text{ A}^{-1} \text{ L}$. A similar treatment was applied to the PFOA removal kinetic data presented in Fig. 3d. Rows # 1–3 of Table 4 correspond to the treatment of mixed PFAS or PFOA in different matrices but using the same microcrystalline (MCD) BDD anode in a parallel plate configuration working in flow-by mode. The normalized kinetic constant $k'_{n,PFOA} = 0.238 \text{ h}^{-1} \text{ A}^{-1} \text{ L}$ of PFOA removal for the real MBR-treated landfill leachates (this study, initial PFOA concentration 0.54 µg/L) is about 13 times lower than for the treatment of PFOA (initial concentration 10 µg/L) in a synthetic mixed PFAS clean solution simulating groundwater impacted by AFFF contaminated soils, and 26 times lower than for treating PFOA in a highly concentrated single compound solution. However, comparing the rate of PFAS removal as a whole, the detrimental effect of the leachate matrix is less pronounced, as $k'_{n,\Sigma PFAS} (0.18 \text{ h}^{-1} \text{ A}^{-1} \text{ L})$ for degrading the ΣPFAS is 6 times lower than that observed in the treatment of mixed PFAS in simulated groundwater (1.073 h⁻¹ A⁻¹ L). Reported results with an ultrananocrystalline diamond anode (UNCD) showed slower rates for PFOA removal when compared to the MCD structure of BDD coating. The better performance of the MCD anodes was explained by the higher sp³ carbon content and lower H-terminated carbon content of the MCD, compared to the UNCD structure [41]. Finally, Maldonado et al. reported results of PFOA degradation in a synthetic solution and in landfill leachates using a flow-through cell that included perforated anode and cathode, both coated with BDD [38]. The normalized rate constant for the degradation of PFOA (row #7 in Table 4) was the same order of

magnitude as in the parallel-plate cell used in the present study (row #2 in Table 4) performed with similar conditions. Recently, Pierpaoli et al. [37] reported PFOA and PFOS degradation using BDD anodes with different boron doping levels and compared the degradation ratio achieved in a phosphate buffer electrolyte solution with that of considering the landfill leachate as background matrix. In their experiments, landfill leachates were spiked with 0.1 mg/L of PFOA or PFOS, concentrations that are 200 and 350 times higher, respectively, than in the MBR-treated landfill leachate analyzed in the present study. Pierpaoli et al. reported that the rates of PFOA degradation using the landfill leachate matrix were reduced by one third to one-half, the interval being dependant on the applied current and boron doping range, compared to the phosphate buffer electrolyte [37]. This conclusion about the effect of the background electrolyte is in good agreement with the observations of our present study.

Finally, the energy consumption for the electrochemical oxidation of PFAS in MBR-treated leachates was calculated. In the experiments conducted in galvanostatic conditions at 800 A/m², the cell voltage was 10.3 V (average along the batch test). In these conditions and considering the rate constant reported in Table 4 ($k_{app,\Sigma PFAS} = 0.505 \text{ h}^{-1}$), the electrical energy per order (EE/O) that is consumed to achieve 90% PFOA and ΣPFAS removals was 112 and 132 kWh m⁻³, respectively. Maldonado et al. reported the EE/O of 28 kWh m⁻³ for removing PFOA in real landfill leachates, although the kinetics of PFOA evolution were insufficiently described in experiments treating real leachate samples [38]. However, they observed negative removal (increasing concentration) for PFPeA, PFBA and PFBS, and the combination of positive and negative removal for individual PFAAs led to a ΣPFAA removal between 38.6% and 73.5%, depending on the leachate sample, in 8 h of electrochemical treatment working at 1500 A/m². The poor removal of PFAS as a whole could be due to the fact that raw leachates with unknown fluorinated precursors were being treated. Therefore, the application of a biological treatment to the raw landfill leachates, as that considered in the present study, seems a suitable approach, as it reduces the organic load of the background matrix and most likely simplifies the PFAS profile.

4. Conclusions

This work reports the electrochemical treatment of raw and MBR-treated municipal solid waste landfill leachates using boron doped diamond (BDD) anodes. The electrochemical treatment of ammonia-free MBR-treated leachates promoted the availability of electrogenerated chlorine species, that added their oxidation potential to that of the hydroxyl radicals electrogenerated on the BDD anodes. In these conditions, the removal of chemical oxygen demand was clearly enhanced during the electrochemical treatment of MBR-treated leachates, compared to the treatment of raw leachates. However, the total organic carbon decreased at similar rates in the raw and MBR-treated leachates, indicating the low activity of chlorine oxidants for the mineralization of the persistent pollutants retained in the MBR-treated leachates.

Furthermore, we exemplified the high performance of BDD electrooxidation for degrading very persistent pollutants through the investigation of the fate of 17 PFAS (10 PFCAs, 6 PFSAs and 6:2 FTSA) contained in the real MBR-treated leachate ($\Sigma_{17} PFAS = 3456 \text{ ng/L}$). The applied current density exerted a paramount influence on PFAS evolution and removal rate. Working at 800 A/m² successfully reduced the Σ₁₇PFAS content by 95% in 6 h, and 1-log (90%) Σ₁₇PFAS reduction was achieved in 4.5 h, when the formation of undesirable perchlorate was still near undetectable. We estimate that the leachate matrix effect reduced PFAS electrooxidation rate to one-sixth, comparing the present study with previous data of mixed PFAS treatment in synthetic contaminated groundwater. Overall, this work demonstrates the viability to remove PFAS and their transformation products from landfill leachates, one of the main secondary sources of PFAS entry to the environment.

CRediT authorship contribution statement

Ane Urriaga: Conceptualization; Formal analysis; Writing; Supervision; Funding acquisition. **Sonia Gómez-Lavín:** Validation; Investigation; Data curation; Writing. **Alvaro Soriano:** Validation; Investigation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

The authors thank the financial support of Grant PDC2021–120905-I00 funded by MCIN/AEI/ 10.13039/501100011033 Spain, and by the “European Union NextGenerationEU/ PRTR”.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2022.107900.

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