



Electrochemical treatment of perfluorooctanoic acid and perfluorooctane sulfonate: Insights into mechanisms and application to groundwater treatment



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HIGHLIGHTS

- Perfluoroalkyl acids oxidized by BDD anodes in electrolyte and groundwater matrices.
- PFOA removal was faster than PFOS removal.
- Direct anodic oxidation mechanism supported by radical scavenger experiment results.
- Treatment in natural groundwater similar to synthetic electrolyte solutions.
- Perchlorate oxidation byproduct treated by downstream biological reduction.

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ABSTRACT

Electrochemical treatment of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) using a nanocrystalline boron-doped diamond (BDD) anode was investigated in a series of bench-scale batch experiments. Experiments focused on assessing the impacts of chloride electrolyte and of hydroxyl radical scavenger *tert*-butyl alcohol (TBA) on both the rates of PFOA and PFOS removal, and the corresponding rates of defluorination. Treatment of PFOA and PFOS in natural groundwater at concentrations that might be observed in the field (0.3 and 0.6 mg/L PFOA and PFOS, respectively) was also evaluated and compared to results obtained in electrolyte solutions with elevated PFOA and PFOS concentrations (15 and 10 mg/L, respectively). Results showed that the presence of chloride and TBA had minimal effects (decreasing rates by <20%) on PFOA/PFOS removal and defluorination for the range of applied current densities (3–50 mA/cm²), at both the low and elevated PFOA/PFOS concentrations. The latter observation is consistent with direct oxidation of PFOA/PFOS at the electrode surface rather than reaction with electrochemically generated hydroxyl radicals. In addition, treatment rates of PFOA and PFOS in natural groundwater were within a factor of two of those measured in electrolyte at a current density of 15 mA/cm² (for both low and concentration experiments). These findings indicate that hydroxyl radical scavengers that may be present in natural groundwater are unlikely to have a major adverse impact on PFOA and PFOS electrochemical treatment. Finally, it was demonstrated that perchlorate produced by BDD oxidation of Cl⁻ could be biologically treated in bioaugmented sand columns, with a 3 order-of-magnitude removal observed within a 9-day residence time.

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1. Introduction

Poly- and perfluoroalkyl substances (PFASs) are an increasing concern due to their toxicity and recalcitrance to many natural

and enhanced degradation mechanisms. Groundwater contamination is often encountered at or near firefighting training areas where aqueous film-forming foams (AFFFs), which are known to contain PFASs, have been used [1,2]. The United States Environmental Protection Agency (USEPA) recently established health advisory levels (HALs) for perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) in drinking water at 0.07 µg/L,

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both individually and combined [3], and a recent report documented that up to 6 million U.S. residents might be exposed to drinking water that exceeds these HALs [4]. As a result, many utilities are facing serious challenges associated with treatment of PFAS-contaminated source waters.

Electrochemical treatment via anodic oxidation is among the most promising PFAS treatment options, with reports of efficient reactions employing both mixed metal oxide (MMO) [5–7] and boron-doped diamond (BDD) anodes [8–10]. Use of BDD is particularly attractive because they are commercially available, have a high overpotential for oxygen generation, resulting in generation of oxidants such as hydroxyl radicals [11], and have been shown previously to defluorinate a wide range of PFASs [12]. At the same time, a notable concern with using BDD at high potentials is the documented generation of perchlorate ions from chloride ions present in the source water [13,14]. Biological reduction of perchlorate in contaminated groundwater (via addition of an appropriate electron donor, e.g., acetate or H₂) has been documented [15,16]. However, to our knowledge, biological perchlorate reduction in electrochemically treated matrices that contain residual PFAS and disinfectants/oxidants (including hydrogen peroxide and active chlorine species) has not been assessed [10,17].

The mechanisms for electrochemical PFOA and PFOS oxidation has generated some debate. Whereas a number of studies have presented evidence that support direct oxidation of PFOA and PFOS at the anode surface with no involvement of hydroxyl radicals in rate-determining steps [8,9,18], other studies present results that suggest that PFAS reactions with hydroxyl radicals are important with respect to rates of PFAS treatment [10,19]. However, these studies were performed using elevated concentrations (≥ 100 mg/L) of PFOA and PFOS, which are orders of magnitude greater than levels typically found in PFAS-impacted groundwater (e.g., < 1 mg/L) [20–23], so observations may not reflect the dominant mechanisms at play during treatment of contaminated source waters. The potential importance of hydroxyl radicals in rate-controlling steps of PFOA and PFOS treatment is of practical importance because natural organic matter, dissolved carbonate species, and hydrocarbon co-contaminants often associated with AFFF releases can act to inhibit PFAS reactions by competitively scavenging hydroxyl radicals.

To date, the vast majority of electrochemical treatment studies [8–10,18,19] have been performed with elevated PFAS concentrations in inert electrolyte (e.g., sodium perchlorate) devoid of other oxidizable inorganic (e.g., chloride) and organic species (e.g., natural organic matter) that may affect the rates of PFAS treatment. The presence of natural organic matter has been shown to adversely impact the electrochemical treatment of halogenated organic contaminants [24], but natural organic matter impacts on PFASs have not been evaluated. Studies performed by Trautmann et al. [12], which examined a variety of perfluorinated carboxylates and sulfonates as well as a fluorotelomer alcohol, demonstrated effective treatment in a natural PFAS-impacted groundwater using a BDD anode, but potential impacts of the natural groundwater constituents on PFAS removal rates and mechanisms were not specifically assessed (i.e., the impacts of chloride or other oxidizable species on the PFAS transformation rate constants and intermediate product generation were not evaluated). Although chloride is rapidly oxidized by BDD anodes, we are unaware of any studies assessing the impact of its presence on electrochemical treatment of PFOA or PFOS.

This study aims to clarify the active mechanisms for PFOA and PFOS oxidation by electrochemical oxidation with BDD electrodes, and assess the influence of a natural water matrix on reaction rates. Experiments examined the effects of known hydroxyl radical scavengers and chloride and sulfate electrolytes on PFOA and PFOS removal and defluorination, and evaluated the generation of

shorter chain perfluorinated intermediate products. While experiments were conducted using elevated PFOA and PFOS concentrations (15 and 10 mg/L, respectively) to quantify defluorination, separate experiments were conducted using field-relevant concentrations of PFOA and PFOS (0.3 and 0.6 mg/L, respectively) added to synthetic solutions and natural groundwater to provide insights into factors influencing treatment under more environmentally relevant conditions. Finally, this work assessed for the first time the feasibility of applying subsurface bioaugmentation for post electrochemical treatment to reduce the perchlorate oxidation byproduct back to chloride prior to discharge.

2. Experimental

2.1. Chemicals and groundwater

PFOA (96% purity) and PFOS ($\sim 40\%$ in H₂O) were purchased from Sigma Aldrich. *tert*-Butyl alcohol (TBA) (reagent grade) was purchased from Spectrum Chemical. NaCl and Na₂SO₄, used to prepare electrolyte solutions, were purchased from JT Baker and Macron Fine Chemicals, respectively. Deionized water (Nanopure system) was used to make the electrolyte solutions. Information on the short chain PFASs used as analytical standards are provided in Table S1 in the Supplementary data (SD) section. Characteristics of the natural groundwater used in this study are provided in Table 1.

2.2. Electrochemical experiments

A picture of the electrochemical treatment system is provided in the Supplementary data (Fig. S1). Electrochemical experiments were performed using a single compartment electrochemical cell and electrodes purchased from Advanced Diamond Technologies (Romeoville, IL). The anode materials consisted of ultrananocrystalline diamond coating (2 μ m) on niobium; the cathode was tungsten. The available surface area of each rectangular electrode was 38 cm², with an electrode spacing of 4 mm.

All experiments were performed in duplicate in batch mode using a polypropylene vessel containing 250 mL of deionized water. The deionized water was spiked with the target level of PFOA or PFOS, and amended electrolyte (either 1500 mg/L Na₂SO₄ or 1500 mg/L Na₂SO₄ + 167 mg/L NaCl); these electrolyte levels were selected to mimic those used in previous PFOA and PFOS electrochemical studies [6]. Urriaga et al. [10] demonstrated that the presence of sulfate (instead of perchlorate which is not further oxidized by BDD anodes) had only a minor impact on PFOA treatment, thus sulfate was not expected to impact assessment of PFOA and PFOS treatment. A parallel experiment was also performed in elec-

Table 1
Characteristics of groundwater used in this study.

	Concentration
Fluoride (mg/L)	<0.2*
Chloride (mg/L)	18
Sulfate (mg/L)	25
Nitrate (mg/L)	5.5
Nitrite (mg/L)	<0.2*
Total Organic Carbon (mg/L)	11
Turbidity (NTU)	1.83
Perchlorate (mg/L)	0.15
Alkalinity (mg/L CaCO ₃)	352
Conductivity (μ mhos/cm)	769
pH	6.7
Hardness (mg/L CaCO ₃)	363

* Compound not detected above method practical quantitation limit.

trolyte solution (containing NaCl) amended with 100 mg/L TBA, a known scavenger of hydroxyl radicals [25]. Experiments conducted with natural groundwater (250 mL) were amended with Na₂SO₄ (final concentration increased to 525 mg/L sulfate) to increase the electrical conductivity so that the voltage applied to the electrodes for a given current density was similar (± 1 V) to the electrolyte solution experiments. Experiments with elevated PFAS concentrations (15 mg/L PFOA, 10 mg/L PFOS) were first conducted to facilitate detection of transformation products, including fluoride; subsequent experiments with low concentrations (0.3 mg/L PFOA, 0.6 mg/L PFOS) were performed to better mimic conditions observed in PFAS-contaminated groundwater [20–23].

All experiments were performed under constant current conditions at room temperature (approximately 20 °C). Power was supplied using an E3646A 60 W Dual Output Power Supply (Agilent). Current densities of 50, 15, and 3 mA/cm² were examined, as the current density has been shown to have a substantial impact on PFOA removal [9,10]. Experiments were performed at galvanostatic conditions and the cell voltage was measured directly on the power supply that was connected to the electrochemical cell. The 250 mL of solution was re-circulated from the polypropylene vessel through the electrochemical cell at 250 mL/min using a peristaltic pump and 0.5 in. tygon tubing. After initiating the experiment, aqueous samples were periodically collected for analysis. Initially, duplicate samples were collected at each timepoint and immediately quenched by mixing with 20 μ L of a sterile 1.5 g/L sodium thiosulfate solution to scavenge any residual oxidant species remaining in the sample [25]. Tests showed that addition of the quenching agent did not influence the extent of PFOA or PFOS oxidation (or any of the transformation products), so this preservation step was discontinued in later experiments. Control experiments were also performed without applied current to account for any losses of PFOA or PFOS not attributable to electrochemical treatment (e.g., sorption).

2.3. Biological reduction of electrochemically generated perchlorate

A screening level biological treatment column experiment was performed to determine if any perchlorate generated by BDD oxidation of Cl⁻ during the electrochemical treatment of PFOA and PFOS could be re-reduced to Cl⁻ by subsequent biological treatment, using methods similar to those employed previously for biologically-enhanced perchlorate reduction [15]. Two stainless steel columns (7.2 cm diameter and 30 cm long) were packed with 2400 g of a medium fine sand; the columns were placed in series. The ends of the columns were sealed using Lexan plates with machined grooves to accept Viton O-rings to seal the column. Column ends were fitted with stainless steel two-way control valves to facilitate water sampling. Electrochemically treated water was introduced upflow through the columns using a peristaltic pump at 3.6 mL/h. Water entering the columns was amended with a carbon-based electron donor (sodium lactate), diammonium phosphate, yeast extract, and molybdenum at target influent concentrations of 900, 10, 100, and 0.1 mg/L, respectively. The total residence time in the columns was approximately 9 days. Influent and effluent samples were periodically collected, filtered, and analyzed for perchlorate, chlorate, and chloride. After 155 days, the downgradient column was further bioaugmented with 50 mL of a suspension (optical density at 550 nm ~ 1.0) of perchlorate-degrading bacterium *Azospira suillum* JPLRND [16,26].

2.4. Analytical

Treated solutions were monitored as a function of time for residual oxidants, pH, anions, and perfluorinated carboxylates and sulfonates. The *N,N*-diethyl-*p*-phenylene diamine (DPD)

method (Spectronic 20D+, Thermo Scientific) was used to determine residual oxidants, including hydroxyl radicals, active chlorine species, and H₂O₂ [25]. An Oakton probe (Part No. WD-35634-14) was used to measure sample pH. Anions were analyzed via ion chromatography using EPA Methods 300.0 (most anions) and 314.2 (perchlorate analysis). Detection limits for most anions were 200 μ g/L; the detection limit for the perchlorate method was 0.25 μ g/L. TBA was analyzed by Chemtech (Mountainside, NJ) using gas chromatograph/mass spectrometry (GC/MS) following EPA Method 8260C (0.5 μ g/L detection limit).

PFASs were analyzed using methods reported previously [6]. Briefly, samples were collected in 20 mL polypropylene vials and were pH neutralized (as needed) to a final pH between pH 5–9. A 50 μ L aliquot of each sample was then diluted in 10 mL of Optima Water (Fisher Scientific) because of the high initial PFOA and PFOS concentrations. This sample was then further diluted for analysis. An aliquot of the diluted sample was transferred to a microcentrifuge tube containing Optima water, Optima methanol (Fisher Scientific), a small aliquot of basic water (0.01% ammonium hydroxide in water), and mass labelled surrogate (at a concentration of 230 ng/L), to obtain a volume of 1500 μ L (80 vol% water and 20 vol% methanol). This ratio was found to minimize surrogate loss and improve chromatography during analysis. The samples were centrifuged at 17,000 relative centrifugal force (rcf) for 10 min, and then 1350 μ L of the solution was transferred to an auto-sampler vial for analysis by liquid chromatography with tandem mass spectrometry (LC-MS/MS). Chromatography was performed using 10 mM ammonium acetate in water, and 10 mM ammonium acetate in methanol. Eluents were delivered initially at a flow rate of 0.6 mL/min by a Shimadzu LC-20AD LC system. The flow rate was decreased to 0.4 mL/min at 4.5 min, and then ramped up again to 0.6 mL/min at 9.5 min. A CTC Analytics Leap Technologies autosampler injected 1 mL of the sample on a 50 mm \times 4.6 mm Gemini C₁₈ column with a 3 μ m particle size, with a C₁₈ guard column. Initial eluent conditions were 90% water, and 10% methanol. The methanol percentage was ramped to 85% over 1.5 min, then to 95% by 9 min, and by 9.5 min before decreasing to 10% over the final 0.5 min. The PFASs were analyzed by an MDS Sciex Applied Biosystems API 3200 in negative electrospray ionization mode under multiple reaction monitoring, and two transitions were monitored for each PFAS. A list of PFASs are found in the [Supplementary information \(Table S1\)](#). Blanks and quality controls were included every eight to ten samples and carry over was minimal. Quality assurance criteria included signal/noise >10 and above the limit of quantitation (LOQ; see [Supplementary data](#) section for definition); LOQs were analyte, matrix, and run dependent, but were generally 6–21 ng/L in an undiluted sample. Depending on the degree of dilution necessary to enable accurate quantitation of the PFAS spiked experiments (i.e., 75–7500-fold dilutions), the dilution-adjusted LOQs ranged between 0.45 and 157.5 μ g/L. Surrogate recoveries were generally >60%, and relative standard deviations for replicate analyses of the same sample were generally <25%.

3. Results

3.1. PFOA and PFOS treatment and defluorination

Fig. 1A shows electrochemical treatment of 15 mg/L PFOA observed at three applied current densities in the absence and presence of chloride ions at ambient temperature. Cell voltages ranged from approximately 4.6 V (lowest current density) to 12 V (highest current density). The corresponding fluoride generation for these same experiments, plotted as the fluoride generated relative to the total fluorine initially in the reactor (bonded within the

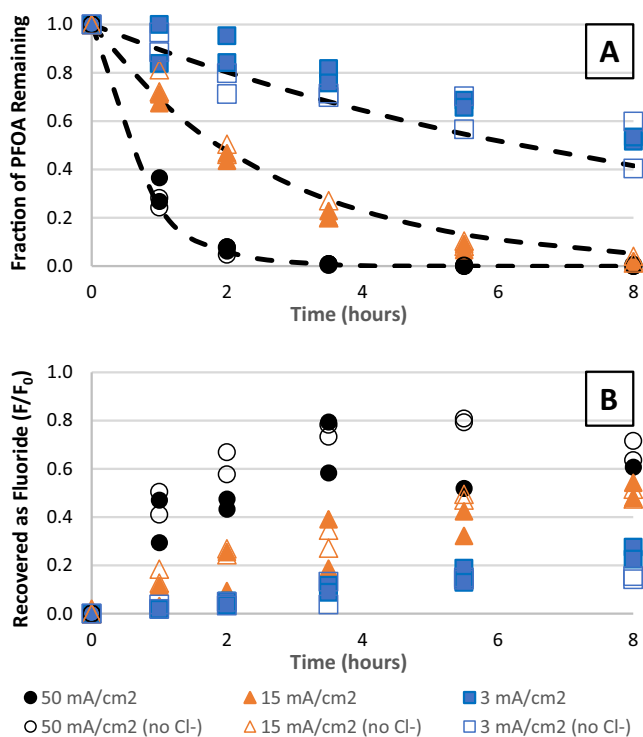


Fig. 1. Influence of applied current density and the presence of chloride ion on (a) PFOA degradation and (b) fluoride release (plotted as fluoride recovered relative to fluoride initially present in PFAS). Reaction conditions: 15 mg/L PFOA, 1500 mg/L Na_2SO_4 , and (if added) 167 mg/L NaCl. Voltages ranged from 4.6 V (lowest current density) to 12 V (highest current density). Duplicate results are shown. Dashed lines represent first-order model fits of treatment data in the absence of chloride. Measured rate constants provided in Table 2.

structure of PFOA), is shown in Fig. 1B. PFOA removal was well-described by a first-order rate law, as indicated by the fits shown in Fig. 1A and in Table 2. Rates of PFOA removal and defluorination increased with increasing applied current density, indicating that observed PFOA treatment rates were current-controlled at the electrodes rather than aqueous mass transfer controlled processes [9,10]. The increase in the PFOA transformation rate constant (Table 2) was approximately proportional to the increase in current density. In comparison, <15% loss of PFOA was observed in

current-free control experiments, likely the result of adsorption to electrochemical system components. During reactions, solution temperature increased slightly ($\leq 2^\circ\text{C}$ for the lower 2 current densities, $\leq 7^\circ\text{C}$ for the highest current density) due to resistive heating, and pH decreased to values as low as pH 4 due to acid production commonly observed at BDD anodes [8].

Somewhat more surprising, the results show that the presence of chloride had a minimal effect on the observed rate constants for PFOA removal and the extent of fluoride ion generation, inhibiting reaction rates by <20%. Chloride oxidation, which formed perchlorate in the experiments shown in Fig. 1, is facilitated by surface reactions on BDD anodes [13]. The minimal impacts of chloride on PFOA oxidation suggests minimal competition between PFOA and chloride (or chloro-oxyanion intermediates) for available reaction on the BDD anode surface, at least for the concentrations examined.

Several studies (e.g., [9]) have shown that PFOA oxidation via electrochemical treatment proceeds via a stepwise mechanism in which C–C bond cleavage occurs between the carbon chain and the carboxylate group, coupled with F^- elimination. This process is repeated, resulting in the intermediate generation of shorter-chain perfluorocarboxylic acids. Consistent with this mechanism, generation of low concentrations of shorter chain perfluorinated carboxylates was observed (perfluorobutanoic acid, perfluoropentanoic acid, perfluorohexanoic acid, and perfluoroheptanoic acid), but at net concentrations $\leq 25\%$ of the total fluorine balance at all times during the experiments (Fig. S2). The observation of short chain perfluorinated carboxylates as intermediate products was generally greater in the experiments conducted at low current density, and the generation of these short chain carboxylic acids was up to 50% greater in the presence of chloride. The increased formation of intermediate transformation products in the presence of chloride may be due to increased surface competition between chlorine species and the perfluorocarboxylic acid intermediates as chain length gets shorter. Total F molar balances (quantified PFASs + fluoride) ranged from 60 to 98% by the end of the experiments, with greater recoveries generally attained for the lower current densities. Perchlorate was generated in all experiments where the electrolyte contained chloride, with perchlorate concentrations ranging from approximately 50 mg/L (18% of the chloride present converted) in the lowest current density experiments to over 250 mg/L (88% of the chloride converted) in the highest current density experiments.

Table 2
Measured rate constants for electrochemical treatment of PFASs.

Target PFAS	C_{init} (mg/L)	Current Density (mA/cm^2)	Matrix ^b	First-order rate constant (h^{-1}) ^a
PFOA	15	3	Na_2SO_4	0.091 ± 0.0008 (0.86)
PFOA	15	15	$\text{NaCl} + \text{Na}_2\text{SO}_4$	0.074 ± 0.0052 (0.95)
			Na_2SO_4	0.37 ± 0.020 (0.98)
PFOA	15	50	$\text{NaCl} + \text{Na}_2\text{SO}_4$	0.41 ± 0.012 (0.99)
			groundwater	0.33 ± 0.017 (0.99)
			Na_2SO_4	1.4 ± 0.027 (0.99)
PFOA	0.3	15	$\text{NaCl} + \text{Na}_2\text{SO}_4$	1.2 ± 0.047 (0.99)
			Na_2SO_4	0.33 ± 0.019 (0.97)
			groundwater	0.34 ± 0.020 (0.97)
PFOS	10	50	$\text{NaCl} + \text{Na}_2\text{SO}_4$	0.49 ± 0.056 (0.97)
			Na_2SO_4	0.37 ± 0.017 (0.99)
			groundwater	0.12 ± 0.016 (0.46)
PFOS	0.6	15	$\text{NaCl} + \text{Na}_2\text{SO}_4$	0.13 ± 0.017 (0.63)
			Na_2SO_4	0.041 ± 0.012 (0.33)
			groundwater	0.25 ± 0.015 (0.97)
PFHpS	1	50	$\text{NaCl} + \text{Na}_2\text{SO}_4$	0.11 ± 0.0098 (0.89)
PFHxS	1	50	$\text{NaCl} + \text{Na}_2\text{SO}_4$	

^a Uncertainties provided as standard error from linear regression of duplicate data sets. R^2 values from regression shown in parentheses. No rate constant measured for PFOS at a current density of 3 mA/cm^2 because only a very weakly decreasing trend in PFOS concentration was observed.

^b Electrolyte solutions prepared with 1500 mg/L Na_2SO_4 and 167 mg/L NaCl. Groundwater composition listed in Table 1 (amended with Na_2SO_4 to bring SO_4^{2-} concentration to 525 mg/L).

PFOA and PFOS removal for both the high (50 mA/cm²) and low (3 mA/cm²) current densities in electrolyte containing chloride are shown in Fig. 2 (corresponding measured rate constants provided in Table 2); PFOA and PFOS experiments were performed separately to distinguish transformation product (e.g., fluoride) generation for each compound. In general, PFOS was found to be less reactive than PFOA, with measured rate constants for oxidation of the former being roughly one third of the latter at comparable conditions; Zhuo et al. [18] also showed that PFOS was less reactive than PFOA during electrochemical treatment using BDD anodes. Unlike PFOA, no generation of shorter chain perfluorinated sulfonates or carboxylates was observed during PFOS treatment in this study, consistent with findings reported by Carter and Farrell [8], who also reported that changes in TOC and PFOS tracked closely to one another during treatment, a finding that suggests that anodic oxidation leads to rapid mineralization. This contrasts with Zhuo et al. [18], who showed that BDD treatment of PFOS resulted in the generation of short chain perfluorocarboxylate intermediates. The reason for these contrasting observations is not readily explained, but may be due to the nature of the BDD anodes and operational conditions used in each study. For the high current density, approximately 75% of the fluorine associated with PFOS degradation was accounted for as fluoride released (which is similar to the ~70% fluoride recovery observed for PFOA in the high current density experiments). For the lowest applied current density, PFOS removal was minimal (19%), which is only slightly greater than PFOS losses observed in absence of applied current, and only 11% of the fluorine associated with the degraded PFOS (i.e., 11% of the 19% PFOS removal) was recovered as fluoride.

The 10 mg/L PFOS electrolyte solution contained approximately 1 mg/L each of perfluoroheptane sulfonate (PFHpS) and perfluoro-

hexane sulfonate (PFHxS); these compounds were present as impurities within the commercial PFOS reagent. As shown in Fig. S3, both of these compounds were removed at a current density of 50 mA/cm², with measured first-order rate constants provided in Table 2. The observed rate constants decreased with decreasing chain length for PFOS through PFHxS, consistent with the observations of others [12,18]. No PFHxS or PFHpS removal (<10% decrease over time) was observed at a current density of 3 mA/cm². Smaller (n < 6) chain perfluorosulfonates remained below the LOQs for all experiments, and no generation of perfluorinated carboxylates above the LOQs was observed.

3.2. Effect of initial PFAS concentration

Results for experiments performed at 15 mA/cm² with a mixture of low concentration PFOA and PFOS (approximately 0.3 and 0.6 mg/L, respectively) are provided in Fig. 3 and Table 2. Consistent with the results observed in experiments using higher PFAS concentrations experiments at 15 mA/cm², chloride had minimal effects on PFOA and PFOS removal, and the measured first-order rate constant for PFOA at low concentration in the presence of PFOS ($0.33 \pm 0.019 \text{ h}^{-1}$) was nearly equal to the first-order rate constant for PFOA at elevated concentration ($0.37 \pm 0.020 \text{ h}^{-1}$). This finding corresponds to the linear region of the classic Langmuir-Hinshelwood model for surface chemical reactions [27]. Also similar to results obtained at elevated PFAS concentrations, PFOA removal was greater than that of PFOS removal. However, at a current density of 15 mA/cm², PFOS removal was not well described by first-order kinetics ($R^2 < 0.65$). The failure of the first order model is not readily explained, but may be due to the lack of sufficient electrode potential at the lower current densities. As shown in Fig. 3 and Table 2, PFOS mass removal was not significantly impacted by the presence of chloride, as approximately 50% PFOS removal was observed with and without chloride over the duration of the experiment.

Generation of shorter-chain perfluorinated carboxylates as intermediates from (presumably) PFOA was also consistent with that observed for the high concentration experiments (Fig. 4). Concentrations of PFHpA and PFHxA decrease by the last sampling event in Fig. 4. It is noted that the PFOS spiking solution contained very low levels (~0.1 mg/L) of PFHxS and PFHpS; both of these compounds showed decreasing trends in concentration during treatment. Generation of shorter chain perfluorocarboxylates and removal of shorter chain perfluorosulfonates were not affected by the presence of chloride, similar to findings for the high PFOA concentration results obtained under similar operating conditions.

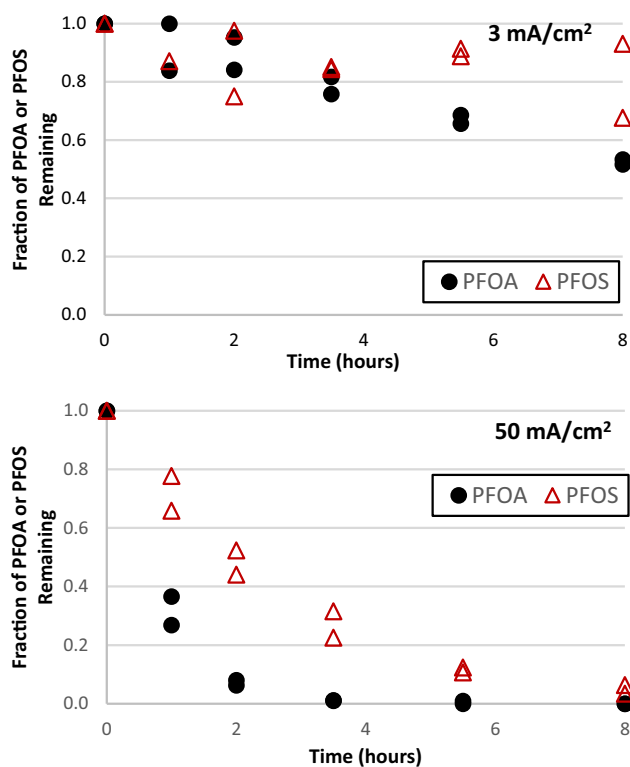


Fig. 2. Comparison of PFOA and PFOS removal during electrochemical treatment using applied current densities of (a) 3 mA/cm² and (b) 50 mA/cm². Each experiment was performed in duplicate in electrolyte containing 1500 mg/L Na₂SO₄ and 167 mg/L NaCl. Concentrations were normalized to the initial PFOA concentration (15 mg/L) or PFOS concentration (10 mg/L).

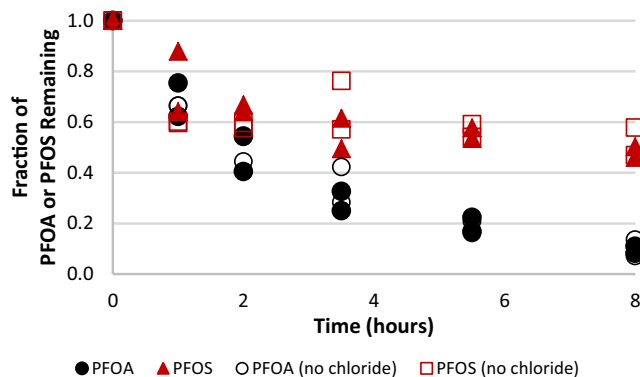


Fig. 3. Electrochemical treatment of low initial concentrations of PFOA (0.3 mg/L) and PFOS (0.6 mg/L) with an applied current density of 15 mA/cm². Each experiment was performed in duplicate in electrolyte containing 1500 mg/L Na₂SO₄ and 167 mg/L NaCl.

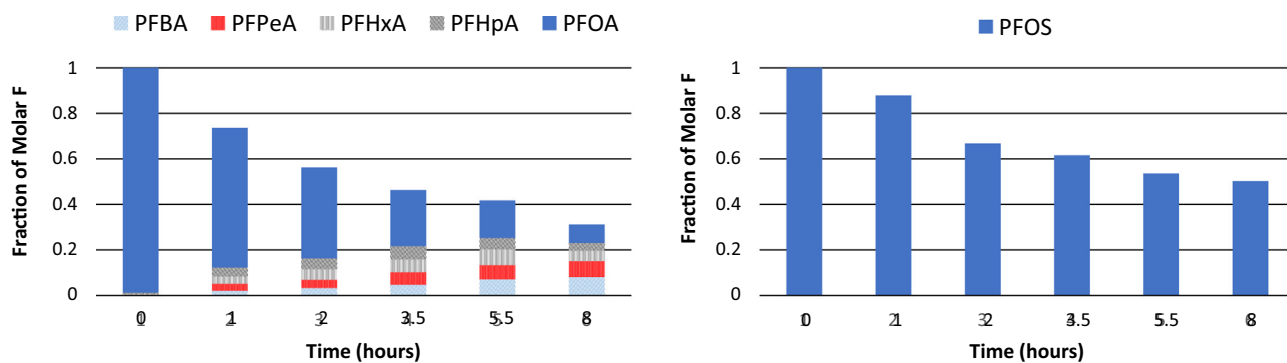


Fig. 4. Removal of PFOA (left) and PFOS (right). Generation of shorter chain perfluorocarboxylates was observed for PFOA. Reaction conditions: 0.3 mg/L PFOA or 0.6 mg/L PFOS, 1500 mg/L Na_2SO_4 , and 167 mg/L NaCl. Each experiment was performed in duplicate, but only results from one of the duplicate experiments is shown for clarity. PFBA = perfluorobutanoic acid, PFPeA = perfluoropentanoic acid, PFHxA = perfluorohexanoic acid, PFHpA = perfluoroheptanoic acid.

Although the low initial concentrations of PFOA and PFOS used in these experiments prevented quantification of fluoride ion release, ion chromatograms did show small unquantifiable peaks corresponding to the elution time of fluoride that increased in size throughout the duration of the experiment.

3.3. Oxidant generation and scavenging

Generation of solution phase oxidants (H_2O_2 and active chlorine species measured via the DPD method) in the absence and presence of chloride is shown in Fig. S4. These results show that the amount of oxidants generated increased with increasing current density, and that the oxidant generation approximately doubled in solutions amended with chloride ions.

Experiments also showed that the addition of TBA, a hydroxyl radical scavenger, had no apparent effect on rates of PFOA or PFOS removal (Fig. S5) or generation of shorter chain perfluorinated intermediates (Fig. S6). In these experiments, TBA concentrations decreased from 100 mg/L to approximately 3 mg/L within 4 h, and to approximately 0.5 mg/L by the end of the 8 h experiment, demonstrating that significant concentrations of hydroxyl radical were likely being generated by the anode during treatment, but scavenging of these radicals had no effect on the degradation or defluorination of either the parent perfluoroalkyl acids or the observed perfluorinated intermediates.

PFOA removal (15 mg/L initial concentration) in a natural groundwater, which also contains a number of known hydroxyl radical scavenging species including chloride, carbonate/bicarbonate, and dissolved organic matter (Table 1), is shown in Fig. 5. The measured first order degradation rate constant in the groundwater ($0.33 \pm 0.017 \text{ h}^{-1}$) was nearly identical to that measured in model electrolyte solutions at comparable conditions ($0.37 \pm 0.020 \text{ h}^{-1}$). Fluoride generation was 23% greater in the natural groundwater system. The behavior of the shorter chain perfluorinated compounds was similar to that observed in electrolyte, with decreases in PFHxA and PFHpA observed by the final sampling event (similar to that observed in Fig. 4). Repeating the natural groundwater experiments with a low concentration mixture of PFOA and PFOS showed that PFOA removal was slightly faster ($0.49 \pm 0.056 \text{ h}^{-1}$) than that measured using higher PFOA concentrations in groundwater ($0.33 \pm 0.017 \text{ h}^{-1}$) or comparable PFOA concentrations in model electrolyte solutions ($0.34 \pm 0.020 \text{ h}^{-1}$) (Table 2). Similar to results obtained in electrolyte, PFOS removal in natural groundwater at 15 mA/cm² was not well described by a first order model ($R^2 = 0.33$). Approximately 27% PFOS mass removal was observed in natural groundwater at a current density of 15 mA/cm², which is just over half that observed in the electrolyte systems. These results indicate that natural groundwater does not have major

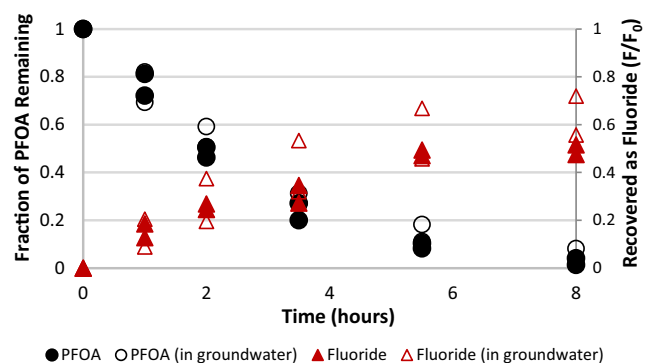


Fig. 5. Comparison of PFOA degradation and fluoride generation during electrochemical treatment in Na_2SO_4 -only electrolyte (solid symbols) with groundwater amended with Na_2SO_4 (open symbols). Applied current density was 15 mA/cm² (8.2 V in groundwater, 7.3 V in electrolyte matrix). Each experiment was performed in duplicate.

adverse impacts on electrochemical treatment of PFOA and PFOS compared to treatment observed in electrolyte.

3.4. Perchlorate treatment

The generation of perchlorate during electrochemical treatment with BDD anodes is a significant obstacle for implementation of this remediation technology since most natural water sources contain appreciable chloride ion. To address this, preliminary experiments were conducted to evaluate the biological treatment of perchlorate in the electrochemically treated solutions. Results of the biological perchlorate treatment experiment conducted in sand columns (to simulate re-injection of PFAS-treated groundwater into aquifers) are summarized in Fig. S7. Biological treatment yielded up to a 3-log decrease in perchlorate levels over the 9 day hydraulic residence time in the sand columns; chlorate concentrations in the effluent were below the detection limit of 0.2 mg/L. Molar decreases in both perchlorate and chlorate were accompanied by a proportional molar increase in chloride. It should be noted that this screening experiment was intended to demonstrate that the electrochemically treated water can be biologically treated to remove perchlorate, and was not intended to assess the process in detail (e.g., to quantify the microbial kinetics or to optimize treatment). The effectiveness of this preliminary treatment study suggests that a biological treatment polishing step can be used to address perchlorate oxidation byproducts of electrochemical treatment systems for PFASs. Further studies are needed to integrate these processes into an optimized treatment train.

4. Discussion

The presence of chloride had no substantial (>20%) impact on PFOA or PFOS removal for the experimental conditions tested, both at high and low concentrations. Fluoride generation in the high concentration experiments also was unaffected by the presence of chloride. These results suggest that the chloride (or its intermediate oxidation products such as chlorate) did not compete with PFOA or PFOS for available reactive surface sites on the BDD anode for the current densities tested, nor did the generation of any chlorine-based reactive oxygen species facilitate the oxidation of PFOS or PFOA. The presence of chloride did result in the formation of chlorate and perchlorate, similar to previous reports applying BDD anodes [13,28,29].

Oxidant generation was shown to increase with increasing current density; similar observations have been made by others using BDD anodes [25,29]. The increased oxidant generation in the presence of chloride likely is due to the generation of active chlorine species such as hypochlorous acid. In the absence of chloride, hydrogen peroxide likely accounts for the majority of the generated oxidants measured (since radical lifetimes are too short to be measured by the ex-situ DPD method). A reasonable (within approximately 10%) mass balance of chlorine was generally maintained in the experiments, with perchlorate and chlorate being the dominant chloride transformation products, even at the lowest current density tested.

The consumption of TBA also provides a measure of hydroxyl radical generation, as TBA consumption via electrochemical treatment with a BDD anode can be primarily ascribed to its reaction with generated hydroxyl radicals [30]. Thus, the observed TBA consumption indicates that substantial levels of hydroxyl radicals were generated at 15 mA/cm² current density. Even assuming that only 1 mol of hydroxyl radical is consumed per mole of TBA transformation, results suggest that the generation of hydroxyl radicals far exceeded the generation of hydrogen peroxide and active chlorine species (as measured via the DPD method). These results are consistent with those of Urriaga et al. [10], who showed substantial hydroxyl radical generation generated during BDD electrochemical treatment of PFOA far exceeded H₂O₂ generation. However, it is possible that TBA removal was, in part, caused by reactions on the anode surface, so observation of TBA removal alone is not confirmation of hydroxyl radical generation.

In the presence of the hydroxyl radical scavenger TBA, PFOA and PFOS removal (and generation of shorter chain perfluorinated as intermediates) was unaffected (Figs. S5, S6, and 4). Interestingly, the rate of chloride removal also was unaffected by the presence of TBA (data not shown). These results suggest that the oxidation of the both chloride and the target perfluorinated compounds (and the subsequent unzipping process of the carbon chain, at least in the case of PFOA) occurred primarily by direct electron transfer reaction on the BDD anode surface [8,9,18,29], and was not affected by the presence of any oxidants generated by the BDD anode, including hydroxyl radicals.

The observation of only relatively low levels (compared to levels of PFOA and PFOS) of the shorter chain perfluorinated transformation products is also consistent with a surface reaction mechanism, as only limited desorption of these compounds from the anode surface likely occurred [31]. The observation that the perfluorosulfonates showed a decreasing rate constant with decreasing chain length (or, with decreasing hydrophobicity), as shown in Table 2, also is consistent with a surface-controlled reaction due to sorption on the anode.

Measured rate constants for PFOA and PFOS removal increased with increasing current density, suggesting that the active sites on the anode surface were not saturated with respect to adsorbed

PFOA or PFOS, and that the observed reaction rates were surface controlled. Fig. S8 shows the PFOA first order rate constants as a function of current density. The first order transformation rate constants for chloride removal also are plotted in Fig. S8. These data show that, consistent with a surface-controlled reaction, the first order rate constants for both chloride and PFOA removal are approximately proportional to the applied current density. The rate constants for PFOA were similar (within a factor of 2) but slightly greater than those determined for chloride, suggesting that PFOA had a greater affinity for the BDD surface than chloride, and/or was more rapidly oxidized than chloride at the BDD surface. While some studies have shown that the presence of chloride increases the rate of organic contaminant removal during BDD electrochemical oxidation [32,33], likely due to oxidation of the target organic contaminants by oxidized chlorine species, the presence of chloride did not enhance the removal rate of PFOA or PFOS. This result suggests that oxidized chlorine species do not facilitate the oxidation of PFOA or PFOS during electrochemical treatment, which also is consistent with a surface-controlled oxidation mechanism for PFOA and PFOS.

PFOS removal at the low current density of 3 mA/cm² was minimal, and the calculated PFOS degradation rate constant at 50 mA/cm² was substantially less than that for PFOA. These results demonstrate that PFOS is more difficult to oxidize than PFOA, similar to the reactivity trend reported for activated persulfate as an oxidant [34] and in previous electrochemical experiments [18]. The increased cell voltage associated with the higher current densities also may have facilitated the observed increases in removal rates with current density, especially for PFOS [10]; the anode potential at 3 mA/cm² may have been insufficient to initiate oxidation.

During electrochemical treatment using BDD anodes, the initial oxidation step has been shown to be removal of an electron from the carboxylate functional group (PFOA) or the sulfonate functional group (PFOS), leading to the formation of functional group radicals [18]. The activation energy needed for this initial radical activation step, using experimental and/or quantum mechanics simulations, is 80 kJ/mole for PFOS [8] and 60 kJ/mole for PFOA [35]. While this difference in activation energies provides a plausible explanation for the observed differences in the PFOA and PFOS rate constants (Table 2), the relative attachment of PFOA and PFOS to active BDD anode sites cannot be ruled out as the cause (in part or in whole) for the observed difference in PFOA and PFOS treatment rates.

While the generation of shorter-chain perfluorocarboxylates and fluoride accounted for up to 61% of the PFOA removed in the high current density experiments, and fluoride generation accounted for up to 75% of the PFOS removed in the high current density experiments, the fate of the remaining fluorine in both the PFOA and PFOS experiments was not determined. Fluorination of the anode surface may account for some of this loss [9]. Previous electrochemical studies also have shown that volatile perfluorinated hydrocarbons (e.g., perfluorooctane) may have been generated [6] that could account for some of the discrepancy in mass balance. Alternatively, shorter chain non-volatile fluorinated byproducts which are not readily observed by LC-MS/MS are also likely forming during treatment. Ochiai et al. [9] noted that PFOA removal resulted in stoichiometric production of CO₂, which suggests that the initial step of PFOA decomposition (i.e., removal of the first C–C bond) is accompanied by complete mineralization. Further examination with emerging high resolution mass spectrometry instrumentation may enable identification of these missing analytes.

The energy used by the electrochemical cell to attain an order of magnitude decrease in PFOA and PFOS at 50 mA/cm² was 180 W-h/L

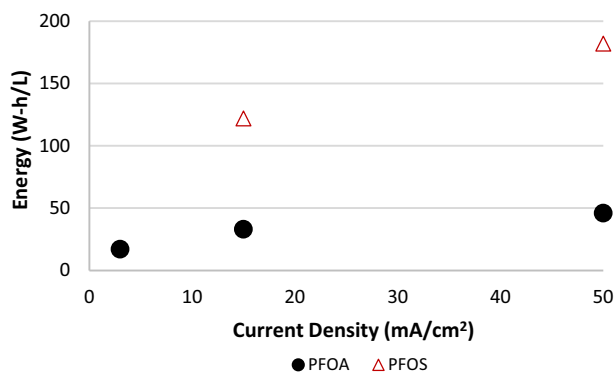


Fig. 6. Comparison of the energy demand for a 50% reduction in concentration for both PFOA and PFOS as a function of applied current density. PFOS removal at 3 mA/cm² was insufficient to determine the energy demand. Experiments were performed in electrolyte (1500 mg/L Na₂SO₄, and 167 mg/L NaCl).

and 500 W-h/L, respectively. For PFOA at 15 mA/cm², the electrochemical energy for an order of magnitude decrease was reduced to 113 W-h/L. A comparison of the electrochemical energy for 50% PFOA and PFOS removal as a function of applied current density is provided in Fig. 6. The energy requirements increased with the applied current density, likely due to increased oxygen evolution that inhibited PFOA and PFOS oxidation. The energy requirements for PFOA oxidation are in reasonable agreement with those measured for doped mixed metal oxide anodes, as summarized by Niu et al. [36].

While BDD anode longevity was not the focus of this study, no decreasing trend in the rate constants determined for PFOA were observed throughout the course of testing performed with a single BDD anode. With approximately 20 8-h batch experiments performed using the same BDD anode, no measurable decrease in PFOA or chloride removal (as indicated by the replicate experiments and by the observed trend in first order rate constants) was observed. Thus, any fluorination of the anode surface that may have occurred did not have a measurable impact on PFOA and chloride removal rates. However, this study was not designed to assess BDD anode longevity with respect to PFOA and PFOS treatment, and further testing of anode longevity, preferably under continuous flow conditions with actual PFAS-impacted source waters, is needed.

5. Conclusions

Results presented herein demonstrate that BDD anodes are effective for treating PFOA and PFOS in waters containing chloride, as well as in natural groundwater. Data indicate that the shorter chain perfluorinated compounds (e.g., PFHpA, PFHxA, PFHpS, PFHxS) are also amenable to treatment using BDD anodes. The presence of chloride, and the subsequent generation of oxidized chlorine species, had only a slight (within 20%) impact on the observed rate of PFOA or PFOS defluorination. PFOA and PFOS removal was consistent with an anode surface reaction being the rate limiting step, as observed removal rates and transformation product generation were not impacted by the presence of an established hydroxyl radical scavenger, and observed removal rates increased with increasing current density. The limited adverse impacts of chloride, hydroxyl radical scavenger, and natural groundwater constituents on PFAS treatment suggests that BDD anodes hold promise as a viable option for treating mixed contaminant groundwater plumes. PFOA oxidation was substantially more rapid than PFOS during electrochemical treatment using the BDD anode used in this study. It is important to note that the results obtained herein were for a specific commercially available BDD

ultrananocrystalline anode (Advanced Diamond Technologies); it is currently unclear how findings would vary for other types of BDD anodes. While perchlorate was generated from chloride as an oxidation byproduct, biological treatment of the electrochemically generated water was shown to be effective in removing the perchlorate. Overall, these results suggest that a treatment train consisting of BDD electrochemical treatment followed by *in situ* biological reduction of the perchlorate and chlorate oxidation byproducts is a promising strategy for remediation of PFAS-contaminated groundwater.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2017.02.107>.

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