Electrochemical treatment of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) in groundwater impacted by aqueous film forming foams (AFFFs)

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HIGHLIGHTS

• Electrochemical treatment of AFFF-impacted groundwater was demonstrated.
• A divided electrochemical cell was used.
• PFOS and PFOA removal was greater than that observed in previous studies using MMO anodes.
• Defluorination was observed for both PFOS and PFOA.
• Other long-chain perfluorinated compounds also were treated.

ABSTRACT

Laboratory experiments were performed to evaluate the use of electrochemical treatment for the decomposition of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), as well as other perfluoroalkyl acids (PFAAs), in aqueous film forming foam (AFF)-impacted groundwater collected from a former firefighter training area and PFAA-spiked synthetic groundwater. Using a commercially-produced Ti/RuO2 anode in a divided electrochemical cell, PFOA and PFOS decomposition was evaluated as a function of current density (0–20 mA/cm2). Decomposition of both PFOA and PFOS increased with increasing current density, although the decomposition of PFOS did not increase as the current density was increased above 2.5 mA/cm2. At a current density of 10 mA/cm2, the first-order rate constants, normalized for current density and treatment volume, for electrochemical treatment of both PFOA and PFOS were $4.6 \times 10^{-5}$ and $7.0 \times 10^{-5} [(\text{min}^{-1})(\text{mA/cm}^2)^{-1}L]$ respectively. Defluorination was confirmed for both PFOA and PFOS, with 58% and 98% recovery as fluoride, respectively (based upon the mass of PFOA and PFOS degraded). Treatment of other PFAAs present in the groundwater also was observed, with shorter chain PFAAs generally being more recalcitrant. Results highlight the potential for electrochemical treatment of PFAAs, particularly PFOA and PFOS, in AFFF-impacted groundwater.

1. Introduction

Groundwater impacts by poly- and perfluoralkyl substances (PFASs) are a growing environmental concern, particularly for perfluorooctyl acids (PFAAs), a subgroup of PFASs that are extremely persistent in the environment [1]. Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), with U.S. drinking water provisional health advisory levels of 0.4 and 0.2 µg/L, respectively, are the two PFAAs currently of greatest interest [2]. Release of these compounds into the subsurface is typically associated with firefighter training activities where aqueous film forming foams (AFFFs) have been applied. While some PFAAs are present in the various AFFF formulations that have been used in firefighter training areas [3], PFAAs can be produced in situ from the degradation of the PFASs present in AFFF [4,5].
Once released to the environment, treatment of PFAAs such as PFOS and PFOA is challenging, as many conventional technologies used to treat organic contaminants in groundwater have proven to be ineffective or inefficient. Treatment approaches such as nanofiltration and advanced UV processes have shown promise for addressing PFAAs [6–8]. Recently, electrochemical treatment using boron-doped diamond (BDD) anodes in undivided cells has been shown to treat both PFOA and PFOS via first order kinetics [9,10]. Fluoride generation was observed in these electrochemical experiments, providing clear evidence of PFOA and PFOS defluorination; however, several studies have noted that perchlorate formation can occur during anodic oxidation [11,12]. Our preliminary studies using BDD anodes for treatment of PFAAs in chloride-containing natural ground waters (which contained approximately 100 mg/L of chloride) resulted in large (>1 mg/L) increases in perchlorate.

Using similar electrochemical treatment approaches in undivided cells, various custom-synthesized mixed metal oxide (MMO) anodes have been shown to treat PFOA, also with apparent first order kinetics and fluoride generation [13–15]. However, MMO anode materials (e.g., Ti/IrO2 and Ti/RuO2) that are commercially available cells, various custom-synthesized mixed metal oxide (MMO) anodes have been shown to treat PFOA, also with apparent first order kinetics and fluoride generation [13–15]. However, MMO anode materials (e.g., Ti/IrO2 and Ti/RuO2) that are commercially available in large quantities, which would likely facilitate the commercial use of MMO electrochemical treatment technologies for groundwater treatment, were simply described as having "poor performance" with respect to PFOA degradation [13].

While previous electrochemical PFAA decomposition research has shown promise, the research typically has not been performed under environmentally relevant conditions. Rather, such research has typically been conducted using a simplified synthetic groundwater matrix with very high PFAA concentrations (e.g., 50 mg/L). Electrochemical treatment typically has consisted of employing an undivided cell using custom-made anodes. Further research is needed to understand electrochemical PFAA decomposition in environmentally and commercially relevant contexts, as several important questions remain unanswered regarding the potential for electrochemical treatment of PFAAs in groundwater. First, natural groundwater is a complex matrix containing many constituents. It currently is unknown, how the natural groundwater matrix will affect electrochemical PFAA treatment. Second, recent studies have shown that PFOA and PFOS contamination in groundwater typically occurs in the presence of a wide range of PFAAs and PFASs [5,16]. The impacts of these mixtures on PFOA and PFOS treatment have not been investigated. In addition, to date, the electrochemical treatment studies for PFOA and PFOA have been performed at concentrations several orders of magnitude above the PFOS and PFOA concentrations that are typically observed in groundwater plumes (i.e., 1–1000 μg/L). Degradation kinetics may be substantially different at the decreased concentrations that are more typical of AFFF-impacted sites. Finally, previous studies have shown that electrochemical treatment of organic compounds can be more effective in divided electrochemical cells rather than undivided cells [17,18]. Thus, the use of Ti/IrO2 or Ti/RuO2 anode materials in divided flow cells may result in improved treatment performance with respect to PFOA and PFOS. However, we are unaware of any published studies reporting on the performance of commercially-available MMO anodes for treatment of PFOA and PFOS in divided flow cells.

The overall goal of this research was to evaluate and demonstrate the electrochemical treatment of PFOA and PFOS in a natural groundwater from an AFFF-impacted former firefighter training area. A commercially-available MMO material, for use in a divided electrochemical cell, was selected for this study. PFOA and PFOS treatment rates were investigated as a function of current density, with respect to PFOA degradation [13].

2. Experimental

2.1. Groundwater collection and synthetic groundwater preparation

Groundwater used in this study was collected from within OU-1 at Ellsworth Air Force Base in South Dakota. A detailed discussion of the PFAS contamination at this site can be found in McGuire et al. [5]. The groundwater was collected from operating extraction wells in the vicinity of a former firefighter training area where AFFF reportedly was used. Groundwater was collected in four 5-gallon gas-tight soda kegs under nitrogen headspace. Collected groundwater was homogenized and stored at 4 °C for laboratory testing. Table 1 provides a summary of the geochemistry of the collected groundwater, as well as PFAA concentrations.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Concentration Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride</td>
<td>107 mg/L</td>
</tr>
<tr>
<td>Sulfate</td>
<td>1400 mg/L</td>
</tr>
<tr>
<td>Nitrate</td>
<td>&lt;0.2 mg/L</td>
</tr>
<tr>
<td>Alkalinity/Conductivity</td>
<td>370 mg/L, 2500 mho/cm</td>
</tr>
<tr>
<td>TOC/COD</td>
<td>pH 23, 27, 7.4 mg/L, mg/L SU</td>
</tr>
<tr>
<td>PFBA</td>
<td>3.9 μg/L</td>
</tr>
<tr>
<td>PFPeA</td>
<td>13 μg/L</td>
</tr>
<tr>
<td>PFHxS</td>
<td>5.7 μg/L</td>
</tr>
<tr>
<td>PFHxA</td>
<td>5.9 μg/L</td>
</tr>
<tr>
<td>PFDA</td>
<td>13 μg/L</td>
</tr>
<tr>
<td>PFNA</td>
<td>&lt;0.70 μg/L</td>
</tr>
<tr>
<td>PFOA</td>
<td>&lt;2.0 μg/L</td>
</tr>
<tr>
<td>PFOA</td>
<td>&lt;1.8 μg/L</td>
</tr>
<tr>
<td>PFBS</td>
<td>17 μg/L</td>
</tr>
<tr>
<td>PFHxS</td>
<td>65 μg/L</td>
</tr>
<tr>
<td>PFHpS</td>
<td>2.2 μg/L</td>
</tr>
<tr>
<td>PFOS</td>
<td>18 μg/L</td>
</tr>
</tbody>
</table>

Table 1 Groundwater geochemistry and perfluoroalkyl acid levels.

The impacts of these mixtures on PFOA and PFOS treatment

Fig. 1. Schematic of experimental set-up. In the electrochemical (EC) cell, the membrane is used to separate the catholyte and anolyte chambers.
The anolyte solution was monitored as a function of time during the duration of each experiment, which typically lasted 6 h. Samples were collected for determination of pH, anions (including perchlorate), and PFAAs. Periodic samples also were collected in the catholyte chamber to evaluate pH increases and to ensure that no PFAAs or potential transformation products were migrating across the membrane.

To further explore potential defluorination, additional experiments at a current density of 1 mA/cm² were performed using a synthetic groundwater prepared with NaCl and Na₂SO₄ concentrations representative of the natural site groundwater (100 and 1500 mg/L, respectively). This synthetic groundwater was amended with a PFOA or PFOS spike (individually in separate experiments) to attain a concentration of 5 mg/L; these elevated concentrations (relative to the concentrations in the natural groundwater) were intended to facilitate identification of potential transformation products during electrochemical treatment. To attain a concentration of 5 mg/L of PFOA, 10 ml of a 1000 mg/L stock dissolved in methanol (Sigma–Aldrich, Cat. No. 171468) was added to 2 L of synthetic groundwater. In separate experiments, 5 mL of a 2000 mg/L PFOS stock (Sigma–Aldrich, Cat. No. 77283) in deionized water was added to 2 L of synthetic groundwater to achieve a concentration of 5 mg/L.

Table 2

<table>
<thead>
<tr>
<th>Compound</th>
<th>20 mA/cm²</th>
<th>10 mA/cm²</th>
<th>2.5 mA/cm²</th>
<th>1.0 mA/cm²</th>
<th>0.0 mA/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFOA(groundwater, 13 µg/L)</td>
<td>0.0073</td>
<td>0.0062</td>
<td>0.0042</td>
<td>0.0017</td>
<td>0.00075</td>
</tr>
<tr>
<td>PFOA(groundwater, 18 µg/L)</td>
<td>0.0061</td>
<td>0.0059</td>
<td>0.0021</td>
<td>NM</td>
<td>0.0027</td>
</tr>
<tr>
<td>PFOA(16 µg/L, synthetic groundwater, pH 2)</td>
<td>0.0060</td>
<td>0.0058</td>
<td>0.0055</td>
<td>0.0046</td>
<td>0.0034</td>
</tr>
</tbody>
</table>

NM = no measurable decreasing trend in concentration observed.
2.3. Analysis of water samples

The pH of each sample was determined by BDH pH test strips (VWR, Cat. No. BDH35309.606). Anions (fluoride and chloride), as well as perchorlate, were analyzed via ion chromatography using EPA Methods 300.0 and 314.2, respectively. For PFAA analysis, samples were collected in 20 mL polypropylene vials and were pH neutralized (as needed) to a final pH between pH 5 and 9. Sample analysis generally followed the procedures outlined in Guello and Higgins [19]. Briefly, an aliquot of each sample was microcentrifuged at 13,000 relative centrifugal force (RCF) for 30 min to remove any particulates. If an interim dilution was warranted (e.g., PFNA concentration >50 μg/L for 30 min to remove any particulates. If an interim dilution was warranted (e.g., PFNA concentration >50 μg/L), a subsample of the centrifuged sample was combined with milliQ water and amended with 10% isopropanol. The centrifuged sample, or interim dilution, was transferred into an autosampler vial containing surrogate standards (200 ng/L), for a final mixture composition of 84% aqueous, 9% isopropanol, 7% methanol. PFNA analysis was accomplished using liquid chromatography with tandem mass spectrometry (LC–MS/MS; Applied Biosystems 3200 Sciex mass spectrometer) operated in negative ionization mode. LC–MS/MS analysis conditions are detailed elsewhere [19]. Two transitions were monitored for each analyte, where the primary transition was used for quantification and the secondary for confirmation. Blanks were included every six samples and carry over was minimal. Quality assurance criteria included signal/noise >30 and above the limit of quantitation (LOQ: see SI for definition); LOQs were analyte, matrix, and run dependent, but were generally 6–21 ng/L. Details on transitions, surrogates, and LOQs are shown in SI.

To investigate the potential generation of volatile organofluorine products, additional experiments with 5 mg/L PFOS or PFOA in synthetic groundwater were performed at a current density of 1 mA/cm². Control experiments, which were performed at a current density of 1 mA/cm² using synthetic groundwater but without addition of any PFOS or PFOA, also were performed. The reactor was not sparged, and headspace gas was sampled as a function of time (reactor vessels were covered with a plastic lid). Employing a similar approach to that of Yamamoto et al. [20], headspace gas samples were analyzed on a gas chromatograph equipped with a mass spectrometer; gas samples were analyzed in selective ion mode with a m/z ratio of 69 to identify CF₄ groups. Standard gases (trifluoromethane, carbon tetrafluoride, octfluoropropane, perfluorohexane, octafluorooctane, hexafluorothane, and 1H-perfluoroctane) were used in an attempt to identify potential transformation products.

3. Results and discussion

3.1. General observations

The voltage remained constant (±5%) during each experiment, and also during the duration of all experiments (for each current density tested), indicating that fouling or deactivation processes were not causing increased resistance at the electrode surfaces. Applied cell voltages for the span of current densities tested ranged from 4 to 13 V.

Electrochemical treatment expectedly resulted in a decrease in pH at the anode, and an increase in pH at the cathode. The anolyte pH results for the current density studies are provided in Fig. 2. Chloride removal in the anolyte also was observed, with chloride gas as the presumed transformation product, as this process has been developed for generation of chlorine gas [21]. Generation of oxidized chlorine species (i.e., chloride, hypohalite, and chlorate) were negligible, and did not account for the stoichiometric decreases in chloride. Trace amounts of perchlorate were observed by the end of treatment at the highest current densities (150 μg/L perchlorate at 20 mA/cm², and 12 μg/L perchlorate at 10 mA/cm²); perchlorate was non-detect (<1 μg/L) in all other experiments.

3.2. PFOA and PFOS removal

Decomposition of PFOA and PFOS during electrochemical treatment followed apparent first-order kinetics. Representative PFOA and PFOS removal data are shown in Fig. 3. Regressed first-order rate constants for PFOA and PFOS over the range of current densities examined are provided in Table 2. Experiments performed with zero applied current served as controls to assess the extent of PFOA and PFOS losses due to sorption. For PFOS, the electrochemical contribution to the observed rate constant is estimated as the difference in the tabulated value of the rate constant with applied current minus that for the no current control.

Because the pH of the anolyte solution decreased to approximately 2 in several experiments and sorption of PFAAs is pH-dependent [22,23], additional zero current controls were performed at a pH of 2 for PFOA, as the observed rate constant for PFOA removal increased with increasing applied current (Table 2) and decreasing pH (Fig. 2). For this low pH control, sulfuric acid was used to lower the pH. Results for the controls indicated that, while measurable decreases in PFOA and PFOS were observed (67% and 13% for PFOS and PFOA controls at neutral pH, respectively), observed removal rates were greater when current was applied (Table 2). The observed PFOA removal was greater in the low pH control (zero current) than in the neutral pH control; this dependence of PFOA sorption on pH makes quantifying the removal of PFOA due to electrochemical treatment versus sorption at the two lowest applied current densities difficult to determine, as the decrease in pH occurs slowly in these experiments. Sparging gases were collected in a base trap to determine if the mechanism for the enhanced PFOA removal at low pH was due to stripping of the PFOA from solution. However, analysis of the base trap (1 L 0.5 M NaOH) showed that only approximately 1% of the PFAA mass loss from the cell could be accounted for by volatilization losses, suggesting that the low pH conditions may have simply enhanced the sorptive losses of PFOA within the electrochemical treatment system.

Previous studies have suggested that the initial degradation steps involved with electrochemical treatment of PFOS and PFOA occur via direct electron transfer at the surface of the anode [13,15]. For PFOA, the rate of observed removal increased with increasing applied current, suggesting that the reactive sites on the electrode were not saturated with respect to PFOA. A similar increasing trend in PFOA decomposition rate through a similar range of current densities was observed by Lin et al. [15] using MMO anodes in electrolyte solution. For PFOS, the rate of observed decomposition decreases in chloride. A single experiment is shown where the applied current density was 10 mA/cm².
increased through a current density of 2.5 mA/cm², then remained steady thereafter. This result for PFOS suggests that reactive sites became saturated at the anode surface; similar observations for PFOS were observed by Carter and Farrell [9], using BDD anodes.

No fluoride generation was observed during the electrochemical experiments in groundwater, although the relatively low levels of PFAAs present in the groundwater would have made fluoride generation difficult to identify (fluoride LOQ of 1 mg/L). In addition, potential generation of fluoride could have been due to the presence of other PFASs in the site groundwater [5], rather than PFOA or PFOS. Thus, the groundwater experiments do not provide any conclusive evidence regarding potential defluorination of PFOA and PFOS. Furthermore, no shorter chain length PFAA (e.g., perflurobutanoic acid, perfluorohexanoic acid) generation was observed, even when looking for these compounds in a base trap for the sparging gases.

3.3. Transformation product investigation

Transformation product generation was further investigated using the synthetic groundwater experiments amended with 5 mg/L of either PFOA or PFOS. Electrochemical treatment results (1 mA/cm²) showed that no measureable fluoride accumulated in the anolyte; sampling of the cathode chamber confirmed that no measurable losses of PFOA, PFOS or fluoride occurred via passage through the membrane. However, because the pH of the anolyte rapidly decreased to 2, which is below the pKₐ of HF (3.2, as reported by Bordwell et al. [24]), volatilization of HF likely occurred. We note that, as hypothesized by Carter and Farrell [9], volatilization losses may also have occurred in the form of HOF. Collection of the sparging gases within a base trap, and subsequent anions analysis of the base trap solution for fluoride, showed that approximately 98% of fluoride in the PFOS that was removed via electrochemical treatment was recovered; 58% of the fluoride in the PFOA that was removed, was recovered. These results suggest substantial defluorination of PFOS and PFOA occurred. Such defluorination, without the observation of substantial quantities of shorter chain length PFAAs, may be explained by the fact that the PFOA and PFOS decomposition reactions occur on the surface of the anodes and transformation products may not enter solution, as suggested by Niu et al. [14].

Investigation of headspace gases during treatment of 5 mg/L PFOS in synthetic groundwater showed an apparent transformation product peak (the GC-analyzed peak area increased over time, and peaks were not observed in control experiments that were not spiked with PFOS). Comparison to standard gases suggested that trace levels of 1H-perfluorooctane were generated, and that the C–S bond was broken. No apparent volatile transformation products were observed for 5 mg/L PFOA in synthetic groundwater. Quantification of volatile transformation products was not possible because the reactor was not gas tight.

3.4. Comparison to other studies and other PFAAs

Table 3 shows a comparison of normalized (with respect to current density and treatment volume) first-order rate constants for electrochemical treatment of PFOA attained in various studies, and with various anode types. In the present study, the calculated values for PFOA and PFOS were 46 × 10⁻⁵ and 70 × 10⁻⁵ [(min⁻¹) (mA/cm²)⁻¹ (L)], respectively. It is noted that, in Table 3, undivided electrochemical cells were used in all studies except the present study. Results obtained herein compare favorably with those attained in other MMO studies, which suggests that commercially-available MMO anodes, employed in a divided electrochemical cell configuration, are a viable approach for PFOA and PFOS treatment of impacted natural groundwater. Results attained using BDD anodes showed the greatest rate constant in Table 3 [10]. However, our initial testing using BDD anodes in an undivided electrochemical cell with the natural groundwater resulted in substantial perchlorate generation. We also note here that a single replicate experiment performed using a commercially available Ti/IrO₂ anode was performed in the groundwater at 10 mA/cm². PFOA and PFOS removal rates were identical to that observed using the Ti/RuO₂ anode, but without any measurable generation of perchlorate (data not shown). While the focus of treatment was on PFOA and PFOS, treatment of the other PFAAs present in the groundwater also were evaluated. Observed first order rate constants at current densities of 0, 10, and 20 mA/cm² are presented in Table 4. These results suggest that not all PFAAs react similarly during electrochemical treatment, highlighting the need for an improved fundamental understanding of these reactions in real groundwater systems. Consistent with the results of Zhuo et al. [25], who investigated the electrochemical oxidation of PFAAs of varying chain length using BDD anodes, results in the present study showed that the shorter chain length PFAAs were generally more recalcitrant to electrochemical treatment (although we note that Zhuo et al. did measure degradation of the shorter chain length compounds). This has been attributed to the fact that the shorter chain compounds adsorb less to the anode surface [25].

4. Conclusions

Using a divided electrochemical cell and a Ti/RuO₂ anode, defluorination of both PFOA and PFOS was observed in a series of bench-scale experiments. This is, to the best of our knowledge, the first demonstrated application of this approach for perfluorinated compounds in AFFF-impacted groundwater. Other PFAAs also were treated electrochemically, but the shorter chain length PFAAs generally were more recalcitrant. Additional work is needed to further evaluate contaminant transformation pathways, to assess treatment of a wider range of PFAAs, to limit formation of perchlorate (if operating at elevated current densities), and to optimize treatment effectiveness.
Acknowledgement

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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.jhazmat.2015.04.024.

References