

## Perfluorooctanoic acid degradation in the presence of Fe(III) under natural sunlight



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### HIGHLIGHTS

- PFOA was photo-chemically decomposed in the presence of Fe(III) and natural sunlight.
- An alternative reaction pathway involves hydroxyl radical as confirmed by EPR.
- Common oxidant-persulfate increased PFOA defluorination extent.

### ARTICLE INFO

#### Article history:

Received 9 July 2013

Received in revised form 23 August 2013

Accepted 1 September 2013

Available online xxx

#### Keywords:

PFOA

Defluorination

Radical

Photolysis

Iron

### ABSTRACT

Due to the high bond dissociation energy (BDE) of C–F bonds (116 kcal/mol), perfluorooctanoic acid (PFOA) is a highly recalcitrant pollutant. Herein, we demonstrate a novel method to decompose PFOA in the presence of sunlight and ferric iron (Fe(III)). Under such conditions,  $97.8 \pm 1.7\%$  of  $50 \mu\text{M}$  PFOA decomposed within 28 days into shorter-chain intermediates and fluoride ( $\text{F}^-$ ), with an overall defluorination extent of  $12.7 \pm 0.5\%$ . No PFOA was removed under visible light, indicating that UV radiation is required for PFOA decomposition. Spectroscopic analysis indicates that the decomposition reaction is likely initiated by electron-transfer from PFOA to Fe(III), forming Fe(II) and an unstable organic carboxyl radical. An alternative mechanism for the formation of this organic radical involves hydroxyl radicals, detected by electron paramagnetic resonance (EPR). The observation that PFOA can be degraded by Fe(III) under solar irradiation provides mechanistic insight into a possibly overlooked natural attenuation process. Because Fe(III) is abundant in natural waters and sunlight is essentially free, this work represents a potentially important step toward the development of simple and inexpensive remediation strategies for PFOA-contaminated water.

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### 1. Introduction

Perfluorooctanoic acid (PFOA) has been detected in various environmental matrices [1–7] and even in human beings [8–11] due to its extensive use in the manufacture of industrial, medical and commercial products [12–14]. PFOA is the subject of increasing regulatory interest because of its potential to bioaccumulate, its environmental persistence [15–18], and growing evidence of its toxicity to humans [19]. The US EPA considers PFOA to be a “likely carcinogen” [20]. Unlike most persistent and bioaccumulative organic pollutants, PFOA is water-soluble ( $9.5 \text{ g/L}$  at  $25^\circ\text{C}$

[21]) and does not sorb strongly to soil or sediments; thus, it has a high migration potential and poses a serious threat to ground and surface water resources.

Due to the presence of multiple, highly stable C–F bonds (BDE = 116 kcal/mol), PFOA and other perfluorinated compounds (PFCs) are very persistent under most natural conditions [15–18], and the development of effective treatment technologies has proven difficult. Biodegradation, one of the primary attenuation mechanisms for most anthropogenic contaminants, appears to be limited. For example, in an attempt to degrade or co-metabolize PFOA, six different microbial communities from a variety of environments were unable to significantly alter the PFOA chemical structure even after 259 days of incubation [15]. Furthermore, abiotic treatment methods (e.g., advanced oxidation using  $\text{H}_2\text{O}_2$  and persulfate) are marginally effective for degrading PFOA [22–27] or

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require relatively harsh conditions (e.g., high temperature (130 °C) [23,26], microwave activation [26], sonolysis [28–30], or strongly acidic conditions [24]).

One potential PFOA degradation mechanism that has received limited attention is photo-decomposition. Taniyasu et al. [31] studied the photolysis of several perfluoroalkyl substances at high altitudes, and reported slow degradation of PFOA (5% removal after 106 days of solar irradiation). Hori et al. [32] and Wang et al. [33] reported that PFOA and shorter chain perfluorocarboxylic acids (PFCAs) could be degraded by UV light in the presence of Fe(III), but many of these experiments were conducted under extreme conditions (i.e., 0.49 MPa pressure and pH 1.5) that are uncommon in the environment. PFOA degradation was postulated to involve organic radicals [33], although no evidence for their production was presented and the role of hydroxyl radicals ( $\bullet\text{OH}$ ), which can be generated in the presence of Fe(III) and UV light [34], was not investigated. Vaalgamma et al. [35] irradiated PFOA for up to 165 h under simulated sunlight ( $290 \leq \lambda \leq 500 \text{ nm}$ ; corresponding to 75.6 days of natural solar radiation) in the presence of ferric ion (2.95 mg/L), but no PFOA removal was observed. This result led the authors to conclude that the photochemical half-life of PFOA will be at least 256 years in the ocean. However, this research was conducted under simulated sunlight, to our knowledge, no previous studies have examined PFOA photo-decomposition in the presence of Fe(III) under real-sunlight exposure.

This study assessed PFOA degradation under natural attenuation conditions in the presence of Fe(III) and sunlight. Electron paramagnetic resonance (EPR) was used to investigate the underlying reaction mechanisms and determine if free radicals are generated by the Fe(III)-sunlight reaction system. Two strong oxidants (persulfate and  $\text{H}_2\text{O}_2$ ), which have been reported to promote PFOA degradation [23,24,26], were also tested to further investigate the photo-decomposition mechanism. Results of this research demonstrate PFOA photo-decomposition and defluorination. Consequently, this study provides insight into PFOA natural attenuation mechanisms and offers a potential platform for novel surface and groundwater treatment technologies.

## 2. Material and methods

### 2.1. Chemicals

Perfluorooctanoic acid (PFOA,  $\text{C}_7\text{F}_{15}\text{COOH}$ , 96%), and its decomposition products: perfluoroheptanoic acid (PFHpA,  $\text{C}_6\text{F}_{13}\text{COOH}$ , 99%), undecafluorohexanoic acid (PFHeA,  $\text{C}_5\text{H}_{11}\text{COOH}$ , 97%), perfluoropentanoic acid (PFPeA,  $\text{C}_4\text{F}_9\text{COOH}$ , 97%), perfluorobutyric acid (PFBA,  $\text{C}_3\text{F}_7\text{COOH}$ , 98%) and pentafluoropropionic acid (PFPrA,  $\text{C}_2\text{F}_5\text{COOH}$ , 97%) were purchased from Sigma–Aldrich Co. (St. Louis, MO, USA). Trifluoroacetic acid (TFA,  $\text{CF}_3\text{COOH}$ ),  $\text{Fe}_2(\text{SO}_4)_3 \cdot 7.5\text{H}_2\text{O}$  and sodium persulfate were purchased from Fisher Scientific (Pittsburgh, PA, USA). LC–MS grade methanol and water were purchased from J.T. Baker (Phillipsburg, NJ, USA). Ammonium acetate was LC–MS grade and purchased from Sigma–Aldrich. All other chemicals were reagent grade or above. All solutions were prepared in deionized water.

### 2.2. Analytical method for PFOA and its decomposition products

PFOA and its decomposition products were analyzed using a high-performance liquid chromatograph (HPLC) Agilent-1100 (Agilent, SF, USA) equipped with a mass spectrometer operated in negative ion electrospray ionization mode. A C18 column ( $2.1 \times 150 \text{ mm}$ ; Agilent) was used with a flow rate of 0.1 mL/min. The mobile phase consisted of (A) 20 mM ammonium acetate and (B) methanol. Separation was achieved using a sequence starting

with 50% B, increasing to 95% B in 10 min, and then returning to 50% B over 10 additional minutes. The column temperature was maintained at 35 °C and the total run time was 20 min. TFA and PFPrA concentrations were measured directly with a Dionex ICS-2000 (Dionex, Sunnyvale, CA) system that consists of an automatic sample injector (AS50), a degasser, a pump, a guard column (Ion pac AS11-HC guard column), and a conductivity detector with a suppressor device. The mobile phase was  $\text{Na}_2\text{B}_4\text{O}_7$  (5 mM) and the flow rate was 1.5 mL/min.

A DX600 ion chromatograph (Dionex), equipped with an AS50 auto-sampler, an ED50 electrochemical detector, a GP50 gradient pump, and a RFICTM IonPac<sup>®</sup> S11-HC column was used to measure fluoride ( $\text{F}^-$ ) and sulfate ( $\text{SO}_4^{2-}$ ) concentrations. The mobile phase was an aqueous solution containing NaOH (30 mM) at a flow rate of 1.5 mL/min. The limits of detection ( $s/n=3$ , inject at 25  $\mu\text{l}$ ) were 0.01 mg/L and 0.03 mg/L for  $\text{F}^-$  and  $\text{SO}_4^{2-}$ , respectively.

### 2.3. Spin trapping of radical species and EPR characterization

5-tert-butoxycarbonyl 5-methyl-1-pyrroline N-oxide (BMPO,  $\text{C}_{10}\text{H}_{17}\text{NO}_3$ ), a commonly used spin trapping agent for various types of free radicals [36–38], was used to generate stable paramagnetic adducts for electron paramagnetic resonance (EPR) characterization. Reaction solutions (48.3  $\mu\text{M}$  (20 mg/L) PFOA and 480  $\mu\text{M}$  (26.8 mg/L) Fe(III)) containing 5 mM BMPO were irradiated with an ultraviolet light source (UV-254) for 5–10 min. Solution containing BMPO only (5 mM) was irradiated to serve as control. The solutions were sampled and the spin-trapped radical species were measured at room temperature using a Bruker EMX EPR spectrometer (Bruker Instruments, Inc., Billerica, MA, USA). The EPR parameters were: microwave frequency = 9.302 GHz; microwave power = 20 mW; modulation amplitude = 1.0 G; modulation frequency = 100 kHz. EPR spectra were simulated using WIN-EPR SimFonia (Bruker Instruments, Inc.). Parameters for spin trapped  $\bullet\text{OH}$  radical were:  $g = 2.0044$  and the hyperfine coupling constants were  $a_{\text{N}} = 14.17 \text{ G}$  and  $a_{\text{H}}^{\beta} = 13.9 \text{ G}$  [36]. Parameters for simulation of the persulfate-only system were:  $g = 2.0039$ ;  $a_{\text{N}} = 14.0 \text{ G}$  and  $a_{\text{H}} = 9.5 \text{ G}$ ; for the persulfate/Fe(III) system:  $g = 2.00347$ ;  $a_{\text{N}} = 14.2 \text{ G}$  and  $a_{\text{H}} = 13.2 \text{ G}$ .

The absorbance of the test solution was measured with a spectrophotometer (Ultraspec 2100 pro, Amersham Biosciences Inc., NJ, USA) using a 1 cm quartz cuvette. Milli-Q water was used as a blank, and the absorbance spectrum was scanned twice between 190 and 600 nm in 2 nm steps against an empty reference cell holder. The blank absorbance was then subtracted from the absorbance of the test samples.

### 2.4. PFOA decomposition experiments

All solar photochemical experiments were performed with a 20-ml solution containing 48.3  $\mu\text{M}$  (20 mg/L) PFOA and 480  $\mu\text{M}$  (26.8 mg/L) Fe(III) (added as  $\text{Fe}_2(\text{SO}_4)_3$ ) in 50-ml sealed borosilicate bottles (VWR, Radnor, PA, USA), which were reported to transmit >80% of UV light (320 to 400 nm) [39]. The relatively high (but not extreme) reactant concentrations were used to facilitate analysis. The initial pH of the reaction solution was 4.6. Based on equilibrium speciation modeling with Visual MINTEQ (Version 3.0), ferric iron was mostly present as  $\text{Fe}(\text{OH})_2^+$  (86.2%) and only 0.05% was present as free Fe(III) (Table S1). For specific assays, sodium persulfate (4 mM) or  $\text{H}_2\text{O}_2$  (4 mM) were added to respective reaction solutions. The samples were placed horizontally on top of the roof of Anderson Biological Laboratories Building, Rice University (Houston, TX) located at N 29° 43' 16", W 95° 23' 41", and 32 m above sea level. Dark controls were constructed using aluminum foil to wrap the bottles and prevent exposure to sunlight. The photochemical

experiment was conducted over a 28-day period (from August 4 to September 2), and the temperature and weather conditions were monitored and are provided in the supporting information (Fig. S1). Temperature increases inside the reaction and control bottles were consistently  $\leq 2$  °C over the course of the experiment (Fig. S2). Prior to analysis, all samples were filtered through a 0.45- $\mu\text{m}$  PTFE filter and stored in 1.5-ml glass vials.

PFOA decomposition experiments were also conducted in the presence of 254 nm UV light to investigate the potential roles of different free radicals. This experiment was conducted in aqueous solutions using a magnetically stirred 60-ml cylindrical quartz reactor surrounded by six 4-W commercial fluorescence lamps (emission wavelength: 254 nm, Philips Co., Netherlands). This bench-scale photo reactor has been previously used for photocatalytic degradation experiments in our lab [40]. All experiments were carried out under air-equilibrated aerobic conditions. During the course of the photochemical reaction, periodic 1-ml samples were withdrawn from the reactor using a syringe, filtered through a 0.45- $\mu\text{m}$  PTFE filter (Millipore), and injected into 1.5-ml HPLC vials for further analysis.

### 3. Results and discussion

#### 3.1. Fe(III)-mediated PFOA degradation under natural sunlight

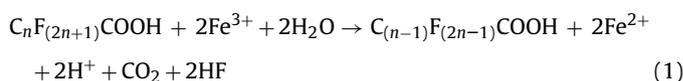
PFOA (48.3  $\mu\text{M}$ , 20 mg/L) decomposed in the presence of Fe(III) (480  $\mu\text{M}$ , 26.8 mg/L) and natural sunlight without any additional input of energy (Fig. 1a). Specifically,  $97.8 \pm 1.7\%$  of PFOA (a C8 compound) was removed within 28 days with concomitant release of  $\text{F}^-$ . The  $\text{F}^-$  concentration in the solution increased from 0 to 1.74 mg/L (0.09 mM) after 28 days, with a defluorination extent ( $[\text{F}^-]$  released/total  $[\text{F}]$  originally in PFOA) of  $12.7 \pm 0.5\%$ . No PFOA decomposition or fluoride release was observed in dark controls (reaction bottles wrapped with aluminum foil). Control experiments using different light sources (simulating UV or visible light) indicate that UV light is primarily responsible for this sunlight induced PFOA decomposition (Fig. S3).

Fig. 1b shows the formation and subsequent degradation of PFOA daughter products over the 28-day experiment. The concentration of C7 daughter products peaked after 7 days and then decreased gradually as C6 daughter products formed. This pattern is consistent with the step-wise decomposition of PFOA from long-chain intermediates to shorter-chain intermediates as indicated by the subsequent generation of C5 and C4 daughter products. The solution pH decreased from 4.6 to 3.7, which could be due to the generation of various types of short-chained PFCAs and subsequent deprotonation (Fig. 2, pathway 2). The fluorine mass balance for this system indicates that after 28 days,  $\text{F}^-$  ion, shorter-chain PFCAs, and PFOA combined account for  $80.5 \pm 10.1\%$  of the total fluorine originally present in the PFOA. The lack of closure in the fluorine mass balance is presumably due to the adsorption of the released fluoride to iron oxide precipitates that were observed at the bottom of the reactor. Iron oxides are known to adsorb fluoride [41]. We emphasize that these PFOA degradation studies were completed under natural conditions with no attempt to optimize the reaction rates. It is likely that more rapid rates could be achieved through modification of one or more experimental parameters. Nevertheless, PFOA decomposition rates may vary under natural environmental conditions due to the presence of other interfering factors, such as turbidity and natural organic matter.

#### 3.2. Proposed PFOA degradation pathway

We postulate that the Fe(III)-mediated degradation of PFOA in the presence of sunlight follows a pathway similar to that proposed

for PFOA decomposition under UV irradiation [33], with some modifications associated with the previously-overlooked involvement of hydroxyl radicals. The PFOA chain would be shortened one carbon atom at a time with subsequent release of two fluoride ions and  $\text{CO}_2$  (Fig. 2), thus implying the possibility of significant mineralization. Two parallel reaction pathways are postulated. In pathway 1, electron transfer occurs from PFOA to Fe(III) when irradiated by UV in sunlight [34], with possible formation of a Fe(III)-PFOA complex [33] and conversion to Fe(II) and an unstable organic free radical ( $\text{C}_7\text{F}_{15}\text{COO}^\bullet$ ). In pathway 2, Fe(III) reacts with water to form  $\bullet\text{OH}$  under UV irradiation, which then oxidizes PFOA to form the same organic radical ( $\text{C}_7\text{F}_{15}\text{COO}^\bullet$ ) as in pathway 1. This unstable organic radical would undergo decarboxylation and subsequent combination with  $\bullet\text{OH}$  to form an unstable perfluorinated alcohol [42,43] prior to defluorination. The reaction per cycle is (Eq. (1)):

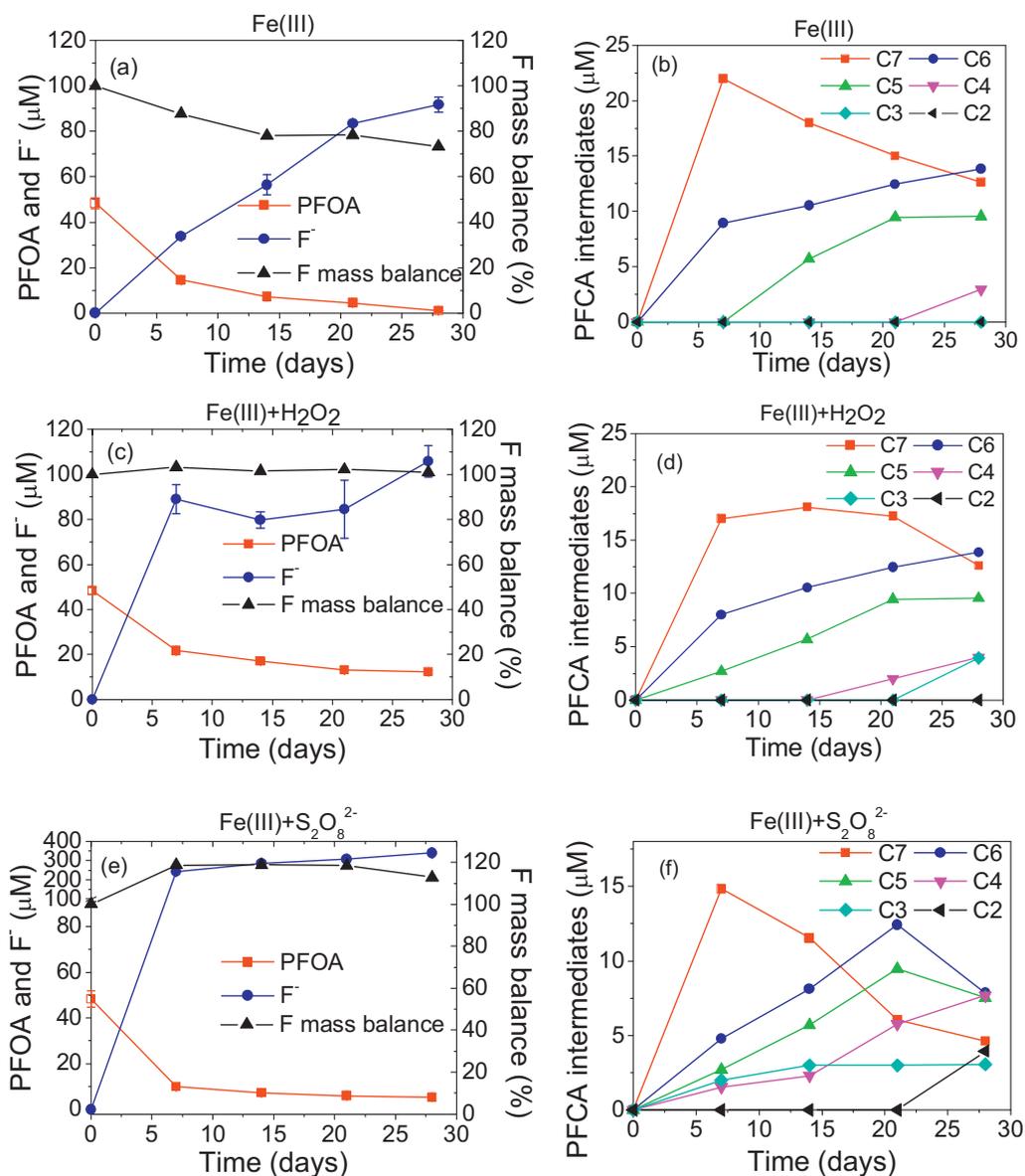


The proposed reaction scheme is supported by HPLC and ion chromatography data showing sequential formation and decomposition of shorter-chain perfluorocarboxylic acids (PFCAs) and fluoride release (Fig. 1). Additional evidence supporting this proposed reaction pathway (provided below) includes EPR data demonstrating the presence of various postulated free radicals and spectroscopic data suggesting the interaction of Fe(III) with PFOA.

#### 3.3. Radical characterization in the Fe(III) system

Characterization of radical generation was accomplished using a combination of EPR techniques and known radical scavengers to gain insight into the PFOA photo-decomposition mechanism. These characterization efforts included investigating the role of hydroxyl radical (formed during the reduction of Fe(III) to Fe(II) by water in the presence of light) as a candidate oxidant responsible for PFOA degradation. Generation of hydroxyl radical was confirmed by the stable spin adduct formed with BMPO. The four-line EPR spectrum of the spin adduct was properly simulated by the hyperfine constants for the nitrogen and proton nuclei given in the methods section [36] by using  $\text{H}_2\text{O}_2$  (under UV irradiation) as a positive control (Fig. 3a). We note that the intensity of  $\bullet\text{OH}$  radicals generated in the PFOA + Fe(III) solution was lower than that in the solution containing Fe(III) alone. This suggests that some  $\bullet\text{OH}$  reacted with PFOA or its degradation products, although the possibility that less  $\bullet\text{OH}$  was produced in the PFOA + Fe(III) solution cannot be ruled out.

To further investigate whether radicals played a critical role in PFOA decomposition, tertiary butyl alcohol (TBA, a  $\bullet\text{OH}$ -specific radical scavenger) or L-histidine (LH, a universal radical scavenger) [44,45] were added. These scavengers served to discern the contributions of different radicals to PFOA defluorination. PFOA decomposition was significantly inhibited after addition of LH (Fig. 3b), corroborating that radical-based mechanisms contribute to PFOA decomposition in the presence of Fe(III). Furthermore,  $\bullet\text{OH}$  scavenging (by TBA addition [46]) significantly reduced the fluoride formation rate, which indicates that  $\bullet\text{OH}$  radical contributed to some PFOA decomposition. It has been previously reported that  $\bullet\text{OH}$  generated from  $\text{H}_2\text{O}_2$  under UV irradiation was only slightly reactive toward PFOA [22,47]. Whether the greater effect of  $\bullet\text{OH}$  in this work was due to the initiation of PFOA decomposition by Fe(III) requires further research. Regardless of the mechanism responsible for higher susceptibility to  $\bullet\text{OH}$ , this is the first documentation of a PFOA photodegradation pathway involving  $\bullet\text{OH}$  radical generated in a Fe(III)-sunlight system.



**Fig. 1.** PFOA decomposition and F<sup>-</sup> release under sunlight irradiation in the presence of (a) Fe(III) alone, (c) Fe(III) and H<sub>2</sub>O<sub>2</sub>, and (e) of Fe(III) and persulfate. Sequential formation and decomposition of shorter-chain perfluorocarboxylic acids (PFCAs) are also shown for these systems in panels (b), (d) and (f), respectively. Error bars represent ± one standard deviation from the mean of 3 replicates. Error bars smaller than symbols are not depicted.

We note that TBA inhibited F<sup>-</sup> release in the first 10 min, but degradation continued even in the presence of excess TBA, indicating that a radical or radicals other than <sup>•</sup>OH were also generated and were active in the system. These are presumed to be fluoroalkyl or/and carboxyl radicals (e.g., C<sub>7</sub>F<sub>15</sub>C<sup>•</sup>, C<sub>7</sub>F<sub>15</sub>COO<sup>•</sup>) [33], which would be generated under sunlight irradiation (Fig. 2). However, such radicals have not yet been detected by EPR. Their detection may require using sufficient PFOA, high intensity UV light pulse and rapid radical trapping method to allow accumulation at detectable levels; this is an objective of future research.

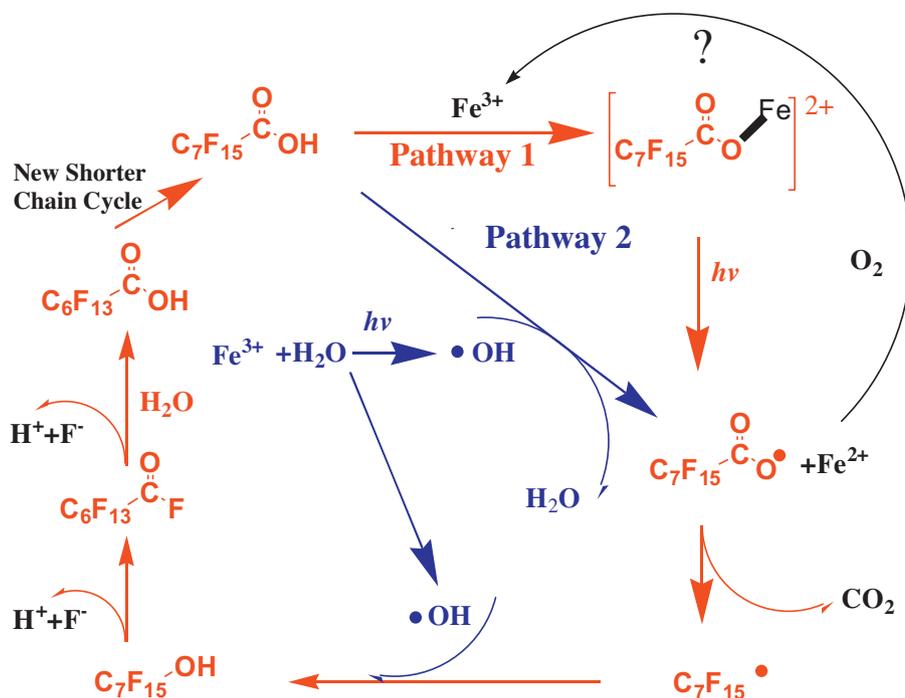
#### 3.4. PFOA photochemical degradation by combination of Fe(III) with H<sub>2</sub>O<sub>2</sub> or persulfate

Several types of common oxidants that generate radicals (e.g., H<sub>2</sub>O<sub>2</sub>, persulfate) can degrade PFOA [48], albeit under conditions of elevated temperature (80 °C) [49,50]. It was thus conjectured that

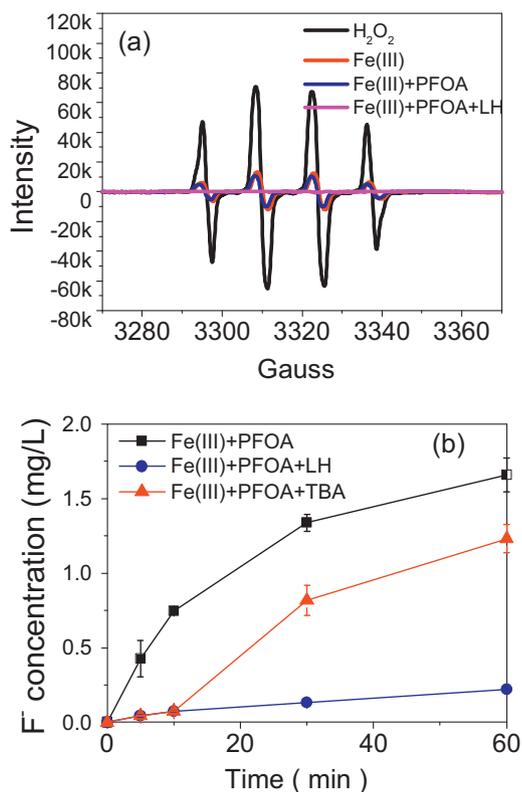
the addition of these oxidants to the Fe(III) system may enhance PFOA decomposition and defluorination extent in the presence of sunlight. Thus, additional tests with H<sub>2</sub>O<sub>2</sub> or persulfate as co-amendments were performed.

Surprisingly, the combination of Fe(III) + H<sub>2</sub>O<sub>2</sub> + sunlight decreased PFOA decomposition significantly ( $p < 0.05$ ) relative to systems without H<sub>2</sub>O<sub>2</sub> (Fig. 1c). Only 74.8 ± 3.1% of PFOA decomposed after 28 days in irradiated systems with Fe(III) and H<sub>2</sub>O<sub>2</sub>, which was lower than the 97.8 ± 1.7% removal observed in the Fe(III) + sunlight system. The concentration of released F<sup>-</sup> reached 2.01 mg/L (0.11 mM) after 21 days, with an overall defluorination extent of 14.7 ± 1.0%. The pattern of shorter-chain intermediates formed in the Fe(III) + H<sub>2</sub>O<sub>2</sub> + sunlight system (Fig. 1d) was similar to that observed in the Fe(III) + sunlight system.

Similarly, the combination of persulfate (S<sub>2</sub>O<sub>8</sub><sup>2-</sup>) and Fe(III) did not enhance the PFOA decomposition in the presence of sunlight, with 88.9 ± 0.8% of PFOA removed in 28 days (Fig. 1e).



**Fig. 2.** Proposed PFOA degradation pathway in the presence of Fe(III) and sunlight. Pathway (in red and black) was proposed by Hori [29] and Wang [30] (with speculated organic radical, unidentified). Pathway (in blue) was proposed by this research,  $\cdot OH$  was identified by EPR analysis. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

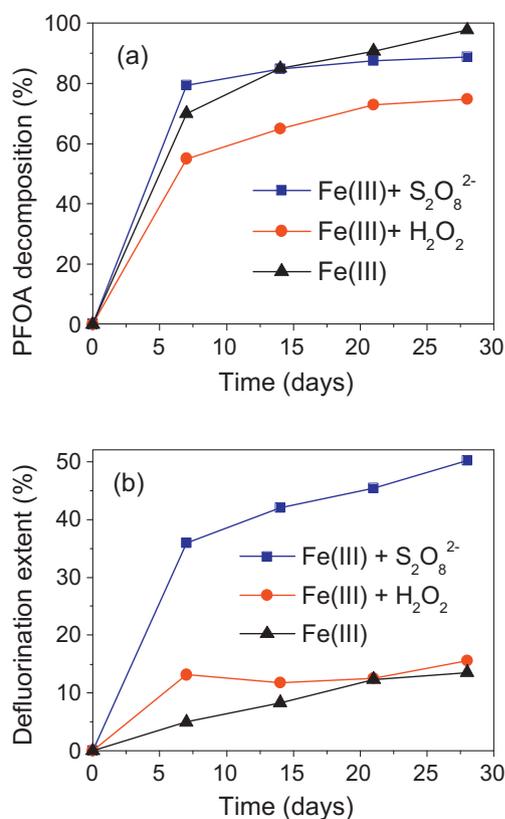


**Fig. 3.** (a) EPR spectra of radicals generated in: Fe(III) control (1 mM);  $H_2O_2$  (2 mM) positive control; Fe(III) (1 mM) and PFOA (20 mg/L); Fe(III) (1 mM), PFOA (20 mg/L) and L-histidine (2 mM, serving as radical scavenger). EPR samples were taken after 10 min UV irradiation; (b) effect of L-histidine (2 mM) and tertiary butyl alcohol (TBA) (2 mM) on  $F^-$  release under UV irradiation. Error bars represent  $\pm$ one standard deviation from the mean of 3 replicates. Error bars smaller than symbols are not depicted.

However, the concentration of  $F^-$  in the  $Fe(III) + S_2O_8^{2-} +$  sunlight system increased from 0 to 4.56 mg/L (0.34 mM) by the end of the test period, which is 3.7-fold higher than that produced in the  $Fe(III) +$  sunlight system, resulting in an overall defluorination extent of  $47.1 \pm 0.8\%$ . We note that PFOA byproducts were degraded faster to shorter-chain PFCAs in the  $Fe(III) + S_2O_8^{2-} +$  sunlight system (Fig. 1f). This suggests that the higher defluorination extent observed in this system might be partly due to faster formation and subsequent degradation of (and release of fluoride from) shorter-chain PFCAs, which are known to be more susceptible to degradation [26].

It is unclear why addition of  $H_2O_2$  or  $S_2O_8^{2-}$  decreased PFOA degradation (Fig. 4a), although the possibility that these oxidants hindered the formation of the postulated  $Fe(III)$ –PFOA complex (pathway 1, Fig. 2) cannot be ruled out, as suggested by spectroscopic analysis (see Section 3.5). The higher extent of defluorination in the oxidant-amended systems (Fig. 4b) is likely due to the generation of more radicals when  $H_2O_2$  or persulfate are added (see Section 3.6), which would enhance the decomposition of PFOA daughter products.

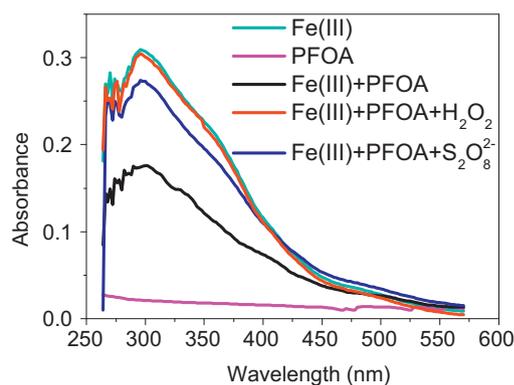
In contrast to the  $Fe(III) +$  sunlight system, the fluorine mass balances for the oxidant-amended systems were much higher, accounting for  $101.8 \pm 2.1\%$  of total fluorine atoms originally present in PFOA in the  $Fe(III) + H_2O_2 +$  sunlight system, and  $109.4 \pm 13.2\%$  in the  $Fe(III) + S_2O_8^{2-} +$  sunlight system. No precipitation was visually evident in these oxidant-amended systems, which corroborates the notion that the fluorine loss observed in the  $Fe(III) +$  sunlight system was attributable to the adsorption of fluorine to iron oxide precipitates. Note that differences in pH alone cannot explain the absence of visible precipitates in the  $H_2O_2$ -amended system (final pH=3.7, same as in the  $Fe(III) + PFOA +$  sunlight system) or the persulfate-amended system (final pH=3.2). Further research is needed to determine the mechanisms by which the added oxidants hindered  $Fe(III)$  precipitation, including the possible formation of peroxide adducts [51,52].



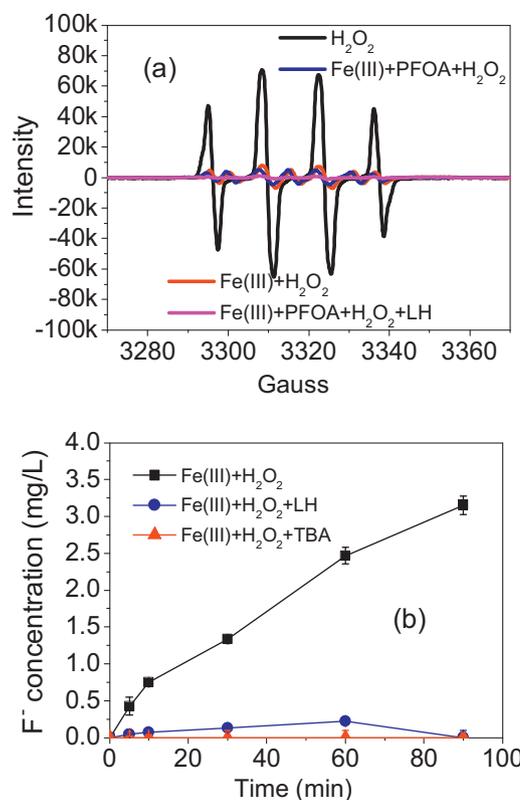
**Fig. 4.** Comparison of PFOA (a) degradation and (b) defluorination by different reaction systems. Addition of persulfate (4 mM) or H<sub>2</sub>O<sub>2</sub> (4 mM) decreased the rate of PFOA degradation, but persulfate significantly enhanced defluorination. Error bars represent  $\pm$  one standard deviation of 3 replicates. Error bars smaller than symbols are not depicted.

### 3.5. Spectroscopy analysis for Fe(III) and PFOA interaction

Interaction between Fe(III) and PFOA in these systems was assessed using spectroscopy measurements in the presence and absence of various reactants. Fe(III) (added as Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>) exhibited a strong absorbance band at 286 nm, while PFOA did not show any absorbance (Fig. 5). When PFOA was added to the Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution, the Fe(III) absorbance peak at 286 nm was reduced, suggesting the formation of a Fe(III)–PFOA adduct(s). We recognize



**Fig. 5.** Absorption spectra of different solutions. The Fe(III) absorption peak decreased dramatically after the addition of PFOA, indicating either formation of Fe(III)–PFOA complex or electron-transfer from PFOA to Fe(III) by photo-activation. Addition of H<sub>2</sub>O<sub>2</sub> increased the Fe(III) absorption peak back to control level, indicating inhibition of the formation (or faster breakdown) the Fe(III)–PFOA adduct, while addition of persulfate increased Fe(III) absorbance but only to a lower level than the control, correlating with the PFOA decomposition and defluorination results.



**Fig. 6.** (a) EPR spectra of radicals generated in Fe(III)–H<sub>2</sub>O<sub>2</sub> (2 mM) system. EPR samples were taken after 10 min UV irradiation; (b) effect of L-histidine (2 mM) and TBA on F<sup>-</sup> release in the Fe(III)–H<sub>2</sub>O<sub>2</sub> system under UV irradiation. Error bars represent  $\pm$  one standard deviation from the mean of 3 replicates. Error bars smaller than symbols are not depicted.

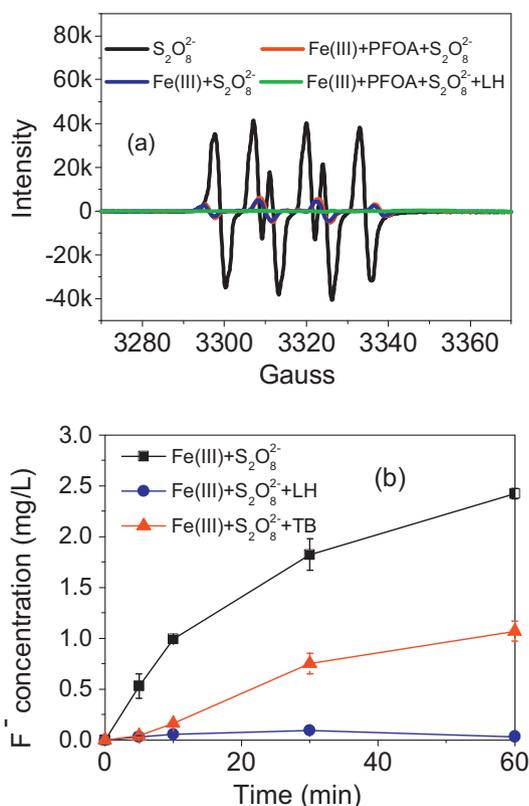
that PFOA addition may decrease the solution pH, and thus affect Fe(III) speciation and absorbance properties. However, control tests (using 0.1 M H<sub>2</sub>SO<sub>4</sub> to acidify the Fe(III) solution) did not alter Fe(III) absorbance (Figure S4), which rules out this potential confounding effect.

When H<sub>2</sub>O<sub>2</sub> was added to the system, Fe(III) absorbance increased back to the level measured in the Fe(III)–alone control, indicating a potential disruption of the putative Fe(III)–PFOA adduct by H<sub>2</sub>O<sub>2</sub> or additional side reactions of Fe(III) with H<sub>2</sub>O<sub>2</sub>, such as ferryl ion (Fe(IV)) formation [53]. In contrast, when persulfate was added to the system instead of H<sub>2</sub>O<sub>2</sub>, the Fe(III) absorbance peak also increased, but to a lesser extent than in the Fe(III)–alone control. This latter result might be due to the lower reactivity of persulfate in the presence of Fe(III) [54] compared to H<sub>2</sub>O<sub>2</sub>, allowing for slower radical generation in a manner that is apparently less disruptive to the putative Fe(III)–PFOA adduct and is thus more compatible for PFOA degradation.

### 3.6. Radical characterization in systems containing Fe(III) with H<sub>2</sub>O<sub>2</sub> or persulfate

In the Fe(III)+H<sub>2</sub>O<sub>2</sub>+sunlight system, F<sup>-</sup> release was almost completely inhibited by either TBA or LH (Fig. 6b), indicating that •OH radical was the main reactive free radical species accounting for PFOA defluorination in this system. In this reaction system, Fe(III) could be reduced to Fe(II) in the presence of PFOA and UV light, and the generated Fe(II) would promote a Fenton-type reaction.

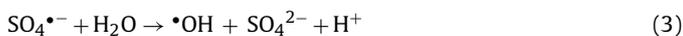
Compared to the Fe(III)+sunlight system, H<sub>2</sub>O<sub>2</sub> generates •OH radical rapidly in the reaction solution, which can subsequently degrade PFOA and its intermediate products. However, the



**Fig. 7.** (a) EPR spectra of different reaction systems: persulfate control (4 mM) (black); persulfate in the presence of Fe(III) (1 mM) (blue); persulfate in the presence of Fe(III) and PFOA (20 mg/L) (red); 4) persulfate, Fe(III) and PFOA in the presence of L-histidine (2 mM, served as radical scavenger) (green). EPR samples were taken after 10 min UV irradiation; (b) effect of L-histidine (2 mM) and TBA (2 mM) on F<sup>-</sup> release in the Fe(III)–S<sub>2</sub>O<sub>8</sub><sup>2-</sup> system under UV irradiation. Error bars represent ± one standard deviation from 3 replicates. Error bars smaller than symbols are not depicted. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

addition of H<sub>2</sub>O<sub>2</sub> led to a lower PFOA degradation rate than the Fe(III) + sunlight system, indicating that the •OH radical (pathway 2 in Fig. 2) is playing a less reactive role in decomposing PFOA than the unidentified (putative) organic radical (pathway 1 in Fig. 2).

Significant amounts of radicals were trapped in the persulfate control system (Fig. 7). These were presumed to be sulfate radicals (Fig. S5a) generated by reaction of persulfate with water [34]. Surprisingly, in the presence of Fe(III), UV irradiation of a persulfate-only solution yielded radicals that exhibit a BMPO adduct line shape that is similar to that of hydroxyl radical (Figure S5b). A likely explanation is that sulfate radicals generated in the Fe(III) + S<sub>2</sub>O<sub>8</sub><sup>2-</sup> + sunlight system were catalyzed by Fe(III) [55] and reacted with water as follows (Eqs. (2) and (3)):



**Table 1**  
Postulated radicals generated in different reaction systems.

Reaction systems	Postulated radicals
PFOA + Fe(III)	•OH, and C <sub>7</sub> F <sub>15</sub> COO•
H <sub>2</sub> O <sub>2</sub>	•OH
PFOA + Fe(III) + H <sub>2</sub> O <sub>2</sub>	•OH, HO <sub>2</sub> • and C <sub>7</sub> F <sub>15</sub> COO•
Persulfate	SO <sub>4</sub> <sup>•-</sup>
PFOA + Fe(III) + Persulfate	•OH and C <sub>7</sub> F <sub>15</sub> COO•

Since persulfate addition likely increased •OH generation but did not enhance PFOA degradation (Fig. 4a), this corroborates the predominance of pathway 1 over pathway 2 (Fig. 2).

#### 4. Conclusions

This study presents evidence that PFOA, long considered an extremely recalcitrant environmental contaminant, can be degraded under natural conditions when sunlight and Fe(III) are present. By detecting shorter-chain byproducts and released fluoride, and by identifying radical species that were generated in systems with and without other oxidants (Table 1), the results support the PFOA degradation pathways proposed in Fig. 2. In this reaction system, PFOA is proposed to be degraded by light-induced electron-transfer from PFOA to Fe(III) (pathway 1) or a new pathway that involves •OH attack (pathway 2), both of which result in the formation of organic radicals. Pathway 2 was corroborated by EPR analysis. The addition of H<sub>2</sub>O<sub>2</sub> and persulfate (both strong oxidants) hindered PFOA decomposition, potentially by favoring pathway 2, which seems less effective. However, the addition of persulfate significantly increased the extent of PFOA defluorination, suggesting that Fe(III)-mediated decomposition could be improved by adding oxidants. Whether other environmental factors (e.g., natural organic matter) inhibit or stimulate this reaction requires further investigation. Overall, this research provides mechanistic insight on PFOA natural attenuation. Importantly, it also offers an innovative and intriguing path for developing a new generation of implementable, sustainable, and cost-effective in situ remediation technologies for PFC-contaminated water.

#### Supporting Information

Weather conditions during PFOA decomposition tests, PFOA degradation in the presence of different irradiation wavelengths, pH effect on Fe(III) absorbance, EPR radical simulations, and Fe(III) speciation in water are provided in the supporting information (SI) section.

#### 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.2013.09.001>.

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