Defluorination of Aqueous Perfluorooctanesulfonate by Activated Persulfate Oxidation

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Abstract

Activated persulfate oxidation technologies based on sulfate radicals were first evaluated for defluorination of aqueous perfluorooctanesulfonate (PFOS). The influences of catalytic method, time, pH and K2S2O8 amounts on PFOS defluorination were investigated. The intermediate products during PFOS defluorination were detected by using LC/MS/MS. The results showed that the S2O82− had weak effect on the defluorination of PFOS, while the PFOS was oxidatively defluorinated by sulfate radicals in water. The defluorination efficiency of PFOS under various treatment was followed the order: HT (hydrothermal)/K2S2O8 > UV (ultraviolet)/K2S2O8 > Fe2+/K2S2O8 > US (ultrasound)/K2S2O8. Low pH was favorable for the PFOS defluorination with sulfate radicals. Increase in the amount of S2O82− had positive effect on PFOS defluorination. However, further increase in amounts of S2O82− caused insignicant improvement in PFOS defluorination due to elimination of sulfate radicals under high concentration of S2O82−. CF3(CF2)nCOOH (n = 0–6) were detected as intermediates during PFOS defluorination. Sulfate radicals oxidation and hydrolysis were the main mechanisms involved in defluorination process of PFOS.

Introduction

Perfluorooctane sulfonate (C8F17SO3−, PFOS) have been widely used in industry as emulsifying agents, surface treatment agents, food containers, fabrics, paper coatings, waxes, fire-fighting foams and polishes [1]. Because of specific characteristics such as unique high surface activity, thermal and acid resistance, and hydro- and lipophilic properties [2], PFOS are considered almost un-degradable in nature. Most conventional degradation technologies are ineffective for degradation of aqueous PFOS since they are inherently recalcitrant to chemical and microbiological treatment [3–6]. Even Advanced oxidation processes (AOPs), which utilize the hydroxyl radical, such as UV/O3, O3/H2O2, UV/H2O2 or Fenton’s reagent, are also relatively ineffective in redox potential of 2.0 V, and can be reduced to sulfate anions as shown below (Eq.1) [21]:

S2O82− + 2e− → 2SO42−

(1)

S2O82− can be activated to produce sulfate radicals (SO4•−) with higher redox potential of 2.6–3.1 V, which are very reactive with a wide range of contaminants. There are two general ways of activating S2O82−: homolysis of the peroxide bond using heat, ultrasound or light (Eq.2) and an oxidation reduction process (analogous to the Fenton reaction) with electron donors, including e− (aq) from radiolysis of water or low-valent metals such as Fe2+ and Ag+ (Eq.3):

S2O82− + Δ, ((( or hv)→ SO42−

(2)

S2O82− + Mn+ → SO42− + SO42− + Mn+1

(3)

Previous studies show that SO42− is more prone to redox reactions than hydroxyl radicals (OH) under neutral conditions, as summarized in the following reactions (Eq.4–6):

●OH + e− → OH− (1.8V / NHE)

(4)
\[
\text{OH} + e + H^+ \rightarrow OH^- (2.7V/NHE) \quad (5)
\]

\[
SO_4^{2-} + e \rightarrow SO_4^{2-} (2.5 - 3.1V/NHE) \quad (6)
\]

SO\(_4^{2-}\) is a strong oxidizing radicals and has been known to react with electron-rich moieties through several reaction pathways, including electron exchange, hydrogen abstraction, and direct oxygen transfer. Because of comparative stability of persulfate, strong oxidation characteristics, and pH-independent effectiveness, persulfate and sulfate radical oxidation have been utilized for the oxidative degradation of a number of organics [22–26]. It also had been reported that perfluorooctanoic acid (C\(_2\)F\(_5\)COOH, PFOA) and other short-chain perfluorocarboxylic acid (C\(_n\)F\(_{2n+1}\)COOH, PFCAs) could be decomposed by sulfate radicals [27–30]. The results show that PFOA and other PFCAs were effectively decomposed to F\(^-\) and CO\(_2\) by using SO\(_4^{2-}\), and almost all of the initial S\(_2\)O\(_8^{2-}\) was transformed to SO\(_4^{2-}\) during the reaction. However, no studies have been reported on persulfate oxidation of PFOS and perfluoroalkyl sulfonate (C\(_n\)F\(_{2n+1}\)SO\(_3\)K).

The present study made first attempt to evaluate the PFOS defluorination effect of S\(_2\)O\(_8^{2-}\) or SO\(_4^{2-}\) using the activated K\(_2\)S\(_2\)O\(_8\) oxidation systems under air atmosphere. The influence of catalytic method (ultraviolet, ultrasound, hydrothermal, ferrous ion), time, pH and K\(_2\)S\(_2\)O\(_8\) concentration on PFOS defluorination were investigated. The concentrations of intermediate products were detected using LC/MS/MS. Finally, the possible defluorination mechanism of PFOS with sulfate radicals was proposed.

**Materials and Methods**

**Materials**

PerfluorooctaneSulfonate (PFOS, C\(_8\)F\(_{17}\)SO\(_3\)K, 98%), Perfluorooctanoic acid (PFOA, C\(_2\)F\(_5\)COOH, 97%), Perfluorooctanesulfonate (PFH\(_x\)A, C\(_8\)F\(_{17}\)COOH, 98%), Tridecafluoroheptanoic acid (PFHxA, C\(_6\)F\(_{15}\)COOH, 98%), perfluoropentanoic acid (PFPA, C\(_5\)F\(_{11}\)COOH, 98%), perfluorooctanoic acid (PFOA, C\(_2\)F\(_5\)COOH, 97%) and perfluorobutyric acid (PFBA, C\(_4\)F\(_9\)COOH, 97%) were purchased from Sigma (USA). Nonafluorobutanesulfonate (PFBS, C\(_4\)F\(_9\)SO\(_3\)K, 98%) was purchased form TCI(Japan). And ammonium acetate (NH\(_4\)\(_2\)CO\(_3\), 99.99%) and Hydrochloric acid (HCl, 98%) was purchased from Sigma (USA). Milli-Q water and sodium hydroxide (NaOH) were purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China). Mill-Q water prepared by Millipore with a conductivity of 18.2 m\(\Omega\)-cm at 25°C was used in all experiments. All aqueous solutions were prepared with ultrapure water prepared using a Thermo Barnstead Nanopure Diamond water purification system.

**Methods**

PFOS stock solution (100 mg/L) was prepared with ultrapure water and then stored in a refrigerator (5°C) before used. The reactions were conducted in batch experiments in polytetrafluoroethylene (PTFE) reactor, due to their superior non-sorption property. Ultraviolet (UV)-activated K\(_2\)S\(_2\)O\(_8\) oxidation system was shown in Fig. 1A: Two 15W low-pressure mercury lamps (Direct-immersion, H model, SUNSHINE, China) emitting light at 254 nm were placed in the reactor. The photoelectric conversion efficiency was 35%–38%. The effective radiating length of the UV tube was 9.5 cm (with a radiating surface area of 113.04 cm\(^2\)) and UV fluence rate was around 40 mW/cm\(^2\). During the irradiation, the UV device was switched on for the first 15 min to warm up the UV lamps. The reactor was placed on constant temperature magnetic stirrer at desired temperature during the reaction time. Ultrasound (US)-activated K\(_2\)S\(_2\)O\(_8\) oxidation system was shown in Fig. 1B: The ultrasonic apparatus consisted of an ultrasonic generator and an oscillator operated at an applied (calorimetric) power of 100 (86)W (TOSO model, China, 40 kHz). The average power density delivered to the reactor was 2W/cm\(^2\). The solution temperature was maintained by a thermostatic container. A sink was placed in the a thermostatic container to keep the temperature of both ultrasound transducer and reactor. During the US process, the thermostatic container device was switched on for the first about 20 to 30 min to keep desired temperature (20°C). According to results of control experiments, the temperature of reaction solution remained about 20°C, was no more than 21°C during the reaction (measured by using mercury’s thermometer). Hydrothermal (HT)-activated K\(_2\)S\(_2\)O\(_8\) oxidation system: The reactor was placed on constant temperature magnetic stirrer at desired temperature during the reaction time. And the reactor was closed during the reaction process to prevent loss of H\(_2\)O and gas product by volatilization. Ferrous ion (Fe\(^{2+}\))-activated K\(_2\)S\(_2\)O\(_8\) oxidation system: the addition quantity of Fe\(^{2+}\) catalyst was 3 mM. The reactor was placed on constant temperature magnetic stirrer at desired temperature during the reaction time.

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**Figure 1. Schematic representation of reactor. (A) UV/K\(_2\)S\(_2\)O\(_8\). (B) US/K\(_2\)S\(_2\)O\(_8\).**

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In all K2S2O8 oxidation systems, an aqueous (Milli-Q) solution (100 mL) of PFOS (100 mg/L; 0.186 mM) were introduced into the reactor. The samples were withdrawn from the reactor at fixed time intervals and quickly quenched in iced water to end reaction [28,29]. Control experiments also had been conducted to make sure the reactions could be quenched in iced water (Fig. S1). The PFOS and F− concentrations were determined by LC/MS/MS and IC, respectively. All the results discussed in this article were average values form at least two experiments. The initial pH values were adjusted at about 7.0 by using standard NaOH and HCl solutions except for “solution pH effect”.

LC/MS/MS. The concentrations of PFOS and the intermediates were measured using liquid chromatography tandem mass spectrometry. Liquid chromatography was performed on an HPLC apparatus equipped with an Agilent model 1200 series (RRLC/6410B Triple Quad RS, USA) and was used for the LC separation of PFOS. The HPLC separation was carried out at 30 °C using a gradient composed of solvent A (10 mM ammonium acetate solution adjusted to pH 4 with the addition of acetic acid) and solvent B (acetonitrile, GR). The gradient expressed as changes in solvent B was as follows: 0 to 2.0 min, a linear increase from 10% to 20% B; 2.0 to 4.0 min, 20% to 45% B; 4.0 to 5.0 min, 45% to 60% B; 5.0 to 6.0 min, 60% to 95% B; 6.0 to 6.1 min, 95% B to 10% B, hold at 4 min. The flow rate was 0.3 mL/min. Ionization was achieved by electro spray in the negative-ion mode. The electrospray conditions were as follows: nitrogen curtain gas flow: 10.0 L/min; gas temperature: 350 °C, nebulizer pressure: 275.8 kPa (40.0 psi), capillary voltage: 100 V. The LC/MS/MS acquisition was performed in the multiple reaction monitor (MRM) mode by following the reactions m/z 413.0–368.8 (PFOA), m/z 363.0–318.9 (PFPrA), m/z 298.9–298.9* (PFHxS) and m/z 263.0–218.9 (PFPA), m/z 213.0–168.9 (PFBA), m/z 163.0–118.9 (PFPA), m/z 113.0–68.9 (TFA), m/z 398.9–98.9 (PFHxS) and m/z 313.0–268.8 (PFHxA), m/z 318.9*–98.8, 79.9* (PFHpA), m/z 309.9–280.9 (PFHxA), m/z 318.9*–98.8, 79.9* (PFHpA), m/z 298.9–298.9* (PFBS). Mass spectrometry acquisition parameters of the intermediates were shown in Table 1.

The sample solution and standard solution were injected into the liquid chromatography tandem mass spectrometry, respectively. MRM spectra of standard solutions of nine kinds of PFCs and peak area of characteristic peaks were built with the correlation coefficient R2 more than 0.99. The linear ranges of each PFCs were 0.001–1 mg/L.

Ion Chromatography. The concentrations of F− and SO42− were determined by an anion-chromatography system (Dionex, ICS-1000, USA) consisting of a degasser, a sampler (1 mL injection volume), a guard column (AS4A-SC 4 × 50 mm, Dionex), a separation column (AS4A-SC 4 × 250 mm, Dionex), a column heater (30 °C), and a conductivity detector with a suppressor. A mixture solution containing 3.5 mM Na2CO3 and 1.0 mM NaHCO3 as the mobile phase was delivered at a flow rate of 1.0 mL⋅min−1. The lowest detection limit of F− and SO42− was 0.02 mg/L and 0.1 mg/L, respectively.

Results and Discussion

Defluorination of PFOS by K2S2O8 oxidation

The defluorination of PFOS (100 mg/L; 0.186 mM) in each system with the initial K2S2O8 amount of 5 g/L (18.5 mM) were shown in Fig. 3.

The S2O82− had weak effect on the defluorination of PFOS. The defluorination efficiency (moles of F− formed/moles of fluorine content in initial PFOS) of PFOS were only 1.45% in solo K2S2O8 system after 12 h, indicating that S2O82− was not an efficient oxidant for degrading PFOS at the room temperature of 20 °C. In contrast, the K2S2O8 showed different defluorination efficiencies of PFOS in the presence of catalyst, such as UV, US, HT and Fe3+. It should be mentioned that these treatments had poor effects on PFOS defluorination when they are used alone. Thus, it can be concluded that the sulfate radical oxidation was mainly responsible for the defluorination of PFOS in activated K2S2O8 oxidation. On the basis of data (Fig. 3) of this research, the varying tendencies of F− concentration were fitted using first-order kinetics equation. According to the fitting results, the apparent rate constants of F− in UV/K2S2O8, US/K2S2O8, HT/K2S2O8 and Fe3+/K2S2O8 were 0.016, 0.004, 0.023 and 0.010 h−1, respectively. Thus, PFOS was defluorinated faster in HT/K2S2O8 system than others. The highest PFOS defluorination efficiency reached 22.52% in HT/K2S2O8 system after 12 h. Temperature has an important influence on free radical and its inducing oxidation reactions. The PFOS move more quickly at high temperature, which increases their probability to react with SO4−. Thus, high temperature could not only activate S2O82− but also promote the reaction process, and HT/K2S2O8 system had showed better defluorination effect than other activated K2S2O8 oxidation systems.

Table 1. Mass spectrometry acquisition parameters of the intermediates. * Quantitative product ion.

| No. | Compound | t0(min) | Prec Ion (m/z) | Prod Ion (m/z) | Frag(V) | Clission energy(V) | Dwell (ms) |
|-----|----------|--------|---------------|---------------|---------|-------------------|------------|
| 1   | PFOA     | 6.45   | 413.0         | 368.9*, 168.8 | 58      | 0, 12             | 80         |
| 2   | PFHxS    | 6.61   | 398.9         | 98.8*, 79.9   | 129     | 40, 52            | 80         |
| 3   | PFHpA    | 6.07   | 363.0         | 318.9*, 168.8 | 56      | 0, 12             | 80         |
| 4   | PFHxA    | 5.59   | 313.0         | 268.9*, 168.8 | 62      | 0, 12             | 80         |
| 5   | PFBS     | 5.66   | 298.9         | 98.8, 79.9*   | 114     | 28, 36            | 80         |
| 6   | PFPA     | 4.85   | 263.0         | 218.9*        | 50      | 0                 | 80         |
| 7   | PFPA     | 2.92   | 213.0         | 168.9*        | 55      | 4                 | 80         |
| 8   | PFPA     | 1.47   | 163.0         | 118.9*        | 60      | 4                 | 80         |
| 9   | TFA      | 1.39   | 113.0         | 68.9*         | 60      | 4                 | 80         |

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The formation of SO$_4^{2-}$ in each system with the initial K$_2$S$_2$O$_8$ amount of 5 g/L (18.5 mM) was also shown in Fig. 4.

In activated K$_2$S$_2$O$_8$ oxidation, SO$_4^{2-}$ radical anions were formed from S$_2$O$_8^{2-}$, which was then react with PFOS. The SO$_4^{2-}$ could be formed through two main ways. One way is that one-electron transfer from reducible agent such as PFOS, S$_2$O$_8^{2-}$ and H$_2$O to SO$_4^{2-}$ (total concentration = 37 mM) and the other way is sulfonic acid group deprivation to form PFOS (total concentration = 0.186 mM). By contrast, the SO$_4^{2-}$ generation from sulfonic acid group deprivation could be negligible, therefore we could assume that all the SO$_4^{2-}$ was product of S$_2$O$_8^{2-}$.

Low formation of SO$_4^{2-}$ under sole K$_2$S$_2$O$_8$ oxidization treatment, implied that S$_2$O$_8^{2-}$ was the major oxidants during the reaction. The activated K$_2$S$_2$O$_8$ oxidation treatment showed different production of SO$_4^{2-}$. Based on these data (Fig. 2), the concentrations of SO$_4^{2-}$ were fitted using first-order kinetics equation. According to the fitting results, the apparent rate constants of SO$_4^{2-}$ in UV/K$_2$S$_2$O$_8$, US/K$_2$S$_2$O$_8$, HT/K$_2$S$_2$O$_8$ and Fe$^{3+}$/K$_2$S$_2$O$_8$ were 0.162, 0.026, 0.233 and 0.131 h$^{-1}$, respectively. Li et al. found that K$_2$S$_2$O$_8$ could be activated by ultrasonic irradiation and degradation rates of TCA was increased from 0.0014 to 0.396 min$^{-1}$ with an increase in the ultrasound frequency from 50 to 400 kHz [31]. However, in present study, low frequency of US (40 KHz) could not effectively decomposes
S₂O₈²⁻ to sulfate radicals. In contrast, S₂O₅²⁻ was fastly converted to SO₄²⁻ under Fe²⁺/K₂S₂O₈ treatment. However, the PFOS defluorination efficiency was only 23.50% after 12 h. One reason for this phenomenon could be that there is lower production of SO₄²⁻ under Fe²⁺/K₂S₂O₈ treatment than UV/ K₂S₂O₈ and HT/K₂S₂O₈ treatment. Homolysis of 1 mol S₂O₅²⁻ produce two moles SO₄²⁻ using heat or light but only one mole SO₄²⁻ production using Fe²⁺ catalyst (Eq.7):

$$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{*}$$  (7)

**Effect of initial solution pH**

Effects of initial pH (3–11) on defluorination of PFOS 0.186 mM (100 mg/L) under each activated K₂S₂O₈ oxidation treatment was shown in Table 2.

During the experimental runs, pH of the PFOS solution dropped as the reaction progressed due to formation of lager amount of SO₄²⁻. Change of pH in K₂S₂O₈ solution during reaction process in activated oxidation systems was shown in Fig. 5. With the reaction going on, pH of the solution dropped, and showed different changing tendency with different initial pH in each activated persulfate oxidation system. The pH of US/ K₂S₂O₈ system slowly decreased as compared with other three systems. It inferred that US had a weaker activating capability than UV, HT and Fe²⁺. Moreover, there was no obvious change in pH in Fe²⁺/K₂S₂O₈ system in 120 min at initial pH of 11.0. Thus, a fixed initial pH was just maintained at the initial stage of PFOS defluorination in UV/K₂S₂O₈ and HT/K₂S₂O₈ systems, and later reaction was conducted under the acidic condition. Even so, PFOS defluorination was varied with initial pH under each activated K₂S₂O₈ oxidation treatment. As shown in Table 2, the PFOS defluorination efficiency decreased with the increase of initial pH under all treatment, especially for Fe²⁺/K₂S₂O₈.

The PFOS defluorination efficiency increased with deceasing of solution pH, because additional sulfate radicals were formed due to acid catalyzation [32]. In addition, sulfate radicals may react with OH⁻ to form more hydroxyl radical under alkaline conditions [26], as shown by Eq. (8) below:

$$SO_4^{*} + OH^- \rightarrow SO_4^{2-} + \cdot OH$$  (8)

The generated hydroxyl radicals generally attack organic molecules through the H-atom abstraction to form water. However, PFOS contain no hydrogen to be abstracted, therefore hydroxyl radicals have a very poor reactivity with PFOS in aqueous solution and slow down the PFOS decomposition rate. Thus, alkaline conditions were unfavorable for the defluorination of PFOS by sulfate radicals. The pH of PFOS solution decrease during the defluorination process, but high initial concentration of OH⁻ need to consume SO₄³⁻, which could weaken the oxidant effect of activated K₂S₂O₈ oxidation. Thus, the PFOS defluorination efficiency decreased with the increase of initial pH under all treatment. In addition, compared with UV/K₂S₂O₈ and HT/ K₂S₂O₈ system, the more decrease in PFOS defluorination under Fe²⁺/K₂S₂O₈ treatment under alkaline conditions could be explained by the formation of Fe(OH)₃ which cause the deactivation of catalyst.

**Effect of S₂O₈²⁻ amounts**

The effect of initial S₂O₈²⁻ amount (0–12.5 g/L) on defluorination of PFOS (100 mg/L) under each activated K₂S₂O₈ oxidation treatment was shown in Fig. 6.

The defluorination efficiency increased under all treatments when the initial amount of S₂O₈²⁻ was increased. However, further increase in the initial amount of S₂O₈²⁻ resulted in saturation, there is no further increase in the PFOS defluorination efficiency. The saturated concentrations of S₂O₈²⁻ were different with the treatment used. Hori et al. reported that sulfate radicals react with S₂O₈²⁻ or themselves (Eq.9, 10). In addition, excess SO₄³⁻ can also react with H₂O (Eq.11) [27]:

$$SO_4^{*} + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8^{*}$$  (9)

$$SO_4^{*} + SO_4^{*} \rightarrow 2SO_4^{2-}$$  (10)

$$SO_4^{*} + H_2O \rightarrow HSO_4^- + \cdot OH \rightarrow SO_4^{2-} + H^+ + \cdot OH$$  (11)

The SO₄³⁻/S₂O₈²⁻, SO₄³⁻/SO₄³⁻ and SO₄³⁻/H₂O reaction could compete with the SO₄³⁻/PFOS for electrons [28]. Thus, a large amounts of SO₄³⁻ were produced along with high concentration of K₂S₂O₈ under activated K₂S₂O₈ oxidation treatment. The scavenging reactions by SO₄³⁻ themselves and with the remaining S₂O₈²⁻ may become significant to decrease PFOS defluorination efficiency. In this case, the systems might have generated much S₂O₈²⁻ and •OH when sulfate radicals too excessive to react with PFOS. Oxidation by S₂O₈²⁻ and •OH are not effective for PFOS and other PFCs because of low rates of reaction at reasonable S₂O₈²⁻ and •OH and their lower oxidation capacity compared with SO₄³⁻. Therefore, further increase in S₂O₈²⁻ concentration resulted in production of larger amounts of SO₄³⁻. The scavenging reactions by SO₄³⁻ themselves and with

| System       | Initial pH | Rate constant (per hour) | Reaction time (h) |
|--------------|------------|--------------------------|-------------------|
|              | 1          | 4                        | 8                 | 12                |
| UV/K₂S₂O₈   | 3.13       | 0.018                    | 0.94              | 5.57              | 15.91              | 19.32              |
|              | 6.91       | 0.016                    | 0.70              | 4.27              | 13.63              | 17.21              |
|              | 11.11      | 0.009                    | -                 | 3.23              | 6.89               | 10.56              |
| US/K₂S₂O₈   | 3.11       | 0.005                    | -                 | 2.47              | 4.90               | 5.82               |
|              | 7.04       | 0.004                    | 0.25              | 1.93              | 3.95               | 5.22               |
|              | 10.92      | 0.003                    | -                 | 0.98              | 3.10               | 3.51               |
| HT/K₂S₂O₈   | 3.11       | 0.025                    | 2.18              | 10.56             | 19.96              | 25.71              |
|              | 6.94       | 0.023                    | 2.47              | 9.35              | 20.33              | 22.52              |
|              | 10.95      | 0.013                    | 0.16              | 4.87              | 10.15              | 15.24              |
| Fe²⁺/K₂S₂O₈ | 3.11       | 0.013                    | 0.44              | 4.93              | 12.57              | 13.88              |
|              | 7.12       | 0.010                    | -                 | 4.36              | 10.31              | 10.68              |
|              | 11.24      | 0.005                    | -                 | 1.77              | 4.02               | 6.07               |
PFOS defluorination by-products

We measured the concentrations of PFOS and its intermediates under UV/K$_2$S$_2$O$_8$ treatment during UV irradiation. Fig. 7 shows the MRM spectra of assigned ionic compounds in the degraded solutions after 4 h by UV/K$_2$S$_2$O$_8$ oxidation.

The concentrations of PFOS and the intermediates at different irradiation time were determined using external standard method. The results were shown in Fig. 8.

The concentrations of PFOA, PFHpA and PFPA first increased and then decreased during the reaction process, and the concentrations of PFHxA, PFBA, PFPrA and TFA gradually increased with the increasing of time. As intermediates, PFCAs were not only the hydrolysis product but also the reactant of following reactions. The formed perfluorinated carboxylic acid undergo a further degradation and shortening of the perfluorocarbon chain. Based on the reaction dynamics of continuous reaction, the concentration of PFCAs should first increase and then decreased during the reaction process. From the results, it can infer that PFHxA, PFBA, PFPrA and TFA could not reached the
maximum at 12 h. On the other hand, there is low concentration of PFHxS and PFBS were maintained at the constant concentration over time. The formation of trace levels of PFHxS and PFBS would be due to the recombination of CF3(CF2)5 and CF3(CF2)3 with SO3 group [8].

Because of the lack of standards of some compounds we could not measure their actual concentration. The unknown fluorines are those not to be confirmed by above analysis. Thus, the irradiation-time dependence of the mass balance of fluorine was also studied in this study. The mass concentration of the inorganic fluorine in the solutions was analyzed using IC at different reaction time. The organic fluorine referred mainly to the fluorine in PFOS and intermediates which had been detected by LC/MS/MS and their mass concentration was calculated from mass ratio between fluorine and parent PFCs (Eq.12).

\[
Y = \sum_{i=0}^{6} (3 + 2i) \times C_{CF_3(CF_2)_iCOO}^- + 17 \times C_{CF_3(CF_2)_7SO_3^-} \\
+ 13 \times C_{CF_3(CF_2)_5SO_3^-} + 9 \times C_{CF_3(CF_2)_3SO_3^-}
\]  

\[\text{(12)}\]

The result of analysis of mass balance of fluorine was given in Table 3. The sum of the fluorine in PFOS, PFCAs and inorganic fluorine accounted for greater than 95% of the fluorine from the degraded PFOS at any point in time during UV/K2S2O8 system. According to the results of analyses of the intermediates and the mass balance of fluorine, it can be inferred that PFCAs were the main intermediates.

PFOS defluorination mechanisms

Previous investigations have provided that PFOS could lose electrons to anode or strong oxidizers, but the mechanism was still in controversy. Kimberly et al. found that an alternative oxidation mechanism is the direct transfer of electrons from PFOS to the BDD (Boron-Doped Diamond) anode as shown in Eq.13 [19].

\[
C_8F_{17}SO_3^- \rightarrow C_8F_{17}SO_4^- + e
\]

\[\text{(13)}\]

Lin et al. reported that hydroxyl radicals attack the perfluorooanion and become quenched into hydroxide ions, leaving perfluorinated radicals for continuing chain reactions that lead to further decomposition [20]. Liu et al. found that the first oxidative attack of PFOS by permanganate may have occurred at the C-S and C-C bonds, which released the -CF2 units and oxidation product of SO4$^{2-}$ to form the shorter chain perfluoroalkyl sulfonates and perfluorochemical products subject to further transformation reactions such as hydrolysis [2].

As another most extensive and typical of PFCs, PFOA oxidation mechanism with SO4$^{2-}$ have previously reported. Both Hori et al. and Lee et al. reported that the PFOA oxidation mechanism with SO4$^{2-}$ was described as follows (Eq.14–18) [27,28]:

\[
C_8F_{17}SO_4^- \rightarrow C_8F_{17}SO_4^- + e
\]

\[\text{(13)}\]
Table 3. Irradiation-time dependence of fluorine element mass balance during decomposition of PFOS in UV/K₂S₂O₈ systems.

| Time (h) | Organic fluorine (mg/L) | Inorganic fluorine (mg/L) | Unknown fluorine (mg/L) |
|----------|-------------------------|---------------------------|-------------------------|
|          | PFOS | Intermediates | F⁻ |                      |
| 0        | 60   | 0             | 0 | 0                     |
| 1        | 58.34| 0.37          | 0.42| 0.87                 |
| 2        | 55.42| 0.99          | 1.6 | 1.99                |
| 4        | 54.46| 2.15          | 2.57 | 0.82                |
| 8        | 48.96| 1.84          | 8.19 | 1.01                |
| 12       | 45.72| 2.53          | 10.34 | 1.41               |

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Figure 9. Possible defluorination pathways of PFOS in the activated K₂S₂O₈ oxidation systems.
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\[ \text{SO}_4^{2-} + \text{C}_2\text{H}_3\text{F}_5\text{COO}^- \rightarrow \text{SO}_4^{2-} + \text{C}_2\text{H}_3\text{F}_5\text{COO}^- \quad (14) \]

\[ \text{C}_2\text{H}_3\text{F}_5\text{COO}^- \rightarrow \text{C}_2\text{H}_3\text{COO}^- + \text{CO}_2 \quad (15) \]

\[ \text{C}_2\text{H}_3\text{F}_5\text{COO}^- + \text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_3\text{OH} + \text{H}_2\text{CO}_2 \quad (16) \]

\[ \text{C}_2\text{H}_3\text{F}_5\text{OH} \rightarrow \text{C}_2\text{H}_3\text{COF} + \text{F}^- + \text{H}^+ \quad (17) \]

\[ \text{C}_2\text{H}_3\text{COF} + \text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_3\text{COO}^- + \text{CO}_2 + \text{H}^+ \quad (18) \]

Based on the results discussed above, the mechanism of oxidative defluorination of PFOS with sulfate radicals could be illuminated. The defluorination of PFOS was as Fig. 9: The oxidation potential of \( \text{SO}_4^{2-} \) is 2.5–3.1 eV, while the C–F bond in PFOS is the most resistant bond \( (\text{E}_0 = 3.6 \text{ eV}) \) and is difficult to be dissociated by \( \text{SO}_4^{2-} \). Therefore, the first oxidative attack of PFOS by \( \text{SO}_4^{2-} \) may have occurred at the C-S bonds, therefore, \( \text{SO}_4^{2-} \) oxidizes PFOS to form \( \text{C}_2\text{H}_3\text{F}_5\text{OH} \), which undergo HF elimination to form \( \text{C}_2\text{H}_3\text{COF} \). Moreover, \( \text{C}_2\text{H}_3\text{COF} \) further undergoes hydrolysis, resulting in the formation of short-chain \( \text{C}_2\text{H}_3\text{COO}^- \). \( \text{PFOS} \) is then oxidized by the SO4 radical. The defluorination efficiency increased with increases of the initial amount of \( \text{S}_2\text{O}_8^{2-} \) under all activated \( \text{K}_2\text{S}_2\text{O}_8 \) oxidation treatment. However, further increase in the initial amounts of \( \text{S}_2\text{O}_8^{2-} \) did not result in further increase in PFOS defluorination efficiency. The main intermediates during the degradation of PFOS were short-chain PFCs. Oxidation and hydrolysis were the main defluorination mechanism of PFOS. PFOS was first lost electron to sulfate radicals and then desulfonated to \( \text{C}_2\text{H}_3\text{F}_7\text{CO}, \text{C}_2\text{H}_3\text{CO}^- \). During the hydrolytic reaction, long-chain PFCAs are decomposed stepwise to form short-chain PFCAs.

**Supporting Information**

**Figure S1** The effects of low temperature (0°C) on the defluorination of PFOS (0.186 mM) with \( \text{S}_2\text{O}_8^{2-} \) (18.5 mM) and \( \text{Fe}^{2+} \) (3 mM) in ice water were investigated. IC spectra of \( \text{F}^- \) and \( \text{SO}_4^{2-} \) before and after reaction were shown in Fig S1. The results showed that no \( \text{F}^- \) and \( \text{SO}_4^{2-} \) was observed after 20 min, and there was less change in concentration of \( \text{S}_2\text{O}_8^{2-} \). Thus, it could be considered that \( \text{S}_2\text{O}_8^{2-} \) was stable in icy water, and the ice water could quench the formation \( \text{SO}_4^{2-} \). Due to the time for sampling was controlled in 10 min, we can considered that this method for quenching reaction could ensure the accuracy of the \( \text{F}^- \) detection.

(TIF)

**Author Contributions**

Conceived and designed the experiments: SWY JHC. Performed the experiments: SWY JHC JS XYL. Analyzed the data: SWY JHC. Contributed reagents/materials/analysis tools: SWY JHC YYH. Wrote the paper: SWY JHC JS YHY XYL. English language editing: JYJ.

**References**

1. Kannan K, Corsolini S, Falanysz J, Fillmann G, Kumar KS, et al. (2004) Perfluorooctane sulfonate and related fluorochemicals in human blood from several countries. Environmental Science & Technology 38, 4489-4495.
2. Liu CS, Shih K, Wang F (2012) Oxidative decomposition of perfluorooctane sulfonate in water by permanganate. Separation and Purification Technology 87, 95–100.
3. Sinclair E, Kannan K (2006) Mass loading and fate of perfluoroalkyl surfactants in the environment. Journal of Environmental Management 79, 155–167.
4. Liu CS, Shih K, Wang F (2012) Oxidative decomposition of perfluorooctane sulfonate in water by permanganate. Separation and Purification Technology 87, 95–100.
5. Sinclair E, Kannan K (2006) Mass loading and fate of perfluoroalkyl surfactants in the environment. Journal of Environmental Management 79, 155–167.
6. Schultz MM, Higgins CP, Huet CA, Luthy RG, Barofsky DF, et al. (2006) Fluorochemical mass flows in a municipal wastewater treatment facility. Environmental Science & Technology 40: 1408–1414.
7. Scholz MM, Higgins CP, Huet CA, Luthy RG, Barofsky DF, et al. (2006) Fluorochemical mass flows in a municipal wastewater treatment facility. Environmental Science & Technology 40: 1408–1414.
8. Holzworth J, Sierra-Alvarez R, Zhou M, Ogden K, Field JA (2005) Anaerobic biodegradability and methanogenic toxicity of key constituents in copper chemical mechanical planarization eluents of the semiconductor industry. Chemosphere 59: 1219–1229.
9. Key BD, Howell RD, Criddle CS (1996) Defluorination of organofluorine sulfur compounds by Pseudomonas sp. strain D2. Environmental Science & Technology 32: 2283–2287.
10. Holzworth J, Sierra-Alvarez R, Zhou M, Ogden K, Field JA (2005) Anaerobic biodegradability and methanogenic toxicity of key constituents in copper chemical mechanical planarization eluents of the semiconductor industry. Chemosphere 59: 1219–1229.
11. Key BD, Howell RD, Criddle CS (1996) Defluorination of organofluorine sulfur compounds by Pseudomonas sp. strain D2. Environmental Science & Technology 32: 2283–2287.
12. Horst FS, Roland JW (2005) Stability of fluorinated surfactants in advanced oxidation processes—A follow-up of degradation products using flow injection-mass spectrometry, liquid chromatography-mass spectrometry and liquid chromatography-multiple stage mass spectrometry. Journal of Chromatography A 1062: 110–119.
13. Yamamoto T, Noma Y, Sakai S, Shibata Y (2007) Photo degradation of perfluorooctanesulfonate by UV irradiation in Water and Alkaline 2-Propanol. Environmental Science & Technology 41: 5660–5665.
14. Herrera V, Alvarez R, Somogyi A, Jacobsen N, Wysocki V, et al. (2008) Reductive defluorination of perfluorooctanesulfonate. Environmental Science & Technology 42: 3260–3264.
15. Park H (2010) Photolysis of aqueous perfluorooctanoate and perfluorooctane sulfonate. Revue Roumaine de Chimie 55: 611–619.
16. Park H, Vecitis CD, Cheng J, Mader BT, Hoffmann MR (2009) Reductive defluorination of aqueous perfluorinated alkyl surfactants: Effects of ionic headgroupand chain length. Journal of Physical Chemistry A 113: 690–696.
17. Moriwaki H, Takagi Y, Tanaka M, Tsuruho K, Okitsu K, et al. (2005) Sonochemical decomposition of perfluorooctane sulfonate and perfluorooctanoic acid. Environmental Science & Technology 39: 3383–3392.
18. Vecitis CD, Park H, Cheng J, Mader BT, Hoffmann MR (2008) Enhanced degradation of perfluorooctanoate and perfluorooctanesulfonate activity at acoustic cavitation bubble interfaces. Journal of Physical Chemistry C 112: 16850–16857.
19. Cheng J, Vecitis CD, Park H, Mader BT, Hoffmann MR (2008) Sonochemical decomposition of perfluorooctane sulfonate and perfluorooctanoic acid. Environmental Science & Technology 42: 8057–8063.
15. Vecitis CD, Park H, Cheng J, Mader BT, Hoffmann MR (2008) Kinetics and mechanism of the sonochemical conversion of the aqueous perfluorinated surfactants, perfluorooctanoate (PFOA), and perfluorooctane sulfonate (PFOS) into inorganic products. Journal of Physical Chemistry A 112: 4261–4270.

16. Cheng J, Vecitis CD, Park H, Mader BT, Hoffmann MR (2010) Sonochemical degradation of perfluorooctane Sulfonate (PFOS) and perfluorooctanoate (PFOA) in groundwater: Kinetic Effects of Matrix Inorganics. Environmental Science & Technology 44: 445–450.

17. Vecitis CD, Wang Y, Cheng J, Park H, Mader BT, et al. (2010) Sonochemical degradation of perfluorooctanesulfonate in aqueous film-forming foams. Environmental Science & Technology 44: 432–430.

18. Hori H, Nagaoka Y, Yamamoto A, Sano T, Yamashita N, et al. (2006) Efficient decomposition of environmentally persistent perfluorooctane-sulfonate and related fluorochemicals using zerovalent iron in subcritical water. Environmental Science & Technology 40: 1049–1054.

19. Carter KE, Farrell J (2008) Oxidative destruction of perfluoroctane sulphonate Using Boron-Doped Diamond Film Electrodes. Environmental Science & Technology 42: 6111–6115.

20. Lin HY, Panchangama SC, Chang C, Andy Hong PK, Hsieh H (2012) Removal of perfluorooctanoic acid and perfluorooctanoate sulfonate via ozonation under alkaline condition. Journal of Hazardous Materials 243: 272–277.

21. Lee YC, Lo SL, Chiueh PT, Liu YH, Chen ML (2010) Microwave-hydrothermal decomposition of perfluorooctanoic acid in water by iron-activated persulfate oxidation. Water Research 44: 886–892.

22. Huang KC, Courtenye KA, Hoag GE (2007) Kinetics of heat assisted persulfate oxidation of methyl tert-butyl ether (MTBE). Chemosphere 49: 413–420.

23. Liang C, Wang ZS, Bruell CJ (2007) Influence of pH on persulfate oxidation of TCE at ambient temperatures. Chemosphere 66: 106–113.

24. Anupam GP, Dionysiou DD, Gonzalez MA (2006) Cobalt-mediated activation of peroxymonosulfate and sulfate radical attack on phenolic compounds. Implications of chloride ions. Environmental Science & Technology 40: 1000–1007.

25. Liang CJ, Bruell CJ, Marley MC, Sperry KL (2003) Thermally activated persulfate oxidation of trichloroethylene (TCE) and 1,1,1-trichloroethane (TCA) in aqueous systems and soil slurries. SoilSediment Contamination 12: 207–220.

26. Waldemir RH, Tratnyek PG, Johnson RL, Nurmij JT (2007) Oxidation of chlorinated ethenes by heat-activated persulfate: Kinetics and products. Environmental Science & Technology 41: 1010–1015.

27. Hori H, Yamamoto A, Hayakawa E, Taniyasu S, Yamashita N, et al. (2005) Efficient decomposition of environmentally persistent perfluorocarboxylic acids by use of persulfate as a photochemical oxidant. Environmental Science & Technology 39: 2383–2388.

28. Lee YC, Lo SL, Chiueh PT, Chang DG (2009) Efficient decomposition of perfluorocarboxylic acids in aqueous solution using microwave-induced persulfate. Water Research 43: 2811–2816.

29. Lee YC, Lo SL, Chiueh PT, Liu YH, Chen ML (2010) Microwave-hydrothermal decomposition of perfluorooctanoic acid in water by iron-activated persulfate oxidation. Water Research 44: 896–892.

30. Lee YC, Lo SL, Kao J, Liu YL (2012) Persulfate oxidation of perfluorooctanoic acid under the temperatures of 20–40 °C. Chemical Engineering Journal 198: 27–32.

31. Li BZ, Li L, Lin K, Zhang W, Lu S, et al. (2013) Removal of 1,1,1-trichloroethane from aqueous solution by a sono-activated persulfate process. Ultrasonics Sonochemistry 20: 853–863.

32. Liang C, Wang ZS, Bruell CJ (2007) Influence of pH on persulfate oxidation of TCE at ambient temperatures. Chemosphere 66: 106–113.

33. Hori H, Nagaoka Y, Moriyama M, Kato Y (2008) Efficient decomposition of perfluorocarboxylic acids and alternative fluorochemical surfactants in hot water. Environmental Science & Technology 42: 7438–7443.