Photodegradation of perfluorooctanoic acid in water under irradiation of 254 nm and 185 nm light by use of persulfate

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Abstract The photodegradation of perfluorooctanoic acid (PFOA) in water using two types of low-pressure mercury lamps, one emitting 254 nm and the other emitting 254 nm and 185 nm, by use of persulfate (K₂S₂O₈) as an oxidant was investigated. PFOA was significantly decomposed under irradiation of 185 nm light, while it was very slow and negligible under 254 nm light irradiation. This was due to its strong absorption of PFOA from deep UV-region to 220 nm and a weak absorption from 220–460 nm. The addition of K₂S₂O₈ led to efficient PFOA decomposition and defluorination no matter what light irradiation. Sulfate radical anion (SO₄⁻), generated by photolysis of K₂S₂O₈, initiated the oxidation of PFOA. Under irradiation of 185 nm light, PFOA was jointly decomposed through 185 nm light photolysis and initiation of sulfate radical. However, under irradiation of 254 nm light, PFOA decomposition was only initiated by sulfate radical. PFOA decomposed and defluorinated much faster under oxygen atmosphere than under nitrogen atmosphere, which suggested that oxygen molecules played an important role in PFOA decomposition.

Keywords Perfluorooctanoic acid; persulfate; photodegradation; UV

Introduction Perfluorocarboxylic acids (PFCAs) are a class of special chemicals used as emulsifying agents in polymer synthesis and as surface treatment agents in photolithography, paper coatings, and waxes and polishes (US EPA, 2003). In recent years, several perfluorinated compounds such as perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) have been widely identified in the environment, including human and marine biota plasma, milk and liver tissue (Holmstrom et al., 2005; Karrman et al., 2005; Kuklenyik et al., 2005; Smithwick et al., 2005, 2006; Van de Vijver et al., 2005; Washburn et al., 2005; Falandysz et al., 2006), water dust, sediments, and domestic sludge (Higgins et al., 2005; Loewen et al., 2005; Shoeib et al., 2005; Yamashita et al., 2005), even in remote areas such as the Arctic (Silva and Mabury, 2004; Berger and Haukas, 2005; Bossia et al., 2005; Karrman et al., 2005; Verreault et al., 2005). Various studies have demonstrated toxicity of PFOS in rat, mice, fish, monkey, and bird (Seacat et al., 2002; Austin et al., 2003; Lau et al., 2004; Newsted et al., 2005; Oakes et al., 2005). As early as May 2000, the 3M Company, a major manufacturer of perfluorocompounds, announced the phase-out of production of PFOS-based compounds due to concerns about the persistence of PFOS in the environment and the potential for long-term environmental effects (3M, 2000, 2003; OECD, 2002; US EPA, 2003). PFOA and PFOS, whose resistance to degradation in ecological systems is ascribed to their C-F bonds, have no known natural decomposition processes. As high as 1 200°C is required for thermal decomposition. Thus, it is necessary to develop effective methods to decompose PFOA to harmless species under mild conditions.

Recently, Hori et al. (2004, 2005, 2006) reported the photochemical decomposition of PFCAs by use of persulfate (S₂O₅²⁻) as oxidant or by a homogeneous photocatalyst,
i.e. tungstic heteropolyacid (\(\text{H}_3\text{PW}_{12}\text{O}_{40}\)) under UV-visible light irradiation (220–460 nm). They argued that PFCAs were oxidized by the photoexcited species (\(\text{SO}_4^2-\) or \([\text{PW}_{12}\text{O}_{40}]^{3-}\)), i.e. one electron was transferred from PFCAs to the photoexcited species. Moriwaki et al. (2005) also reported the sonochemical decomposition of PFOS and PFOA under air or argon atmosphere. And they concluded that PFOS and PFOA were mostly pyrolysed at the interfacial region between the bulk solution and the cavitation bubbles where the temperature was as high as several thousands due to sonication.

Water pollution is a serious problem throughout the world. According to the UN’s latest figures, approximately 40% of the world’s population of more than two billion people face water shortage. Chemical industry is at the forefront of the water management challenge because of increasing government pressure on effluent discharge, raw water usage, increasing water demands, and general lack of available water in many locations (Wang et al., 2001). Advanced oxidation processes (AOPs) hold great promise to provide alternatives for better protection of public health and the environment. Ultraviolet light (UV) process has been used to degrade numerous organic contaminants in water, such as nitrobenzene (Bhatkhande et al., 2004), humic substances (Wang et al., 2001), and nitrophenols (Kamble et al., 2003), since PFOA has strong absorption from deep UV-region to 220 nm but a weak absorption from 220 to visible light. Thus, we expect to utilize 185 nm light irradiation to directly photolyse PFOA and at the same time utilize \(\text{K}_2\text{S}_2\text{O}_8\) to enhance PFOA decomposition. In the present work, the influences of oxidant \((\text{K}_2\text{S}_2\text{O}_8)\), reaction atmospheres \((\text{O}_2, \text{N}_2)\), and UV light \((185 \text{ nm and } 254 \text{ nm light})\) on PFOA decomposition were investigated.

Methods

Materials and photochemical reactor

Perfluorobutanoic acid (\(\text{C}_3\text{F}_7\text{COOH}\), PFBA, 99%), perfluoropentanoic acid (\(\text{C}_4\text{F}_9\text{COOH}\), PFPeA, 97%), perfluorooctanoic acid (\(\text{C}_7\text{F},\text{COOH}\), PFPeA, 97%) and perfluorooctanoic acid (\(\text{C}_7\text{F}_13\text{COOH}\), 96%) were purchased from Aldrich Chemical Co. (New Jersey, USA). Perfluorohexanoic acid (\(\text{C}_5\text{F}_{11}\text{COOH}\), PFHxA, 97%) was purchased, from Sigma-Aldrich Chemical Co. (Tokyo, Japan). Persulfate \((\text{K}_2\text{S}_2\text{O}_8, \text{99%})\) was purchased from Zhong Guancun Chemical Co. (Beijing, China).

The photochemical decomposition experiments were conducted in a tubular glass reactor with an inner diameter of 55 mm. Two kinds of 23 W low-pressure mercury lamps were used as UV light sources, one only emitting 254 nm light (UV light), and the other emitting 254 nm and a small amount of 185 nm light (VUV). The lamp was placed in the centre of the reactor with quartz tube protection (external diameter 25 mm). The reaction temperature was kept constant with a cooling water jacket around the reactor. An aqueous solution (1000 mL) of PFOA (25 mg·L\(^{-1}\)) and \(\text{K}_2\text{S}_2\text{O}_8\) (407 mg·L\(^{-1}\)) was put into the reactor. Oxygen or high pure nitrogen were continuously bubbled into the reactor through a ceramic plate with a flow rate of 100 mL·min\(^{-1}\). The reaction temperature was maintained at 25 °C.

Analyses

The concentrations of \(\text{F}^-\) and \(\text{SO}_4^{2-}\) were determined by an ion-chromatography system (761 compact IC, Metrohm) consisting of a manual sample injector (sample injection volume: 20 \(\mu\)L), a guard column (4.6 mm i.d. 10 cm length, TSKguard column Super IC-A, Japan), a separation column (4.6 mm i.d. 15 cm length, TSKgel Super IC-Anion, Japan), a column oven (40 °C), and a conductivity detector with a suppressor device. The mobile phase was a mixture of \(\text{Na}_2\text{B}_4\text{O}_7\) (5 mM), \(\text{H}_3\text{BO}_3\) (12 mM), \(\text{NaHCO}_3\) (0.5 mM), with a flow rate of 1.0 mL·min\(^{-1}\). The limit of detection (LOD) was 0.01 mg·L\(^{-1}\).
The concentrations of PFCAs were measured by HPLC-MS with an Alliance 2695 liquid chromatograph interfaced with ESI mass spectrometer (ZQ 4000, Waters, USA) in the negative ion mode. Samples were separated by a Tosoh DBS C18 column (4.6 mm i.d. 25 cm length, Supelco, Japan) with a mobile phase of a mixture of methanol (A) and aqueous CH₃COONH₄ (10 mM) (B) at a flow rate of 0.2 mL·min⁻¹. The gradient was operated from 20 to 100% A for 8 min, and held at 100% eluent A for 2 min, then decreased in 20 min to 20% A. The samples were electrosprayed at a flow rate of 0.2 mL·min⁻¹ for mass spectrometric analysis. The electrospray potential was −4.5 kV, and the cone voltage was 20 V. The heated capillary temperature used was set to 150°C. Nitrogen was used as the collision gas (0.34 MPa). The full scan \( m/z = 50–500 \) mass spectra were obtained with a triple-stage quadrupole mass spectrometer TSQ700 (Finnigan MAT, San-Jose, CA, USA). Analysts were identified and quantified using selective ion monitoring (SIM). Ions selected for monitoring in this study included PFOA \( (m/z = 413) \), PFHpA \( (m/z = 363) \), PFHeA \( (m/z = 313) \), PFPeA \( (m/z = 263) \), PFBA \( (m/z = 213) \). The typical TIC chromatography is shown in Figure 1. The limit of detection (LOD) was 1 ng·L⁻¹.

The quantification of CO₂ was carried out by gas chromatograph (Agilent 6890N, USA) with a thermal conductivity detector. The analytic method was according to the produce outlined by Hori et al. (2004).

**Results and discussion**

**Photodegradation of PFOA by K₂S₂O₈ under oxygen atmosphere**

Photochemical decomposition of PFOA in the presence of K₂S₂O₈ was conducted with the initial concentration of PFOA (25 mg·L⁻¹) and K₂S₂O₈ (407 mg·L⁻¹) under 185 nm or 254 nm light irradiation in the oxygen atmosphere. Control experiment (direct photolysis) was carried out as the same condition as the photochemical experiment except without K₂S₂O₈. Figure 2 shows the degradation and defluorination ratios of PFOA. Since PFOA has a strong absorption from deep UV region to 200 nm and weak absorption from 220 to 270 nm, PFOA was effectively decomposed under 185 light nm irradiation, whereas hardly decomposed under 254 light nm irradiation. The degradation ratios of

![Figure 1 TIC chromatogram of PFOA and its decomposition products](https://iwaponline.com/wst/article-pdf/54/11-12/317/431312/317.pdf)
PFOA were 87.4 and 4.8% for VUV photolysis and UV photolysis, respectively. Compared to direct photolysis, addition of K$_2$S$_2$O$_8$ significantly enhanced PFOA degradation and defluorination. The degradation and defluorination ratios of PFOA improved by K$_2$S$_2$O$_8$ were about 0.06 and 13.2 times after 120 min of 185 nm light irradiation, and the corresponding values were 1.5 and 15.8 times under 254 nm light irradiation. This indicated the enhancement of PFOA decomposition with K$_2$S$_2$O$_8$ was higher under 254 nm light irradiation than 185 nm light irradiation. PFOA decomposition was followed by pseudo-first-order kinetics at initial reaction periods (60 min). Therefore, the pseudo first-order rate constant was useful as a measure for photodegradation reactivity. The degradation rate constants (min$^{-1}$) of PFOA for photochemical decomposition (under 185 nm and 254 nm light irradiation) and photolysis (under 185 nm and 254 nm light irradiation) experiments, obtained by the slope from this period, were 1.44, 0.81, 1, and 0.68, respectively, indicating that rate constants PFOA degradation increased significantly with K$_2$S$_2$O$_8$ and 185 nm light irradiation.

**Intermediate products during PFOA photochemical decomposition**

Although the photodecomposition rate of PFOA in the presence of K$_2$S$_2$O$_8$ under 185 nm light irradiation clearly showed a higher rate than that under 254 nm light irradiation, the product distributions in the two systems were similar. No other by-products other than F$^-$, SO$_2^{2-}$, CO$_2$, and shorter-chain PFCAs were detected, indicating that this photochemical reaction was very selective. The formation of F$^-$, SO$_2^{2-}$, and CO$_2$, with reaction time is shown in Figure 3. In the case of photochemical decomposition under 254 nm light irradiation, after 120 min reaction, the concentrations of fluorine ion and CO$_2$ gas were up to 164.74 µM and 83.40 µM, while the corresponding values were 385.26 µM and 180 µM.
and 197.78 μM under 185 nm light irradiation. The formation rates of fluorine ion and CO₂ were much faster than those under 254 nm light irradiation.

As mentioned in the sections above, the defluorination ratio was much lower than the corresponding PFOA decomposition ratio, which implied that, besides fluorine ion, other intermediate products containing fluorine formed with PFOA decomposition. The reaction samples were identified with HPLC-MS. The products were separated and quantified by liquid chromatography and qualified with mass spectrometry. In addition, the external standards also were used to confirm the results. The identified intermediate products of PFOA decomposition were shorter chain PFCAs including PFHpA (C₆F₁₃COO⁻), PFHxA (C₅F₁₁COO⁻), PFPeA (C₄F₉COO⁻), and PFBA (C₃F₇COO⁻).

The amounts of consumed substrates were in balance with those of products, indicating that stoichiometric photodecomposition occurred in this system. On the other hand, the recovery ratios of carbon, sulfur, and fluorine were 96.7%, 96.94%, and 97.89%, respectively. Figure 4 shows the irradiation-time dependence of the formation of shorter chain PFCAs with K₂S₂O₈. The concentration of PFCAs with longer chain, such as PFHpA, firstly reached to maximum and then decreased, while others increased with time continuously, indicating that the intermediate products also decomposed and defluorinated under irradiation. Furthermore, before the concentration of product decreased, the concentration of product with longer chain was larger than that with shorter chain, indicating that PFCAs formed and decomposed stepwise toward shorter chain PFCAs. The concentration of intermediates under 254 nm irradiation were much lower than those under 254 nm light irradiation, further indicating that photochemical decomposition of PFOA under 185 nm light irradiation was much more effective than under 254 nm light irradiation.

The photochemical decomposition of PFOA in the presence of K₂S₂O₈ under 185 nm light irradiation under high pure nitrogen atmosphere was also conducted. The product distributions were similar to those under oxygen atmosphere. Product distribution of PFOA decomposition by K₂S₂O₈ nitrogen atmosphere after 120 min of 185 nm light irradiation is listed in Table 1.

When photolysis was carried under 185 nm light irradiation in nitrogen atmosphere, it seemed that K₂S₂O₈ had little influence on PFOA degradation but significantly affected decomposition of intermediates. While under oxygen atmosphere, addition of K₂S₂O₈ significantly enhanced PFOA decomposition. The formation of F⁻ was much higher in the presence of K₂S₂O₈ than without K₂S₂O₈ whether under oxygen or nitrogen, indicating that the use of K₂S₂O₈ increased defluorination of PFOA.

![Figure 4](https://iwaponline.com/wst/article-pdf/54/11-12/317/431312/317.pdf)
Compared with nitrogen atmosphere, PFOA degradation and defluorination were faster under oxygen atmosphere. The degradation and defluorination ratios were enhanced 17.18% (10.51% in control experiment) and 76.16% (1.23% in control experiment control), respectively. This indicated oxygen played an important role in PFOA degradation, which was similar to the report by Hori et al. (2004). Hori et al. showed the oxygen took part in PFOA decomposition. They used water H2(18O) and oxygen gas (16O2) to elucidate the origin of oxygen in the products, and the results indicated that water and oxygen gas acted as the oxygen source for short-chain PFCAs and CO2.

Mechanisms of PFOA decomposition

Under 185 nm light irradiation with K2S2O8 degradation and defluorination of PFOA took place immediately. PFHpA was formed firstly by dissociation of two F from PFOA because C5F13COO was first detected intermediate, and then shorter chain PFCAs were detected, followed by more CF2-unit-shortened species: PFHxA, PFPeA, and PFBA. These observations indicated short chain PFCAs formed in a stepwise manner from longer chain PFCAs. And according to the amount of fluoride ion formed in the reaction, the decomposition of intermediate continued to produce F−. The photodefluorination was a successive process.

Based on the data from our reaction system and the reports from literature (Yin et al., 2001; Hori et al., 2004), we postulate a degradation mechanism for PFOA under 185 nm light irradiation. Under 185 nm light irradiation, PFOA firstly decomposes to form excited-state PFOA* (Equation 1), and unstable PFOA* cleaves the C–C bond between C7F15 and COOH group. The C7F15 radical in water undergoes hydrolysis to produce the PFCA with one less CF2 unit, C6F13OOH:

\[
PFOA \xrightarrow{hv} \text{PFOA}^* \tag{1}
\]

When K2S2O8 is added into the reaction solution, K2S2O8 is significantly photolysed under 185 nm and 254 nm light irradiation since it has strong absorption from deep UV-region to visible light. Photolysis of K2S2O8 produces two sulfate radical anions (SO42−) (Equation 2), which is a strong oxidant to oxidize various organic compounds in aqueous system (Davies et al., 1984):

\[
S_2O_5^{2−} \xrightarrow{hv} 2SO_4^{2−} \tag{2}
\]

The sulfate radical anions (SO42−) oxidize PFOAn to form reactive radical PFOA+ (Equation 3), which leads to the C–F bond cleavage neighbouring to COOH group.

\[
SO_4^{2−} + PFOA \rightarrow SO_4^{2−} + PFOA^+ \tag{3}
\]

The active and unstable intermediate C7F15 radicals undergo the following pathway: the F atom is replaced with an electron to form the thermally unstable alcohol C7F15OH, which undergoes HF elimination to form C6F15COF, and this acid fluoride undergoes

| Table 1 Product distribution after PFOA decomposition by K2S2O8 (µM) |
|-----------------|------------------|
|                 | N2               | N2 (control) | O2   | O2 (control) |
| C7F15COOH       | 12.60            | 12.63       | 4.39 | 7.61         |
| C6F13COOH       | 20.24            | 26.32       | 19.03| 38.46        |
| C5F11COOH       | 17.70            | 12.44       | 14.35| 8.61         |
| C4F9COOH        | 4.09             | 9.36        | 5.85 | 4.33         |
| C3F7COOH        | 0.42             | not detected| 0.42 | not detected |
| F−              | 221.05           | 154.74      | 385.26| 154.21       |
| CO2             | 112.27           | 76.6        | 197.78| 78.46        |

Control experiments were conducted at the same condition except without K2S2O8.
hydrolysis to give \( \text{C}_6\text{F}_{13}\text{COOH} \) (PFHpA); the \( \text{F} \) atom forms dissociated \( \text{F}^- \) ion in reaction aqueous solution. In addition, with increasing irradiation time, the C–C bond between \( \text{C}_6\text{F}_{13} \) and COOH is cleaved, and \( \text{C}_6\text{F}_{13} \) radicals would undergo the same reaction route as \( \text{C}_7\text{F}_{15} \) radical to give the PFCAs with one less CF\(_2\) unit, \( \text{C}_5\text{F}_{11}\text{COOH} \). In the same manner, PFCAs bearing shorter perfluoroalkyl groups are formed in a stepwise manner from PFCAs that bear longer perfluoroalkyl acids. In addition, the concentration of \( \text{S}_2\text{O}_5^- \) in the initial aqueous solution was 2.14 mM, and the amount of \( \text{SO}_{4}^- \) reached 4.2 mM after 120 min of irradiation. This showed all sulfur species used in this reaction were eventually transformed into \( \text{SO}_2^- \). In a word, both PFOA and \( \text{K}_2\text{S}_2\text{O}_8 \) were excited to form reactive radicals under 185 nm light irradiation, and sulfate radical anion \( \left( \text{SO}_4^- \right) \) generated by photolysis of \( \text{K}_2\text{S}_2\text{O}_8 \) acted as an important oxidant to oxidize PFOA.

However, the direct photolysis of PFOA under 254 nm light was very slow and negligible; therefore, PFOA decomposition was mostly initiated sulfate radical anions \( \left( \text{SO}_4^- \right) \) by \( \text{K}_2\text{S}_2\text{O}_8 \) photolysis under 254 nm light.

**Conclusions**

PFOA was effectively decomposed under 185 nm light irradiation, while it was hardly decomposed under 254 nm light irradiation. Addition of \( \text{K}_2\text{S}_2\text{O}_8 \) enhanced both decomposition and defluorination of PFOA, no matter what light irradiation. The decomposition of PFOA under 185 nm light irradiation was induced by the excitation of PFOA. Addition of \( \text{K}_2\text{S}_2\text{O}_8 \) introduced another mechanism for PFOA decomposition. Persulfate was excited into sulfate radical anion by absorbance of UV light, and the sulfate radical anion initiated the oxidative degradation of PFOA. While under 254 nm light irradiation, PFOA decomposition was mainly under the later reaction mechanism. PFOA decomposed and defluorinated much faster under oxygen atmosphere than under nitrogen atmosphere, suggesting that oxygen played an important role in PFOA decomposition.

**References**


