

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 ($K_2S_2O_8$) 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 $K_2S_2O_8$ led to efficient PFOA decomposition and defluorination no matter what light irradiation. Sulfate radical anion ($SO_4^{\cdot-}$), generated by photolysis of $K_2S_2O_8$, 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 ($S_2O_8^{2-}$) 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 (SO_4^- 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 (O_2 , N_2), and UV light (185 nm and 254 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%), perfluoroheptanoic acid ($\text{C}_6\text{F}_{13}\text{COOH}$, PFHpA, 96%) and perfluorooctanoic acid ($\text{C}_7\text{F}_{15}\text{COOH}$, 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 ($\text{K}_2\text{S}_2\text{O}_8$, 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 ($25 \text{ mg}\cdot\text{L}^{-1}$) and $\text{K}_2\text{S}_2\text{O}_8$ ($407 \text{ mg}\cdot\text{L}^{-1}$) 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 $100 \text{ mL}\cdot\text{min}^{-1}$. The reaction temperature was maintained at 25°C .

Analyses

The concentrations of F^- and SO_4^{2-} were determined by an ion-chromatography system (761 compact IC, Metrohm) consisting of a manual sample injector (sample injection volume: $20 \mu\text{L}$), 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), H_3BO_3 (12 mM), NaHCO_3 (0.5 mM), with a flow rate of $1.0 \text{ mL}\cdot\text{min}^{-1}$. The limit of detection (LOD) was $0.01 \text{ mg}\cdot\text{L}^{-1}$.

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 $\text{CH}_3\text{COONH}_4$ (10 mM) (B) at a flow rate of $0.2 \text{ mL}\cdot\text{min}^{-1}$. 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 $0.2 \text{ mL}\cdot\text{min}^{-1}$ 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 $150 \text{ }^\circ\text{C}$. Nitrogen was used as the collision gas (0.34 MPa). The full scan ($m/z = 50\text{--}500$) mass spectra were obtained with a triple-stage quadrupole mass spectrometer TSQ700 (Finnigan MAT, San-Jose, CA, USA). Analytes 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 $1 \text{ ng}\cdot\text{L}^{-1}$.

The quantification of CO_2 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 $\text{K}_2\text{S}_2\text{O}_8$ under oxygen atmosphere

Photochemical decomposition of PFOA in the presence of $\text{K}_2\text{S}_2\text{O}_8$ was conducted with the initial concentration of PFOA ($25 \text{ mg}\cdot\text{L}^{-1}$) and $\text{K}_2\text{S}_2\text{O}_8$ ($407 \text{ mg}\cdot\text{L}^{-1}$) 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 $\text{K}_2\text{S}_2\text{O}_8$. 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

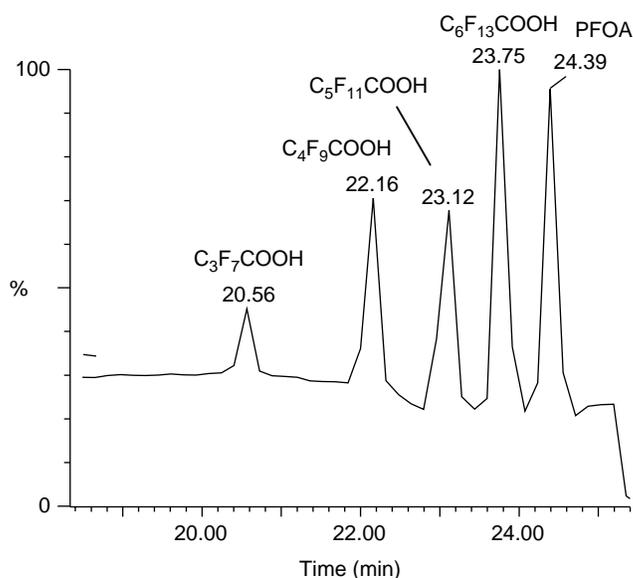


Figure 1 TIC chromatogram of PFOA and its decomposition products

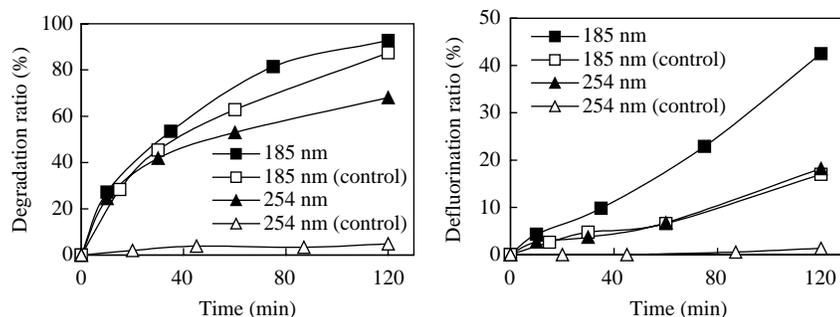


Figure 2 Degradation and defluorination ratios of PFOA in the presence of $K_2S_2O_8$ under oxygen atmosphere

PFOA were 87.4 and 4.8% for VUV photolysis and UV photolysis, respectively. Compared to direct photolysis, addition of $K_2S_2O_8$ significantly enhanced PFOA degradation and defluorination. The degradation and defluorination ratios of PFOA improved by $K_2S_2O_8$ 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 $K_2S_2O_8$ 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 $K_2S_2O_8$ and 185 nm light irradiation.

Intermediate products during PFOA photochemical decomposition

Although the photodecomposition rate of PFOA in the presence of $K_2S_2O_8$ 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_4^{2-} , CO_2 , and shorter-chain PFCAs were detected, indicating that this photochemical reaction was very selective. The formation of F^- , SO_4^{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 $164.74 \mu\text{M}$ and $83.40 \mu\text{M}$, while the corresponding values were $385.26 \mu\text{M}$

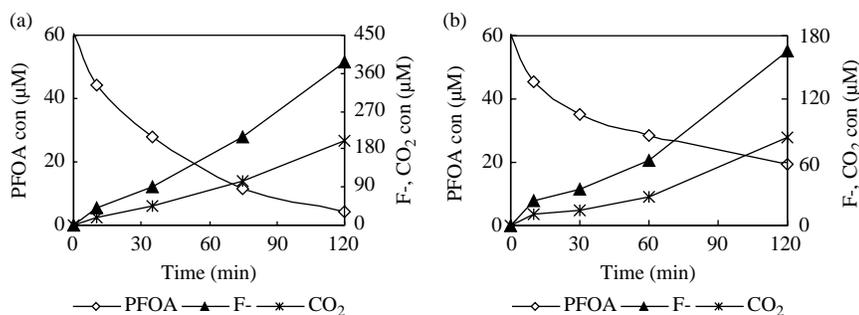


Figure 3 F^- and SO_4^{2-} formed under 185 nm (a) and 254 nm (b) irradiation

and $197.78 \mu\text{M}$ under 185 nm light irradiation. The formation rates of fluorine ion and CO_2 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 ($\text{C}_6\text{F}_{13}\text{COO}^-$), PFHxA ($\text{C}_5\text{F}_{11}\text{COO}^-$), PFPeA ($\text{C}_4\text{F}_9\text{COO}^-$), and PFBA ($\text{C}_3\text{F}_7\text{COO}^-$).

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 $\text{K}_2\text{S}_2\text{O}_8$. 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 185 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 $\text{K}_2\text{S}_2\text{O}_8$ 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 $\text{K}_2\text{S}_2\text{O}_8$ 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 $\text{K}_2\text{S}_2\text{O}_8$ had little influence on PFOA degradation but significantly affected decomposition of intermediates. While under oxygen atmosphere, addition of $\text{K}_2\text{S}_2\text{O}_8$ significantly enhanced PFOA decomposition. The formation of F^- was much higher in the presence of $\text{K}_2\text{S}_2\text{O}_8$ than without $\text{K}_2\text{S}_2\text{O}_8$ whether under oxygen or nitrogen, indicating that the use of $\text{K}_2\text{S}_2\text{O}_8$ increased defluorination of PFOA.

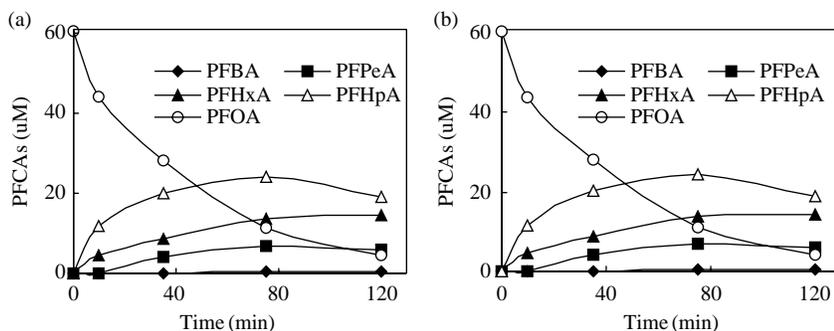


Figure 4 Changes in the concentration of $\text{CF}_3(\text{CF}_2)_n\text{COOH}$ ($n = 3-5$) with $\text{K}_2\text{S}_2\text{O}_8$ under oxygen atmosphere. (a) 185 nm light irradiation; (b) 254 nm light irradiation

Table 1 Product distribution after PFOA decomposition by $K_2S_2O_8$ (μM)

	N_2	N_2 (control)	O_2	O_2 (control)
$C_7F_{15}COOH$	12.60	12.63	4.39	7.61
$C_6F_{13}COOH$	20.24	26.32	19.03	38.46
$C_5F_{11}COOH$	17.70	12.44	14.35	8.61
C_4F_9COOH	4.09	9.36	5.85	4.33
C_3F_7COOH	0.42	not detected	0.42	not detected
F^-	221.05	154.74	385.26	154.21
CO_2	112.27	76.6	197.78	78.46

Control experiments were conducted at the same condition except without $K_2S_2O_8$

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 $H_2(^{18}O)$ and oxygen gas ($^{16}O_2$) 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 CO_2 .

Mechanisms of PFOA decomposition

Under 185 nm light irradiation with $K_2S_2O_8$ degradation and defluorination of PFOA took place immediately. PFHpA was formed firstly by dissociation of two F from PFOA because $C_5F_{13}COO^-$ was first detected intermediate, and then shorter chain PFCAs were detected, followed by more CF_2 -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 C_7F_{15} and COOH group. The C_7F_{15} radical in water undergoes hydrolysis to produce the PFCA with one less CF_2 unit, $C_6F_{13}OOH$:



When $K_2S_2O_8$ is added into the reaction solution, $K_2S_2O_8$ 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 $K_2S_2O_8$ produces two sulfate radical anions ($SO_4^{\bullet-}$) (Equation 2), which is a strong oxidant to oxidize various organic compounds in aqueous system (Davies *et al.*, 1984):



The sulfate radical anions ($SO_4^{\bullet-}$) oxidize PFOA to form reactive radical PFOA⁺ (Equation 3), which leads to the C–F bond cleavage neighbouring to COOH group.



The active and unstable intermediate C_7F_{15} radicals undergo the following pathway: the F atom is replaced with an electron to form the thermally unstable alcohol $C_7F_{14}OH$, which undergoes HF elimination to form $C_6F_{12}COF$, and this acid fluoride undergoes

hydrolysis to give $C_6F_{13}COOH$ (PFHpA); the F atom forms dissociated F^- ion in reaction aqueous solution. In addition, with increasing irradiation time, the C–C bond between C_6F_{13} and COOH is cleaved, and C_6F_{13} radicals would undergo the same reaction route as C_7F_{15} radical to give the PFCAs with one less CF_2 unit, $C_5F_{11}COOH$. 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 $S_2O_8^{2-}$ in the initial aqueous solution was 2.14 mM, and the amount of SO_4^- reached 4.2 mM after 120 min of irradiation. This showed all sulfur species used in this reaction were eventually transformed into SO_4^{2-} . In a word, both PFOA and $K_2S_2O_8$ were excited to form reactive radicals under 185 nm light irradiation, and sulfate radical anion (SO_4^-) generated by photolysis of $K_2S_2O_8$ 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 (SO_4^-) by $K_2S_2O_8$ 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 $K_2S_2O_8$ 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 $K_2S_2O_8$ 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.

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