



# Photodegradation of perfluorooctanoic acid by 185 nm vacuum ultraviolet light

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## Abstract

The photodegradation of persistent and bioaccumulative perfluorooctanoic acid (PFOA) in water by 185 nm vacuum ultraviolet (VUV) light was examined to develop an effective technology to deal with PFOA pollution. PFOA degraded very slowly under irradiation of 254 nm UV light. However, 61.7% of initial PFOA was degraded by 185 nm VUV light within 2 h, and defluorination ratio reached 17.1%. Pseudo first-order-kinetics well simulated its degradation and defluorination. Besides, fluoride ion formed in water, 4 shorter-chain perfluorinated carboxylic acids (PFCAs), that is, perfluoroheptanoic acid, perfluorohexanoic acid, perfluoropentanoic acid, and perfluorobutanoic acid. These were identified as intermediates by LC-MS measurement. These PFCAs consecutively formed and further degraded with irradiation time. According to the mass balance calculation, no other byproducts were formed. It was proposed that PFCAs initially are decarboxylated by 185 nm light, and the radical thus formed reacts with water to form shorter-chain PFCA with one less  $\text{CF}_2$  unit.

**Key words:** photodegradation; perfluorooctanoic acid; perfluorinated carboxylic acid; vacuum ultraviolet

## Introduction

In recent years, several perfluorinated acids especially perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) have been identified worldwide in the environment including in human and marine biota plasma, milk and liver tissue (Falandyisz *et al.*, 2006), water, dust, sediments, and domestic sludge (Yamashita *et al.*, 2005; Loewen *et al.*, 2005; Shoeib *et al.*, 2005; Van der Vijver *et al.*, 2003, 2005), and even in the remote Arctic region (Kannan *et al.*, 2005). Many studies have demonstrated their toxicity to rat, mice, fish, monkey, and bird (Lau *et al.*, 2004; Oakes *et al.*, 2005). These chemicals are too stable to be degraded in the natural environment or by known methods, such as biology, ozonation, photolysis, or photocatalysis. As a result, they persist and bioaccumulate in the environment. Thus, it is necessary to develop effective methods to degrade PFOA to harmless species under mild conditions.

Recently, Hori *et al.* (2004, 2005) reported the photochemical decomposition of PFCAs by the use of persulfate ( $\text{S}_2\text{O}_8^{2-}$ ) as oxidant or by a homogeneous photocatalyst, that is, tungstic heteropolyacid ( $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ) under UV-Visible light irradiation (220–460 nm). Moriwaki *et al.* (2005) also reported the sonochemical decomposition of PFOS and PFOA under air or argon atmosphere.

Vacuum ultraviolet (VUV,  $100\text{ nm} < \lambda < 200\text{ nm}$ ) was

usually used to decontaminate water and air or to modify the solid surface (Oppenlander *et al.*, 2000; Zhang *et al.*, 2004). Either a low-pressure mercury lamp ( $\lambda=185\text{ nm}$ ) or excimer lamps (for  $\text{Xe}_2^*$ ,  $\lambda=172\text{ nm}$ ) were used as the VUV radiation source. Organic contaminants can be photolyzed directly or degraded through water photolysis pathway, in which water is homolyzed into hydrogen atom and hydroxyl radical (Heit *et al.*, 1998).

Although photochemical degradation of PFOA by use of persulfate has been reported (Hori *et al.*, 2004), the photodegradation of PFOA by VUV light has never been reported as yet. Since PFOA has strong absorption from deep UV-region to 220 nm and weak absorption from 220 nm to visible light region, 185 nm VUV light was utilized to excite PFOA, leading to the cleavage of the C–C or C–F bond. In the present study, the degradation and defluorination of aqueous PFOA by 185 nm VUV light under an atmosphere of nitrogen were studied, and its degradation products and mechanism were discussed.

## 1 Experimental section

### 1.1 Materials

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 ( $\text{C}_7\text{F}_{15}\text{COOH}$ , PFOA, 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). All these chemicals were used as received.

## 1.2 Photodegradation procedures

The photodegradation experiments were conducted in a tubular glass reactor (Fig.1) with an inner diameter of 55 mm. Two types of low-pressure mercury lamps were used to provide UV or VUV illumination. One mainly emitted 254 nm UV light (15 W, hereafter referred to as 254 nm), and the other emitted mainly 254 nm and a small amount of 185 nm UV light (15 W, hereafter referred to as 185 nm). The lamp was placed in the center of the reactor with quartz tube protection (external diameter 25 mm). The reaction temperature was maintained at 40°C with a cooling water jacket around the reactor. The reactor was filled with an aqueous solution (800 ml) of PFOA. The high purity nitrogen gas was continuously bubbled into the reactor through a porous glass plate at the flow rate of 100 ml/min.

The pH value of 0.1 mmol/L PFOA (41.4 mg/L) aqueous solution was 3.7. In all experiments, pH value was not adjusted.

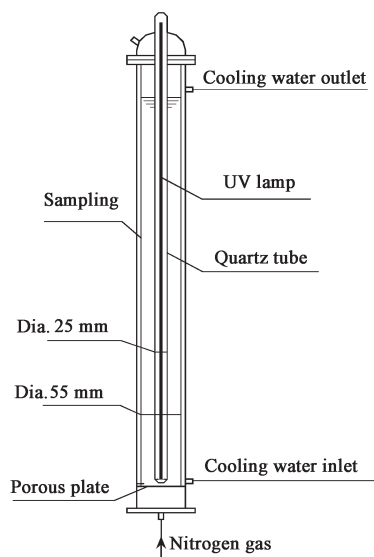


Fig. 1 Schematic diagram of the photochemical reactor.

## 1.3 Analyses

PFOA and the organic intermediates were measured by LC-MS (ZQ 4000, Waters, USA) in negative ion mode. Tosoh DBS C18 column (4.6 mm i.d., 25 cm length, Supelco, Japan) was used for separation. The mobile phase was a mixture of methanol (A) and aqueous  $\text{CH}_3\text{COONH}_4$  (10 mmol/L) (B). The gradient expressed as changes in solvent A was as follows: 0–8 min, a linear increase from 20% to 100%; 8–10 min, held at 100%; 10–20 min, a linear decrease from 100% to 20%; 20–25 min, held at 20%. The flow rate was set at 0.2 ml/min. The sample was electrosprayed for mass spectrometric analysis. And the electrospray potential was  $-4.5$  kV, the cone voltage was 20 V. The heated capillary temperature was set at 150°C. High-purity nitrogen gas was used as the collision gas (0.34 MPa). After photochemical degradation, the samples

were analyzed using selective ion monitoring (SIM) mode. Ions selected for monitoring included PFOA ( $m/z = 413$ ), PFHpA ( $m/z = 363$ ), PFHeA ( $\text{C}_5\text{F}_{11}\text{COOH}$ ) ( $m/z = 313$ ), PFPeA ( $m/z = 263$ ), PFBA ( $m/z = 213$ ). In addition, the external standards were used to quantify the concentration.

The concentration of fluoride ion ( $\text{F}^-$ ) in aqueous solution was determined by an ion chromatography system (761 compact IC, Metrohm). Defluorination ratio ( $R$ ) was then calculated as follows:

$$R = \frac{C_{\text{F}^-}}{C_0 \times 15} \times 100 \quad (1)$$

where,  $C_{\text{F}^-}$  is concentration of fluoride ion, mmol/L;  $C_0$  is initial concentration of PFOA, mmol/L. Moreover, the factor 15 corresponds to the number of fluorine atoms contained in the PFOA molecule.

## 2 Results and discussion

### 2.1 Photodegradation and defluorination

As mentioned above, PFOA is chemically inert. In the experiments, PFOA degraded very slowly under the irradiation of 254 nm UV light, and only a very small amount of fluoride ion was detected after 2 h of irradiation (Fig.2). This result is similar to that reported by Hori *et al.* (2004). They showed that 89.5% of initial PFOA degraded and fluoride ion was formed after 72 h irradiation by a 200-W xenon-mercury lamp (main wavelength 220–460 nm).

However, PFOA degraded very fast under the irradiation of 185 nm VUV light. As shown in Fig.2, 61.7% of initial PFOA (25 mg/L) degraded after 2 h of irradiation. And the amount of fluoride ion also increased continuously with increasing time, which means that PFOA was significantly defluorinated by 185 nm VUV. Defluorination ratio reached as high as 17.1% after 2 h irradiation, that is, averagely more than 4 fluorine atoms were broken off from one degraded PFOA molecule.

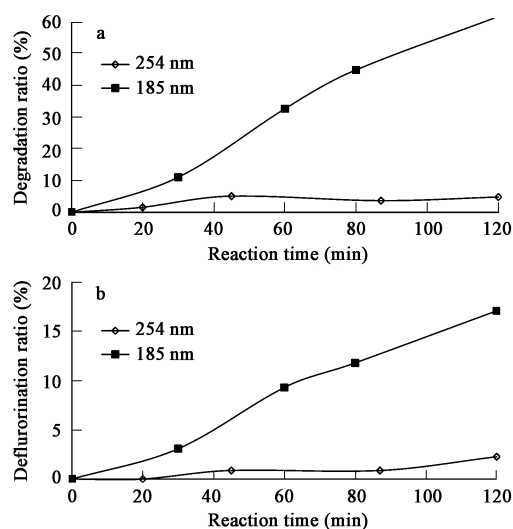


Fig. 2 Degradation (a) and defluorination (b) of PFOA by 185 nm and 254 nm UV light. Initial concentration of PFOA was 25 mg/L.

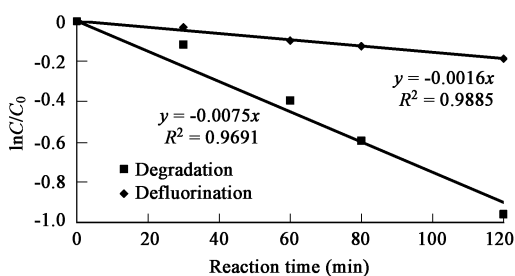


Fig. 3 Kinetics of PFOA degradation and defluorination by 185 nm VUV light.

The first-order kinetics was used to simulate the degradation and defluorination of PFOA by 185 nm VUV light, and a good result was obtained as shown in Fig.3. The corresponding rate constants were  $0.0075 \text{ min}^{-1}$  and  $0.0016 \text{ min}^{-1}$ , respectively.

## 2.2 PFOA degradation intermediates

Besides fluoride ion, other products were also formed when PFOA degraded under the irradiation of 185 nm VUV light. As shown above, defluorination ratio was much lower than the corresponding PFOA degradation ratio, which means PFOA is not completely transformed into  $\text{CO}_2$  and fluoride ion instantly. Through LC-MS analysis, 4 perfluorinated carboxylic acids, including PFHpA ( $\text{C}_6\text{F}_{13}\text{COOH}$ ), PFHxA ( $\text{C}_5\text{F}_{11}\text{COOH}$ ), PFPeA ( $\text{C}_4\text{F}_9\text{COOH}$ ), and PFBA ( $\text{C}_3\text{F}_7\text{COOH}$ ) were identified as degradation intermediates. Typical TIC chromatography of PFOA and its degradation intermediates are shown in Fig.4.

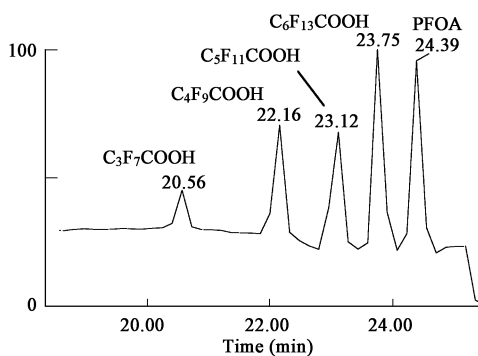


Fig. 4 TIC chromatography of PFOA and its degradation products.

Fig.5 shows the degradation of PFOA and formation of intermediates with irradiation time. Within 6 h of reaction time, PFHpA (containing 7 carbon atoms) initially reached a maximum concentration within less than 1 h, and PFHxA (containing 6 carbon atoms) reached its maximum concentration after 2 h. The concentration of these two intermediates then decreased with irradiation time. And concentrations of PFPeA (containing 5 carbons) and PFBA (containing 4 carbons) continuously increased with time. Besides, the concentration of PFPeA was always higher than that of PFBA. These phenomena indicate that the intermediates with longer chains form initially, and it further degrades into intermediates with shorter chains on a step-by-step basis.

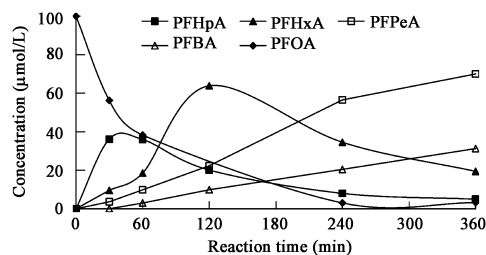


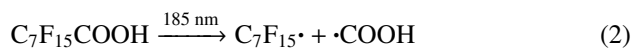
Fig. 5 Time dependence of PFOA and its degradation products.

According to concentrations of PFOA and its intermediates at any reaction time, the loss of organic fluorine and organic carbon and their changes with irradiation time were calculated. And comparing the loss of organic fluorine and formation of fluoride ion in the solution, it was found that they were nearly the same, which means all lost fluorine transforms into fluoride ion, and that besides shorter chain PFCAs, no other intermediate containing fluorine atom forms. In addition, the ratio of lost fluorine to lost carbon was found to be about 2, which implies that PFOA and its intermediates lose one  $\text{CF}_2$  unit on a step-by-step basis during their degradation.

## 2.3 PFOA degradation mechanism

As shown in the above section, PFOA is transformed to shorter-chain perfluorinated carboxylic acids besides fluoride ion under the irradiation of 185 nm VUV light, losing  $\text{CF}_2$  unit on a step-by-step basis. Hori *et al.* (2004, 2005) and Moriwaki *et al.* (2005) reported the same degradation products of PFOA although they used different degradation methods.

As shown in Fig.6, PFOA has strong absorption from 190 nm to 220 nm. Limited by the measurement method, the absorption at 185 nm was not obtained. However, extrapolated from Fig.6, it is reasonable to predict that PFOA also has strong absorption at the wavelength of 185 nm. On the basis of the above-mentioned results and discussion, the following degradation mechanism was proposed. First, PFOA is excited by 185 nm VUV light and is photolyzed into  $\text{C}_7\text{F}_{15}\cdot$  and  $\cdot\text{COOH}$  radicals.



Then  $\text{C}_7\text{F}_{15}\cdot$  radical immediately reacts with water (water acts as a nucleophilic reagent to attack the end carbon atom), and accordingly  $\text{C}_6\text{F}_{13}\text{COOH}$  (PFHpA) and fluoride ion forms.

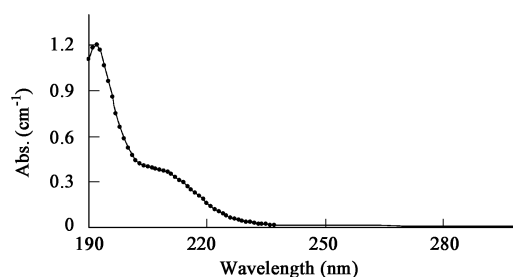


Fig. 6 UV absorption of aqueous PFOA solution (50 mg/L).

The intermediate C<sub>6</sub>F<sub>13</sub>COOH further degrades to form C<sub>5</sub>F<sub>11</sub>COOH (PFHeA) in a similar way. Finally, a series of perfluorinated carboxylic acids including PFHpA, PFHeA, PFPeA, and PFBA form during PFOA degradation. Moreover, PFCA with longer chains first reaches a maximum concentration and then decreases with irradiation time.

### 3 Conclusions

Although PFOA is chemically inert and degrades very slowly under irradiation of 254 nm UV light, it was found that PFOA degraded very fast under the irradiation of 185 nm VUV light. Within 2 h, 61.7% of PFOA (25 mg/L) degraded, and defluorination ratio reached 17.1%. Degradation and defluorination of PFOA were in good agreement with pseudo-first-order kinetics, with rate constants of 0.0075 min<sup>-1</sup> and 0.0016 min<sup>-1</sup>, respectively.

Besides formation of fluoride ion, perfluorinated carboxylic acids including PFHpA, PFHeA, PFPeA, and PFBA were identified as intermediates by LC-MS, which were formed successively. According to the mass balance calculation, the degradation of PFOA and its intermediates always leads to loss of a CF<sub>2</sub> unit step-by-step, and lost fluorine atom completely transforms to fluoride ion. PFOA has strong absorption in the deep UV region, which makes it tend to be decarboxylated by 185 nm VUV light. The radical thus formed reacts with water to form PFHpA (C<sub>6</sub>F<sub>13</sub>COOH). PFHpA further degrades, and other shorter-chain PFCAs consecutively form in a similar way.

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