



Ferric ion mediated photochemical decomposition of perfluorooctanoic acid (PFOA) by 254 nm UV light

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ABSTRACT

The great enhancement of ferric ion on the photochemical decomposition of environmentally persistent perfluorooctanoic acid (PFOA) under 254 nm UV light was reported. In the presence of 10 μM ferric ion, 47.3% of initial PFOA (48 μM) was decomposed and the defluorination ratio reached 15.4% within 4 h reaction time. While the degradation and defluorination ratio greatly increased to 80.2% and 47.8%, respectively, when ferric ion concentration increased to 80 μM , and the corresponding half-life was shortened to 103 min. Though the decomposition rate was significantly lowered under nitrogen atmosphere, PFOA was efficiently decomposed too. Other metal ions like Cu^{2+} and Zn^{2+} also slightly improved the photochemical decomposition of PFOA under irradiation of 254 nm UV light. Besides fluoride ion, other intermediates during PFOA decomposition including formic acid and five shorter-chain perfluorinated carboxylic acids (PFCAs) with C7, C6, C5, C4 and C3, respectively, were identified and quantified by IC or LC/MS. The mixture of PFOA and ferric ion had strong absorption around 280 nm. It is proposed that PFOA coordinates with ferric ion to form a complex, and its excitation by 254 nm UV light leads to the decomposition of PFOA in a stepwise way.

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1. Introduction

Perfluorinated compounds (PFCs) are widely used to manufacture fluorinated polymer, and fluoro-surfactants [1,2] because of their excellent physical and chemical properties. In recent years, PFCs especially perfluorooctanoic acid (PFOA) and perfluorooctanyl sulfonate (PFOS) have received much attention because they were ubiquitously detected in various environmental media [3–11] and in the body of wildlife [12,13] and human beings [14–17]. Though their sources, fate and transport in the environment are not well understood, it has been known that they are directly released into the environment or indirectly formed [18]. These compounds show high stabilization due to the strong C–F bonds and their natural decomposition pathway is unknown. According to assessment on available toxicity studies, the Science Advisory Board of US EPA recommends that PFOA is a “likely carcinogen” [19]. Now PFOA and PFOS have been generally recognized as a new kind of environmentally persistent organic pollutant (POP).

3M company, the major manufacturer of perfluorinated compounds, voluntarily phased out production of most of PFOS and POSF-based chemicals by the end of 2002 [20]. Furthermore, on

January 2006, US EPA launched a global stewardship program to reduce PFOA emissions and its presence in products by 95% by 2010, aiming for complete elimination by 2015 [21]. In order to abate the potential harm to human health and wildlife of PFOA and other PFCAs in the environment, it is necessary to develop feasible methods to decompose these compounds into harmless materials under mild conditions.

To our knowledge, Hori et al. have reported that PFOA can be efficiently decomposed by using a homogeneous photocatalyst, i.e. $\text{H}_3\text{PW}_{12}\text{O}_{40}$ [22] or by using persulfate ion ($\text{S}_2\text{O}_8^{2-}$) [23] as photochemical oxidant under UV–vis light irradiation (220–460 nm) in the presence of oxygen gas. On the other hand, Zhang et al. [24,25] investigated 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. These authors thought that electron transfer from PFOA to the photo-excited species played an important role in the degradation of PFOA. Moriwaki et al. [26] reported the sonochemical decomposition of PFOA under air or argon atmosphere. And they suggested that the cavitation phenomena produced by ultrasonic irradiation made PFOA molecules pyrolyzed at the interfacial region between the cavitation bubbles and the bulk solution.

Iron is one of the most abundant transition metals in Earth and a main constituent of atmospheric particulate matters and it plays a critical part in many chemical and biological processes. Inorganic ferric iron species have been known as active chromophore

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for many years, and FeOH^{2+} is recognized as the most photoactive species particularly in the near UV region. The complexes of ferric ion with simple carboxylic acids exhibits obvious photochemical behavior [27]. Many studies indicated the existence of ferric ion improved the degradation of organic pollutants. Although Hori et al. [28] recently reported that photochemical decomposition of short-chain (C_3 – C_5) PFCAs were induced by Fe^{3+} with 220–460 nm light under rigorous conditions, i.e. pressure 0.49 MPa and pH 1.5. PFOA is more widely detected in the environment than other PFCAs, and bioaccumulation of PFCAs is directly related to length of perfluorinated carbon-chain [29,30]. It is more necessary and valuable to know whether and how PFOA is decomposed. In the present study, we firstly demonstrated the photochemical decomposition of PFOA in the presence of low-level ferric ion by 254 nm UV light under rather mild conditions.

2. Experimental

2.1. Chemical reagents

Pentadecafluorooctanoic acid monohydrate ($\text{C}_7\text{F}_{15}\text{COOH}\cdot\text{H}_2\text{O}$, PFOA, 96%), perfluoroheptanoic acid ($\text{C}_6\text{F}_{13}\text{COOH}$, PFHpA, 96%), perfluoropentanoic acid ($\text{C}_4\text{F}_9\text{COOH}$, PFPeA, 97%), perfluorobutanoic acid ($\text{C}_3\text{F}_7\text{COOH}$, PFBA, 99%) and perfluoropropionic acid ($\text{C}_2\text{F}_5\text{COOH}$, PFPa, 97%), 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). Ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3\cdot x\text{H}_2\text{O}$) was purchased from Zhongguancun Chemical Co. (Beijing, China). Oxygen (99.9%) and Nitrogen (99.99%) gases for the reaction were supplied by Beijing Longhui Jingcheng Gas Company (Beijing, China). All chemicals were used without further purification and deionized water was used in all the experiments.

2.2. Photochemical reaction procedures

The photochemical reactions were conducted in a glass tubular reactor with inner diameter 55 mm. A low-pressure mercury lamp (23 W, Bright Star Light & Electricity Industry Co., Guangdong, China) emitting 254 nm UV light was placed in the center of the reactor with two-layer quartz tubes protection (external diameter 25 mm and internal diameter 23 mm). Deionized water was introduced into jacket between two-layer quartz tubes to filter any 185 nm UV light from the low-pressure mercury lamp. PFOA stock solution (500 mg L^{-1}) was prepared with deionized water and stored in a refrigerator. A fresh aqueous solution of $\text{Fe}_2(\text{SO}_4)_3$ was prepared at the beginning of experiment and used at once in order to avoid any change [31]. In a typical photochemical reaction experiment, 500 mL mixture of PFOA ($48\text{ }\mu\text{M}$) and $\text{Fe}_2(\text{SO}_4)_3$ with various ferric ion concentration was filled into the reactor. The initial pH of reaction solution ranged from 4.0 to 3.5 depending on the concentration of ferric salt. Oxygen, air or nitrogen gas was continuously bubbled into the reactor through a microporous glass plate with a flow rate at 100 mL min^{-1} during the whole reaction. The photochemical reactions were conducted at room temperature with a cooling water jacket around the reactor. At a regular time interval, the liquid aliquots were sampled for analysis.

2.3. Analyses

Concentration of PFOA and its degradation products were determined by HPLC interfaced with an electro-spray mass spectrometry (LC/MS). HPLC separation was performed on an Alliance 2695 liquid chromatograph with a Discovery® C18 column (150 mm length \times 2.1 mm i.d., 5 μm packing material, Supelco, USA). A mixture of methanol and 5 mM ammonium acetate (pH 6) aqueous

solution as mobile phase, was delivered with a flow rate of 0.2 mL min^{-1} . The gradient started at 40% methanol followed by 10-min ramp to 80% methanol, a 5-min hold, and then 2-min ramp reverting to initial conditions followed by 5-min stabilization time. The column temperature was kept at $40\text{ }^\circ\text{C}$. Detection was performed with a Waters ZQ 4000 (Waters, USA) operating in the negative ion mode. The electro-spray conditions were as follows: capillary voltages -2.0 kV , the cone voltage 12 V, collision gas nitrogen (0.34 MPa), desolvation gas flow rate 350 L h^{-1} , source temperature $120\text{ }^\circ\text{C}$. Quantitation was monitored as corresponding $[\text{M}-\text{H}]^-$ ion for PFOA and its degradation products in selective ion monitoring mode, and relating the area of analyte to the area of external standards. The calibration curves of perfluorinated carboxylic acids were established before samples analysis. The calibration concentration ranged from 0.05 mg L^{-1} to 2 mg L^{-1} . And the linear correlation factors (R^2) of these calibration curves were larger than 0.99. The limit of detection (LOD) of these compounds estimated from a signal-to-noise ratio (3:1) was as low as 0.001 mg L^{-1} .

Concentrations of fluoride ion (F^-) and formate ion were determined by a Metrohm ion-chromatography (761 compact IC, Switzerland). Sample was injected into Metrosep A supp 5 column (150 mm length \times 4.0 mm i.d.) with a Metrosep R guard column. A mixture solution containing 3.2 mM Na_2CO_3 and 1 mM NaHCO_3 as mobile phase, was delivered with a flow rate of 1.0 mL min^{-1} . The limit of detection (LOD) was 0.01 mg L^{-1} . Defluorination ratio was calculated as follows:

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

where C_{F^-} is concentration of fluoride ion, mM, C_0 is initial concentration of PFOA, mM. And the factor 15 corresponds to the number of fluorine atoms in PFOA molecule.

Concentration of ferrous ion (Fe^{2+}) during reaction was measured by spectrophotometric method using 1,10-phenanthroline as an indicator. The absorbance of the $\text{Fe}(\text{II})$ -phenanthroline complex at 510 nm ($\epsilon_{510} = 1.1 \times 10^4\text{ M}^{-1}\text{ cm}^{-1}$) was measured to determine the concentration of Fe^{2+} [32,33]. UV-vis spectra of the solution were determined by DR/4000U spectrophotometer (HACH, USA) (path length 10 mm).

3. Results and discussion

3.1. Effect of Fe (III) on photochemical decomposition of PFOA

It is well known that PFOA is very stable under 254 nm UV light. In our experiments, the direct photolysis of PFOA by 254 nm UV light was very slow and negligible whenever bubbled with oxygen, air or nitrogen gas, and only a very small amount of fluoride ion was detected after 4 h irradiation (shown in Fig. 1). However, the addition of $50\text{ }\mu\text{M}$ ferric ions led to a fast photochemical decomposition of PFOA, about 78.9% PFOA with initial concentration of $48\text{ }\mu\text{M}$ was decomposed within 4 h (Fig. 1a). In addition, ion chromatography analysis indicated simultaneous increase of fluoride ion in the solution with PFOA decomposition (Fig. 1b), the defluorination ratio reached 38.7% within 4 h reaction time, i.e. on an average 5.8 organic fluorine atoms contained in PFOA were transformed into inorganic fluoride ion, which further proved the efficient photochemical decomposition of PFOA in the presence of ferric ion.

Besides inorganic fluoride ion, organic intermediates formed during photochemical decomposition of PFOA were also determined with LC/MS or IC. Five shorter-chain perfluorinated carboxylic acids, i.e. $\text{C}_6\text{F}_{13}\text{COOH}$, $\text{C}_5\text{F}_{11}\text{COOH}$, $\text{C}_4\text{F}_9\text{COOH}$, $\text{C}_3\text{F}_7\text{COOH}$ and $\text{C}_2\text{F}_5\text{COOH}$ were identified and quantified with LC/MS. Trifluoroacetic acid (CF_3COOH) was identified with LC/MS, however, it

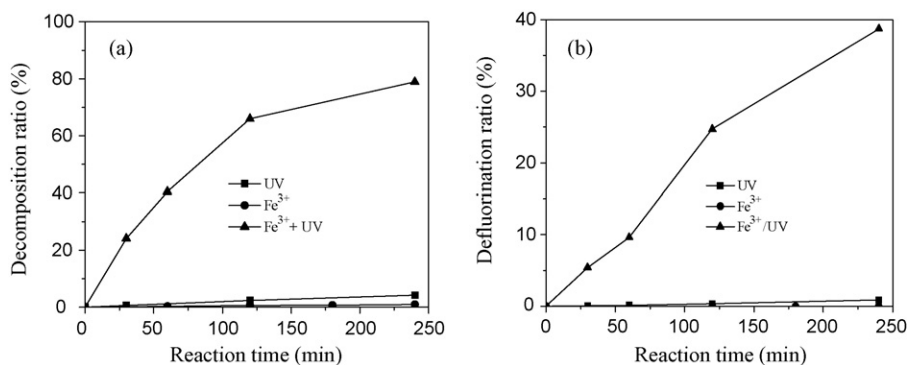


Fig. 1. (a) Photochemical decomposition of PFOA and (b) defluorination of PFOA under oxygen atmosphere. $[\text{PFOA}]_0 = 48 \mu\text{M}$, $[\text{Fe}^{3+}]_0 = 50 \mu\text{M}$.

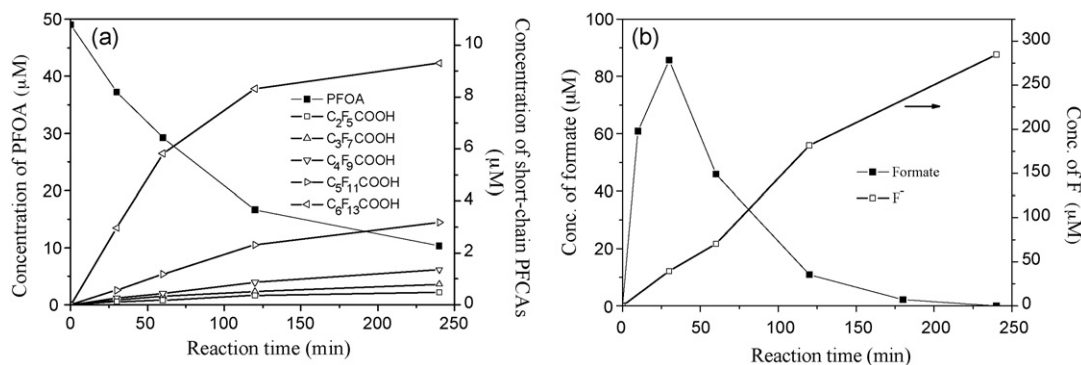


Fig. 2. Change of (a) PFOA and its decomposition intermediates and (b) formate and fluoride ion with reaction time under oxygen atmosphere. $[\text{PFOA}]_0 = 48 \mu\text{M}$, $[\text{Fe}^{3+}]_0 = 50 \mu\text{M}$.

was not quantified due to its low concentration in this study. The formation of these above PFCAs accompanying with PFOA decomposition was shown in Fig. 2(a). The concentration of all these shorter-chain PFCAs continuously increased during the whole 4 h reaction time, and PFOA with longer carbon-chain showed the higher concentration, i.e. the concentration order was as follows: $\text{C}_6\text{F}_{13}\text{COOH} > \text{C}_5\text{F}_{11}\text{COOH} > \text{C}_4\text{F}_9\text{COOH} > \text{C}_3\text{F}_7\text{COOH} > \text{C}_2\text{F}_5\text{COOH}$. And $\text{C}_6\text{F}_{13}\text{COOH}$ was the richest species formed during the whole reaction and it reached maximum concentration of $9.31 \mu\text{M}$ at the end of reaction, which is about 3.4 times higher than that of the second richest decomposition product, i.e. $\text{C}_5\text{F}_{11}\text{COOH}$.

It is worth noting that formate ion was detected by IC. As shown in Fig. 2(b), the formate ion quickly reached its maximum concentration of about $87.0 \mu\text{M}$ within 30 min and then it quickly decreased to $10.9 \mu\text{M}$ at 120 min and to less than $2.17 \mu\text{M}$ at 180 min reaction time. To our knowledge, it is the first time to observe the formation of formic acid during PFOA decomposition. The formation of formic acid indicated that the C–C bond between C_7F_{15} and COOH may be cleaved firstly during PFOA decomposition. Hori et al. [22,23] pointed out that CO_2 was identified in the gas phase when photochemical decomposition of PFOA under the condition of 0.48 MPa oxygen gas. In the present study, the reaction was conducted in an open system, and any possible products in the gas phase such as CO_2 were not determined.

3.2. Effect of reaction atmosphere on PFOA decomposition

The effects of bubbling gases including nitrogen, air and oxygen gas on the photochemical decomposition of PFOA in the presence of $50 \mu\text{M}$ ferric ion were investigated. Fig. 3 shows the decomposition ratio and defluorination ratio of PFOA after 4 h reaction when bubbled with different gases. After 4 h reaction, the decomposi-

tion ratio of PFOA and defluorination ratio was up to 73.6% and 35.1%, respectively, when bubbled with air. And when bubbled with oxygen gas, it was about 78.9% and 38.7%, which is a little higher than that when bubbled with air. However, the decomposition and defluorination ratio of PFOA was much lower when bubbled with nitrogen gas, and it was only 40% and 13.4%, respectively. Therefore, the presence of molecular oxygen is beneficial to improving the degradation and defluorination of PFOA.

3.3. Effect of ferric concentration on PFOA decomposition

As mentioned above, the coexistence of ferric ion and irradiation of 254 nm UV light caused the effective photochemical decomposition of PFOA. In this section, the effect of concentration of

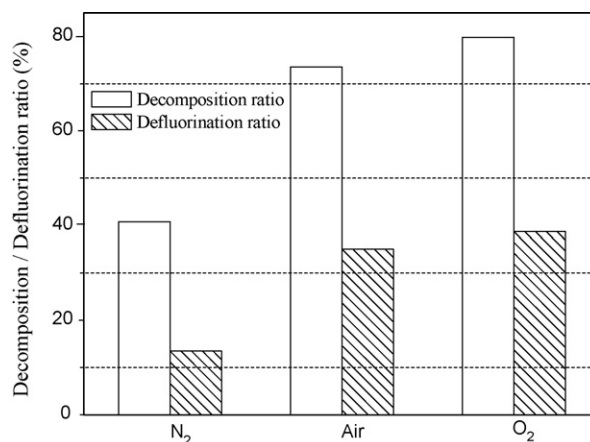


Fig. 3. Effect of bubbling gas on decomposition and defluorination of PFOA. $[\text{PFOA}]_0 = 48 \mu\text{M}$, $[\text{Fe}^{3+}]_0 = 50 \mu\text{M}$.

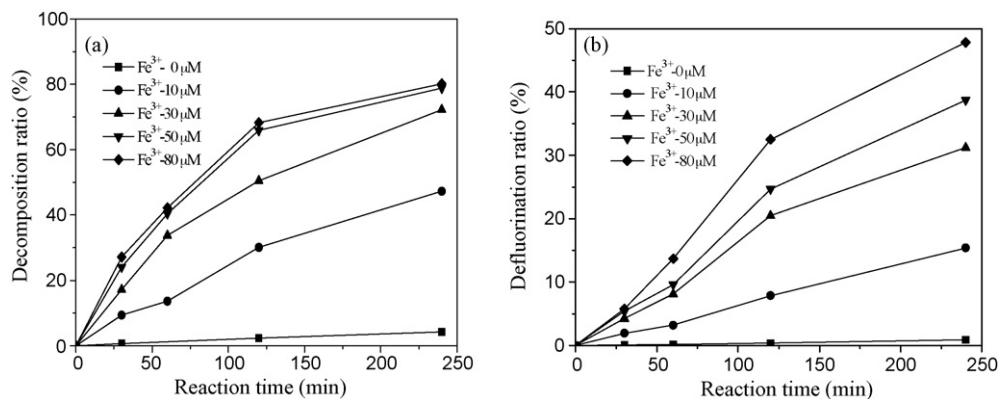


Fig. 4. (a) Decomposition and (b) defluorination of PFOA in the presence of various ferric concentration under oxygen atmosphere. $[PFOA]_0 = 48 \mu\text{M}$.

Table 1
Rate constants and half-life of PFOA in the presence of various ferric concentrations

| Fe^{3+} concentration (μM) | Decomposition rate constant k_1 (min^{-1}) ($\times 10^{-3}$) | Defluorination rate constant k_2 (min^{-1}) ($\times 10^{-3}$) | Ratio of k_1/k_2 | PFOA $t_{1/2}$ (min) |
|--|--|---|--------------------|----------------------|
| 0 | 0.2 | – | – | 4333 |
| 10 | 2.7 | 0.7 | 3.86 | 260 |
| 30 | 5.3 | 1.6 | 3.31 | 132 |
| 50 | 6.5 | 2.1 | 3.10 | 107 |
| 80 | 6.7 | 2.8 | 2.39 | 103 |

$[PFOA]_0 = 48 \mu\text{M}$, oxygen atmosphere.

Table 2
Decomposition and defluorination ratio in the presence of different metal ions

| Metal ion | Decomposition ratio (%) | Defluorination ratio (%) |
|-----------------------------------|-------------------------|--------------------------|
| Without metal ion | 4.2 | 0.9 |
| 50 μM Mn^{2+} | 4.2 | 0.9 |
| 50 μM Mg^{2+} | 5.2 | 1.0 |
| 50 μM Zn^{2+} | 5.4 | 1.1 |
| 50 μM Cu^{2+} | 7.4 | 1.3 |
| 30 μM Fe^{2+} | 68.8 | 26.0 |
| 30 μM Fe^{3+} | 72.2 | 31.2 |

$[PFOA]_0 = 48 \mu\text{M}$, after 4 h, oxygen atmosphere.

ferric ion ranging from 10 μM to 80 μM on the decomposition of PFOA under oxygen atmosphere was investigated. The variation of decomposition ratio and defluorination ratio in different cases was plotted in Fig. 4. In the range of investigated ferric ion concentration, decomposition of PFOA was accelerated by increasing ferric ion concentration, as well as the defluorination rate. Within 4 h reaction, PFOA decomposed 47.3% in the presence 10 μM ferric ion, and the defluorination ratio was 15.4%. While it greatly increased to 72.2% and 31.2%, respectively, when the ferric ion concentration increased to 30 μM . However, the increasing trend became slow when the ferric ion concentration further increased to over 50 μM , particularly for PFOA decomposition.

Both PFOA decomposition and defluorination fitted the first-order kinetics as shown in Fig. 5. Table 1 listed first-order rate constants for decomposition (k_1) and defluorination (k_2), as well as the half-life of PFOA in the presence of various ferric ion concentration. The decomposition rate constant in the presence of 80 μM ferric ion was about 33.5 times higher than that by direct photolysis,

reaching $6.7 \times 10^{-3} \text{min}^{-1}$, and the corresponding half-life was shortened from 4333 min to 103 min. The defluorination rate constant was much lower than the degradation rate constant because PFOA did not immediately decompose into fluoride ion and formic acid in one step, however some shorter-chain PFCA formed during PFOA decomposition as demonstrated above. The ratio of k_1/k_2 was about 3.86 when the ferric ion concentration was 10 μM , however it decreased to 2.39 when the ferric ion concentration increased to 80 μM , which implied that higher ferric ion concentration was in favor of defluorination and complete mineralization of PFOA and its decomposition intermediates.

3.4. Effect of other metal ions

In addition to Fe^{3+} , the effects of Mg^{2+} , Mn^{2+} , Cu^{2+} , Zn^{2+} and Fe^{2+} on the photochemical decomposition of PFOA were also investigated. These metal ions are common trace cations in natural water. Table 2 indicates the effects of these common cations on PFOA

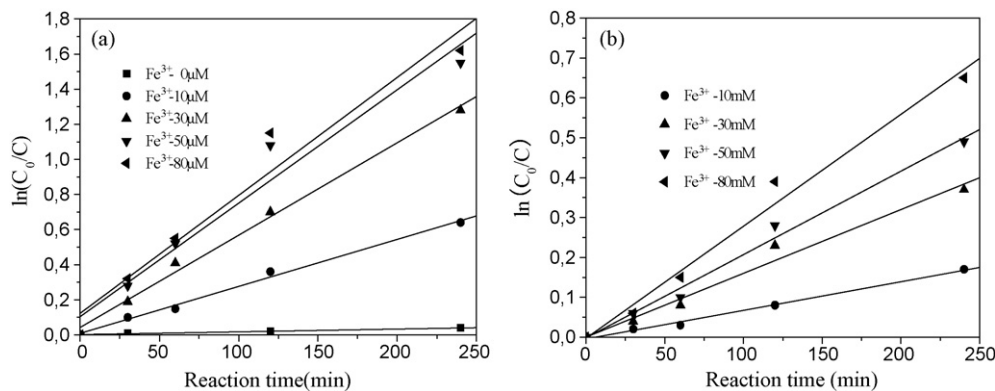


Fig. 5. Pseudo-first-order kinetic curve of PFOA (a) decomposition and (b) defluorination in the presence of various Fe^{3+} concentration under oxygen atmosphere. $[PFOA]_0 = 48 \mu\text{M}$.

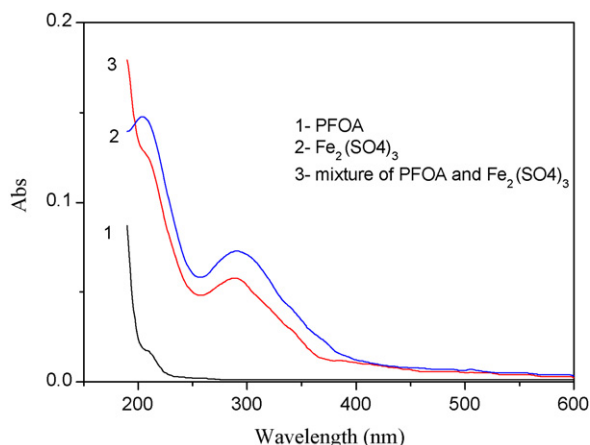
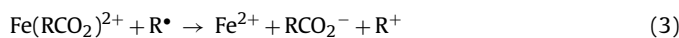
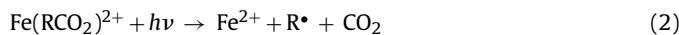


Fig. 6. UV-vis spectra of PFOA (48 μM), $\text{Fe}_2(\text{SO}_4)_3$ (50 μM) and mixture of PFOA (48 μM) and $\text{Fe}_2(\text{SO}_4)_3$ (50 μM).

decomposition and defluorination. As shown in Table 2, addition of 50 μM Mn^{2+} did not enhance the PFOA decomposition at all. On the other hand, addition of Mg^{2+} , Zn^{2+} or Cu^{2+} slightly enhanced the PFOA decomposition. While the addition of 30 μM Fe^{2+} resulted to efficient decomposition and defluorination of PFOA, very close to the effect of 30 μM Fe^{3+} . The effect of Fe^{2+} mainly resulted from the fact that Fe^{2+} was quickly oxidized to Fe^{3+} during reaction under oxygen atmosphere.

3.5. Decomposition mechanism of PFOA

Fig. 6 shows the UV-vis absorption spectra of aqueous solution of PFOA, $\text{Fe}_2(\text{SO}_4)_3$, and the mixture of PFOA and $\text{Fe}_2(\text{SO}_4)_3$, respectively. As reported in literature [22], PFOA had strong absorption from the deep UV-region to 220 nm and very weak absorption from 220 nm to 270 nm. The aqueous solution of $\text{Fe}_2(\text{SO}_4)_3$ (pH 3.9) had very strong absorption from deep UV region to 400 nm and an absorption peak around 280 nm. The mixture of PFOA and $\text{Fe}_2(\text{SO}_4)_3$ also had absorption spectra similar to that of $\text{Fe}_2(\text{SO}_4)_3$, however the absorption intensity was somewhat lower than that of $\text{Fe}_2(\text{SO}_4)_3$, which indirectly indicated the formation of a complex between PFOA and Fe^{3+} . It is well known that ferric ion easily forms complex with carboxylate and the complex formed may photolyze to Fe^{2+} and an organic radical through the ligand-to-metal charge transfer [27]:

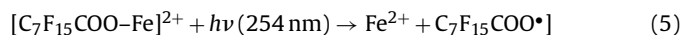
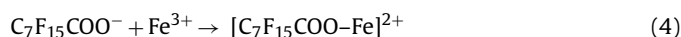


The existence of photo-induced ferrous ion (Fe^{2+}) in our reaction system was verified. The amount of Fe^{2+} after 4 h reaction was about 0.4% of the initial amount of Fe^{3+} (50 μM), which implied that PFOA also could be photochemically decomposed in a similar way in the presence of ferric ion. Hori et al. [28] also reported that about 0.7% of the initial amount of Fe^{3+} (5.0 mM) was transformed to Fe^{2+} after 24 h reaction under oxygen atmosphere during the photochemical degradation of perfluoropentanoic acid. And they supposed that the complex between Fe^{3+} and $\text{C}_2\text{F}_5\text{COOH}$ was a prerequisite species for the photochemical degradation of $\text{C}_2\text{F}_5\text{COOH}$ under 220–460 nm light according to ESR spectrum of the mixture solution of iron (III) sulfate and $\text{C}_2\text{F}_5\text{COOH}$.

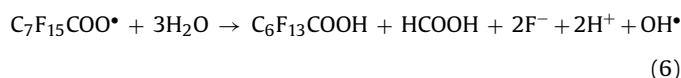
As mentioned above, during PFOA decomposition, fluoride ion was also continuously formed, and formic acid was first accumulated in the first 30 min and then decreased. Furthermore, five shorter-chain perfluorinated carboxylic acids containing C7, C6,

C5, C4 and C3, respectively, were detected during PFOA decomposition, and their concentrations in the reaction system also continuously increased and had the following sequence during the whole reaction time: $\text{C7} > \text{C6} > \text{C5} > \text{C4} > \text{C3}$. These observations implied that PFOA decomposed in a stepwise way, i.e. PFOA firstly was transformed to $\text{C}_6\text{F}_{13}\text{COOH}$ with a less CF_2 unit than PFOA, and then $\text{C}_6\text{F}_{13}\text{COOH}$ to $\text{C}_5\text{F}_{11}\text{COOH}$, $\text{C}_5\text{F}_{11}\text{COOH}$ to $\text{C}_4\text{F}_9\text{COOH}$, $\text{C}_4\text{F}_9\text{COOH}$ to $\text{C}_3\text{F}_7\text{COOH}$, and $\text{C}_3\text{F}_7\text{COOH}$ to $\text{C}_2\text{F}_5\text{COOH}$. The reduced CF_2 unit from the PFCAs was transformed to formic acid (or further oxidized as CO_2) and fluoride ion.

According to the above discussions and experimental results, the following mechanism for photochemical decomposition of PFOA in the presence of ferric ion is proposed. First, a complex between PFOA and ferric ion is formed, and then the complex is excited and photolyzed by 254 nm UV light.



The radical generated in the reaction (5) rapidly reacts with water, as a result $\text{C}_6\text{F}_{13}\text{COOH}$ with less CF_2 unit than the original PFOA, formic acid as well as fluoride ion are formed.



The reduced iron ion (Fe^{2+}) reacts with oxygen or with hydroxyl radical in the absence of oxygen, thus the ferric ion is regenerated.



The intermediate $\text{C}_6\text{F}_{13}\text{COOH}$ is further decomposed to shorter-chain PFCA in a similar way, and the formic acid is further oxidized to CO_2 . Finally, PFOA is transformed to various shorter-chain perfluorinated carboxylic acids and fluoride ion. If the reaction time is long enough, PFOA and its organic intermediates will be completely mineralized to CO_2 and fluoride ion.

4. Conclusion

Environmentally persistent perfluorooctanoic acid was hardly decomposed under the irradiation of 254 nm UV light, while the addition of trace ferric ion (Fe^{3+}) greatly induced the efficient decomposition and defluorination of PFOA, which fitted the first-order kinetics. Though the decomposition ratio of PFOA under nitrogen atmosphere was much lower than that under oxygen or air atmosphere, PFOA did efficiently be decomposed under nitrogen atmosphere. The concentration of ferric ion greatly influenced the decomposition rate of PFOA. Both the decomposition and defluorination ratio of PFOA increased with increase of ferric ion concentration. The decomposition rate constants increased from $2.7 \times 10^{-3} \text{ min}^{-1}$ to $6.7 \times 10^{-3} \text{ min}^{-1}$ when the ferric ion concentration increased from 10 μM to 80 μM , and the corresponding defluorination rate constant increased from $0.7 \times 10^{-3} \text{ min}^{-1}$ to $2.8 \times 10^{-3} \text{ min}^{-1}$. Other metal ions such as Cu^{2+} and Zn^{2+} also slightly enhanced the decomposition of PFOA by 254 nm UV light.

Besides fluoride ion, organic intermediates including formic acid and five shorter-chain perfluorinated carboxylic acids were identified and quantified with IC or LC/MS, and the PFCA with longer carbon-chain had the higher concentration than that with shorter carbon-chain. It is proposed that PFOA coordinate with ferric ion to form a complex, and its excitation by 254 nm UV light leads to the decomposition of PFOA in a stepwise way.

Acknowledgements

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