



## Factors influencing aqueous perfluorooctanoic acid (PFOA) photodecomposition by VUV irradiation in the presence of ferric ions



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### HIGHLIGHTS

- PFOA can be completely defluorinated in relatively long time (72 h).
- $\cdot\text{OH}$  radical shows profound impact on the reoxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ .
- Persulfate inhibits the defluorination of PFOA in studied system.
- The environmental matrix effect is firstly demonstrated.

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### ABSTRACT

In this study, four photochemical reaction parameters, including the reaction atmosphere, extra inorganic oxidant, inorganic anion and organic matter, were investigated in an aqueous environment to determine their effects on perfluorooctanoic acid (PFOA) photodecomposition. The photochemical defluorination of PFOA was conducted by vacuum ultraviolet light (VUV) using ferric ions as the catalyst. Both direct photolysis and photocatalysis were involved in the reaction. PFOA was completely decomposed by VUV irradiation with and without ferric ions within 72 or 144 h, respectively. There was no significant evidence indicating that the type of atmosphere (oxygen, nitrogen, or air) had any effect on the decomposition results. However,  $\cdot\text{OH}$  radicals generated during the photolysis process profoundly affected the decomposition of PFOA. The introduction of persulfate inhibited the mineralization of PFOA in the VUV/ $\text{Fe}^{3+}$  system. Inorganic anions hindered the defluorination of PFOA in the following order:  $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{NO}_3^- \sim \text{Cl}^- > \text{ClO}_4^-$ . The adverse effects of organic matter, including volatile organic compounds and dissolved natural organic compounds, were also examined. This study is beneficial to the understanding of the photodecomposition of other similar perfluorinated compounds (PFCs).

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### Introduction

Perfluorinated compounds (PFCs), especially perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), have caused public concerns in relation to their widespread occurrence in the environment, wildlife and humans [1,2]. The widespread use of perfluorinated compounds as the raw materials and products of manufacturing is due to their typical chemical properties such as

high interfacial activities, and high thermal and chemical stabilities [3]. They are bioaccumulative and toxic to aquatic life, other animals and human beings [4]. The United States Environmental Protection Agency (US-EPA) and the European Environment Agency (EEA) have imposed strict restrictions on the usage of PFOA [5,6]. However, PFOA is increasingly detected in aquatic environments because of its high solubility and persistent stability in water. The main sources of PFOA in water are PFOA-containing industrial wastewater, domestic wastewater, landfill leachate and widely used fire-extinguishing foam [1,7]. Reportedly, as a result of its strong C–F bond and the electronegativity of fluorine, PFOA is also resistant to biological degradation as well as the common oxidation processes that generate non-selective hydroxyl radicals [8,9].

Recently, various treatments for the degradation of PFOA have been investigated. Advanced oxidation technologies (AOTs), especially UV-based AOTs, are reported as highly promising for the

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decomposition of PFOA [10–14]. Photochemical degradation is the most frequently investigated method for the study of PFOA decomposition. PFOA can be decomposed by vacuum ultraviolet (VUV) irradiation due to its absorption in the deep UV region (<200 nm) [15]. However, the defluorination process is slow and inefficient. Although the direct UVC photolysis of PFOA can be ignored, PFOA can be efficiently decomposed with the introduction of oxidants, such as periodate, persulfate, ferric ions, and carbonate [12,16–19]. The effective enhancement with oxidants results from the generation of specific radicals or the formation of PFOA complexes. In the past few years, the photochemical degradation of PFOA in the presence of ferric ions has been of interest because of the beneficial effect of ferric ions in different photoprocesses [14,20–22]. Hori et al. first reported the degradation of shorter-chain perfluorinated carboxylic acids bearing C<sub>3</sub>–C<sub>5</sub> perfluoroalkyl groups by UV photolysis in the presence of ferric ions [9]. Wang et al. explored the photochemical decomposition of PFOA by UV irradiation (254-nm) using ferric ions as the photocatalyst in oxygen atmosphere [17]. Ferric ions are suggested to form complexes with PFOA, and the transfer of electrons from the PFOA to the photo-excited species leads to the decomposition of PFOA. A study by Masaki et al. focused on the effects of pH and coexisting inorganic anions (NaCl and NaSO<sub>4</sub>) on the decomposition of PFOA by UV light treatment combined with ferric ions [23]. They found that PFOA could be effectively eliminated at a pH of 2.0 due to an abundance of hydroxyl radicals that was generated by the reaction in the presence of ferric ions and UV light. The existence of SO<sub>4</sub><sup>2-</sup> restricted the degradation of PFOA because of its interference with the complexation of PFOA and the ferric ions. Our earlier research also illustrates the enhancements derived from ferric ions during the defluorination of PFOA and its intermediates under VUV irradiation. PFOA could be more efficiently defluorinated at pH 3–4, a result that differed from the treatment with UV light in the presence of ferric ions [24]. However, the effects of other experimental factors (e.g., reaction atmosphere, antioxidant, intermediates) and environmental factors (e.g., coexisting inorganic and organic species) on the defluorination of PFOA has been minimally examined. Various matrix components significantly affect the PFOA defluorination efficiency and mechanism, which had not been clarified until now. It is therefore necessary to illustrate this point, and the results are expected to be beneficial in designing more effective photodegradation systems for the treatment of PFOA and other PFCs.

The effects of the reaction atmosphere and oxidant as well as the coexisting ions and organic compounds in water in relation to the defluorination of PFOA were the focus of this study. The decomposition of PFOA was conducted with VUV irradiation in the presence of ferric ions. The effects on PFOA defluorination efficiency of certain factors, including intermediates, reaction atmosphere and extra oxidant, were assessed. Moreover, the effects of the environmental matrix, including inorganic ions and organic compounds commonly found in surface and ground water, on the PFOA photochemical defluorination kinetics were discussed in this article.

## 2. Materials and methods

### 2.1. Chemicals

Perfluorooctanoic acid (PFOA, 95%) and perfluoroheptanoic acid (PFHpA, 98%) were supplied by Alfa Company, USA. Perfluorohexanoic acid (PFHxA, 98%) and perfluoropentanoic acid (PFPeA, 98%) were obtained from Tokyo Kasei, Japan. Perfluorobutanoic acid (PFBA, 99%) and trifluoroacetic acid (TFA, 97%) were provided by Adamas Reagent, Switzerland. Perfluoropropionic acid (PFPA, 97%) was provided by Acros Organics. Potassium

persulfate and hydrogen peroxide as well as the sodium salts of chloride, nitrate, perchlorate, sulfate, and bicarbonate were purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China). Methanol, acetone, isopropyl alcohol, ethyl acetate, toluene, p-xylene, m-xylene, ethyl benzene, and ammonium acetate were purchased from Sinopharm Chemical Reagent Co. Ltd, China. The methyl-t-butyl-ether (MTBE), methyl isobutyl ketone (MIBK) and humic acid standards were obtained from Aladdin, China. All of the chemicals were used without further purification. Ultrapure water was prepared using a Millipore Milli-Q ultrapure water system (USA) and was used in all of the experiments.

### 2.2. Photochemical defluorination procedure

Photochemical defluorination reactions were performed in a 600-mL Teflon cylindrical reactor at the operating wavelengths of 185 and 254 nm using a low-pressure vacuum ultraviolet lamp (5 W, Philips Lighting Co., Guangdong, China). The lamp was placed in the center of the reactor with quartz tube protection. The applied irradiation wavelengths were mainly 254 nm with a small amount of 185 nm (determined as 12–15%). In a typical run, a 500-mL mixture of PFOA (36 μM) and FeCl<sub>3</sub>·6H<sub>2</sub>O (20 μM) was added to the reactor in the beginning. This amount of ferric ions was selected according to our previous study [24]. That is, under our experimental conditions, a dosage of 20 μM was beneficial for the defluorination of PFOA. The pH was not adjusted. No additional gases were supplied during the entire reaction, except when testing for the effects of the reaction atmosphere. The entire photochemical reactor was set in a standing-temperature cultivator, and the reactions were conducted at room temperature for all of the runs. The reaction solution was sampled for analysis at regular time intervals.

In our previous study, we indicated that acidic conditions (pH = 3–4) were more beneficial for PFOA defluorination [24]. The pH of PFOA with a concentration of 36 μM was approximately 4.1 ± 0.1. With the introduction of 20 μM Fe<sup>3+</sup>, the pH of the mixture dropped to 3.9 ± 0.1. For all of the runs conducted in our study, the initial pH of the reaction solution ranged from 4.1 to 3.7, except when testing the effects of HCO<sub>3</sub><sup>-</sup>. The influence of pH was insignificant and negligible in the pH range tested. When testing the effects of HCO<sub>3</sub><sup>-</sup>, the pH value increased from 3.9 to 7.85, which depended on the concentration of HCO<sub>3</sub><sup>3-</sup>.

The effects of the reaction atmosphere on PFOA defluorination was evaluated by continuously supplying nitrogen, oxygen or nothing (400 mL/min flow rate). Nitrogen or oxygen gases were bubbled for approximately 30 min before switching on the VUV lamp. The presence of extra oxidants, inorganic ions and organic compounds during PFOA photodecomposition was evaluated. Aqueous solutions of PFOA and other compounds were prepared before starting the experiment and were used immediately.

### 2.3. Analysis

The concentrations of PFOA and other PFCAs were quantified by LC-MS/MS. Fluoride ions (F<sup>-</sup>) were detected using an ion-chromatography system (ICS-90, Dionex). Fe<sup>2+</sup> and the dissolved trivalent iron species (Fe(III)) in the sample solutions were determined using spectrometry with 1,10-phenanthroline according to testing methods used for industrial wastewater and related reports [19]. The detection conditions were described in detail in the [supplementary data](#).

The defluorination ratio was calculated as follows:

$$\text{Defluorination ratio} = \frac{C_F}{C_0 \times 15} \times 100 \quad (1)$$

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