Insights into perfluorooctane sulfonate photodegradation in a catalyst-free aqueous solution

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Photodegradation in the absence of externally added chemicals could be an attractive solution for the removal of perfluorooctane sulfonate (PFOS) in aqueous environment, but the low decomposition rate presents a severe challenge and the underlying mechanisms are unclear. In this study, we demonstrated that PFOS could be effectively degraded in a catalyst-free aqueous solution via a reduction route. Under appropriate pH and temperature conditions, a rapid PFOS photodegradation, with a pseudo-first-order decomposition rate constant of 0.91 h\(^{-1}\), was achieved. In addition, hydrated electrons were considered to be the major photo-generated reductive species responsible for PFOS photodegradation in this system. Its production and reduction ability could be significantly affected by the environmental conditions such as pH, temperature and presence of oxidative species. This study gives insights into the PFOS photodegradation process and may provide useful information for developing catalyst-free photodegradation systems for decomposing PFOS and other persistent water contaminants.

Perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) have been widely used in the industrial production sectors over decades, due to their excellent thermal, chemical stability and surface activity. However, they are also environmentally persistent and bio-accumulative, and have high developmental toxicity, immunotoxicity, and hepatotoxicity. With a growing awareness of the hazards of these compounds, their production and application have been restricted by some countries so far. Nevertheless, in many countries they are still being manufactured and extensively used, resulting in still high environmental concentration and even raising concentration in some regions. Thus, effective approaches for degradation of these compounds are needed.

The PFOS/PFOA degradation involves the cleavage of carbon-fluorine bonds, which requires advanced treatment approaches, such as photochemical, sonochemical, subcritical, microwave-hydrothermal, electrochemical and plasma chemical degradation. Amongst these, the photodegradation process has drawn great interest due to its operational simplicity and the potential to directly utilize the inexhaustible solar energy. Compared with PFOA, PFOS is more difficult to degrade due to the presence of ionic headgroup. In existing photochemical PFOS degradation systems, extra chemicals, e.g., alcohol, ferric ion, iodide or persulfate were usually added to allow an efficient degradation, but this also increases the costs and arouses environmental concerns. Therefore, it is interesting to know whether an efficient photodegradation of PFOS could also be achieved in a catalyst-free system (i.e., without addition of extra chemicals) and how this process occurs.

This study aims to shed light on the photodegradation process of PFOS in a catalyst-free aqueous solution and elucidate the underlying mechanisms. The roles of water photolysis-derived oxidative or reductive species in PFOS degradation were investigated by selectively adding specific promoters or inhibitors, such as oxygen, hydrogen peroxide, nitrous oxide, tert-butanol, or by adjusting the pH and temperature. The findings in this study may provide useful information and guidance for future optimization of PFOS photodegradation processes.

Results

Photodegradation of aqueous PFOS. The photodegradation of neat aqueous PFOS under UV irradiation of medium pressure mercury lamp (500 W) was investigated. Figure 1 shows a gradual decline of PFOS...
concentration over time, accompanied by increased fluoride and sulfate ions. This result confirmed that the carbon-fluorine and carbon-sulfur bonds of PFOS, despite their weak light absorbance (Figure S1), were broken to form sulfate and fluoride ions under UV irradiation. In addition, no degradation of PFOS was observed after 6-h irradiation when a xenon lamp (500 W) was used as the light source. Thus, it could be inferred that UVC band (λ: 100–280 nm) should be responsible for the PFOS photodegradation in the medium pressure mercury lamp system. In all the samples, the mole ratios of the formed sulfate ions to the decomposed PFOS ranged from 0.98 to 1.16, and the defluorination ratios were between 0.82 and 1.03. All these results suggest a high decomposition degree of PFOS. Nevertheless, the complete degradation of 37.2 μM PFOS under the present conditions took more than 11 days.

Here, a powerful light source, with a UVC intensity (λ ≤ 290 nm, mainly around 254 nm) of 20 mW·cm⁻² according to chemical actinometry (iodide/iodate)25, was used. However, the degradation rate (κ = 0.012 h⁻¹, adjusted R² = 0.9503) was not significantly increased compared to a previous study (κ = 0.0054 h⁻¹) with a much lower UV intensity (λ = 254 nm) of 3.73 mW·cm⁻², indicating that light intensity might not be a limiting factor in our system.

Photodegradation of organic compounds can take place through direct and/or indirect photolysis. According to Eq. 1, both oxidative species (e.g., hydroxyl radicals (·OH), and reductive species (e.g., hydrogen atoms (H⁺) and hydrated electrons (eaq⁻)), could be generated from water splitting under UV irradiation21.

\[ H_2O + hv \rightarrow e_{aq}^- \cdot OH, H^+, H_3O^+ \] (1)

The presence of these species in irradiated solution was confirmed by the electron paramagnetic resonance analysis (Figure S2). Photodegradation of PFOS might be attributed to direct photolysis and/or an attack by these aggressive species. To clarify this, we tested the PFOS decomposition rates under specifically controlled oxidative or reductive conditions.

We first investigated the PFOS degradation in a non-buffered aqueous solution, and found a substantial decrease in the solution pH from 7.4 to 3.5 during 6-h reaction (Figure S3). This should be attributed to the formation of acidic compounds such as hydrofluoric acid (HF, pKₐ = 3.1422) and hydrosulfate (HSO₄⁻, pKₐ = 1.9923) during PFOS degradation. For instance, 5% of PFOS (37.2 μM) mineralization would reduce the pH value from neutral to about 4.5. Thus, in order to eliminate the pH impact on PFOS degradation, 6.0 mM phosphate buffer solution (PBS) was used in the subsequent experiments. A significant increase in the PFOS decomposition rate (κ = 0.13 h⁻¹, adjusted R² = 0.9999) was observed (Figure S4). Although PBS had an intense absorbance in UVC band (λ ≤ 220 nm, Figure S1), the enhanced degradation was likely associated mainly with the stable pH rather than the phosphate-induced adsorption (discussed below).

**PFOS resistance to oxidative degradation.** To validate the possible role of oxidative species in PFOS photodegradation, an oxidative solution environment was created by purging O₂ or dosing with H₂O₂. Notably, although O₂ and H₂O₂ will quench some radicals, such as hydroxyl radicals, UV/O₂ and UV/H₂O₂ systems can provide more reactive oxygen species (ROS) than UV alone system. In the oxygenation test, O₂ was continuously supplied to maintain a high dissolved oxygen level (0.81 mM, estimated according to a O₂ partial pressure of 101 kPa at 90°C)26. In another test, 30% (w/w) H₂O₂ solution was continuously dosed at a rate of 1.0 mL·h⁻¹. Thus, given the H₂O₂ decomposition under UV irradiation was compensated by the continuous H₂O₂ addition, the effective concentration of H₂O₂ was estimated to be 8.8 mM.

The PFOS decomposition profiles and the fitted results under the above conditions are shown in Figure 2. The PFOS photodegradation was substantially suppressed under oxygenated conditions (κ = 0.003 h⁻¹) and even more so under the H₂O₂-dosing condition (κ = 0.0062 h⁻¹) compared to the control (κ = 0.058 h⁻¹). Apparently, the oxidative species generated in the presence of O₂ or H₂O₂ were ineffective and even detrimental to the PFOS photodegradation. This is consistent with a previous report that hydroxyl radicals could not decompose PFOS under relatively mild conditions24. Therefore, reductive degradation should be the main route of PFOS decomposition in our system, which process could be considerably impaired by the presence of oxidative species. On one hand, O₂, H₂O₂ and the generated ROS might directly quench some photo-generated reactive species. On the other hand, a fraction of the UV photons might be absorbed by O₂ or H₂O₂ (Figure S1)24, reducing the available photons for PFOS decomposition.

**PFOS photodegradation attributable to reduction.** To validate the above hypothesized mechanism, the degradation of PFOS in the presence of N₂O or t-BuOH was investigated. N₂O can convert hydrated electrons (Eq. 2) or hydrogen atoms (Eq. 3) to hydroxyl radicals25-26, while t-BuOH can convert hydroxyl radicals to the less reactive radicals (Eq. 4) and react with hydrogen atoms with a low reactivity constant (Eq. 5)25-27.
\[ e_{aq}^{-} + \text{N}_2\text{O} + \text{H}_2\text{O} \rightarrow \cdot \text{OH} + \cdot \text{OH} + \text{N}_2 \quad k = 9.1 \times 10^9 \text{ M}^{-1}\text{s}^{-1} \quad (2) \]

\[ \text{H}^- + \text{N}_2\text{O} \rightarrow \cdot \text{OH} + \text{N}_2 \quad k = 2.1 \times 10^8 \text{ M}^{-1}\text{s}^{-1} \quad (3) \]

\[ \cdot \text{OH} + (\text{CH}_3)_2\text{COH} \rightarrow \text{CH}_2(\text{CH}_3)_2\text{COH} + \text{H}_2\text{O} \quad k = 6 \times 10^8 \text{ M}^{-1}\text{s}^{-1} \quad (4) \]

\[ \cdot \text{OH} + (\text{CH}_3)_2\text{COH} \rightarrow \text{CH}_2(\text{CH}_3)_2\text{COH} + \text{H}_2 \quad k = 1 \times 10^5 \text{ M}^{-1}\text{s}^{-1} \quad (5) \]

Figure 3 illustrates the PFOS decomposition rate profiles and fitted results in the presence or absence of different scavengers. As expected, N\(_2\)O (8.4 mM, calculated assuming the N\(_2\)O partial pressure of 101 kPa and according to its solubility at 80 °C\(^{29}\)) significantly lowered the decomposition rate (\(k = 0.052 \text{ h}^{-1}\)) compared with the control (\(k = 0.094 \text{ h}^{-1}\)), confirming that PFOS photodegradation could be suppressed by the formed hydroxyl radicals\(^{25}\). Meanwhile, the addition of t-BuOH (1.0 mM) drastically increased the degradation rate (\(k = 0.60 \text{ h}^{-1}\)). All these evidences suggest that PFOS in the aqueous solution was mainly subjected to reductive photodegradation.

**Effects of solution pH and temperature.** The above conclusion was also supported by the results obtained under different pH and temperature conditions, because both factors could influence the production and consumption of reductive species and hence lead to different PFOS degradation performances. An investigation of the photodegradation at different pHs shows that the PFOS decomposition rates and defluorination ratios decreased at a lower pH, and almost no decomposition was observed at pH 2.4 after 6-h irradiation (Figure 4 and Table S1). Thus, the rapid decrease in pH might be a critical reason responsible for the slow PFOS degradation in the non-buffered solution. Considering, the low pKa value of PFOS (\(-3.27\)), direct photolysis of PFOS was unlikely to occur in our system, while photoreductive decomposition should be the only route. In addition, as shown in Figure 5, a positive correlation between the PFOS photodegradation rate and the solution temperature (from 35 to 100 °C) was observed (also see Table S2 for more details). The activation energy for the initial defluorination of PFOS in the aqueous solution was mainly subjected to reductive photodegradation. A higher level of reductive species in the solution and accelerated PFOS degradation might be encouraged by the raised pH and temperature. The underlying mechanism is detailed below.

**Discussion**

Photodegradation without chemical-dosing in aqueous solution is a promising process to treatment PFOS, but a low degradation efficiency presents a severe limitation at the present stage\(^{10,13}\). This study attempts to find out the reason behind such a slow PFOS degradation. The results indicate that the PFOS photodegradation in a catalyst-free aqueous solution was a reduction process, in which reductive species such as hydrogen atoms and/or hydrated electrons from water photolysis play important roles. The production of these reductive species could be significantly affected by solution pH and temperature. According to Eq. 6, the high-concentration hydroniums (H\(_3\)O\(^+\)) in acidic solution would quench the hydrated electrons to form hydrogen atoms. Thus, the suppressed degradation at acidic pH suggests that hydrated electrons, rather than hydrogen atoms, might be the major contributors for the PFOS degradation. In addition, the thermodynamic analysis also indicates that the hydrogen atoms (standard reduction potential \(E^0 \approx -2.1 \sim -2.3 \text{ V}\)) could not break the primary and secondary carbon-fluorine bonds of PFOS \((E \approx -2.7 \text{ V})\), while hydrated electrons could \((E \approx -2.7 \sim -2.9 \text{ V}\)). A higher temperature tend to increase the hydrated...
electrons generation and thus also favor PFOS degradation. Therefore, hydrated electrons should be the key reductive species responsible for the PFOS photodegradation in the present study, although more direct evidences are still to be provided.

$$e_{aq}^{-} + H_2O^+ \rightarrow H^- + H_2O \quad k = 2.3 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$$  \hspace{1cm} (6)

Based on the above analysis, we hypothesize the following mechanism for the PFOS photodegradation in a simple aqueous solution. Firstly, hydrated electrons are generated from water photolysis (Eq. 1) and/or the charge-transfer-to-solvent reaction of hydroxide ions (Eq. 7). A fraction of these generated hydrated electrons are immediately quenched via the recombination with the concurrently photo-generated hydroxyl radicals, $H_2O^-$, and even water molecules, while another fraction reduces PFOS. Then, the reduction products of PFOS, (i.e., after defluorination and/or desulfonation), which are less persistent owing to lower fluorination nature of the ionic headgroup, undergo rapid further degradation (photolysis, oxidation and/or reduction) and mineralization. In this complicated reaction process, there might be some other degradation products, such as formic acid and fluoride-contained metabolites. Especially, short-chain perfluorocarboxylic acids, namely, $C_nF_{2n}$, were expected to form during PFOS photodegradation. However, they were not detected in our study, probably due to their rapid decomposition under the tested conditions. For instance, $C_6F_{14}COO^-$ decomposed at a high rate of 2.78 h$^{-1}$ at pH 7.0 and 90°C (Figure S6), while PFOS at 0.058 h$^{-1}$. Notably, defluorination ratio under this chemical-free conditions (typically > 70%) was higher than under iodide-dosing conditions, probably because the hydroxyl radicals generated along with the hydrated electrons (Eq. 7) in our study were also involved in the subsequent processes to yield fluoride.

With the deep understanding of the catalyst-free PFOS photodegradation, an efficient photodegradation of aqueous PFOS may be enabled by enforcing appropriate pH, temperature, and anoxic conditions. To optimize this process, we explored the PFOS decomposion under different pH and temperature combinations. Figure 6 shows that the decomposition rate was only slightly increased when the temperature was raised from 90 to 100°C at pH 7.0 (see Table S2 for more details). However, a significantly increased degradation was observed at pH 11.8. In contrast, no degradation was observed in the absence of UV irradiation. Thus, by applying an alkaline pH of 11.8, K$_3$PO$_4$ only). In case of H$_2$O$_2$ or t-BuOH addition, these reactions could be warmed up by the lamp. To resolve this problem, a water bath was used to control the temperature of the solution, which was monitored using a thermometer. Reactor B was made of a double layered quartz tube (semi-sealed as Reactor A), but without stirring and temperature monitoring. It was smaller and fed with 200 mL reaction solution. Due to a relatively slow heat exchange, the temperature of the solution was maintained at about 90°C (measured using a thermometer after the experiment) during the UV irradiation, with the assistance of a water bath.

The deoxygenated (purgue nitrogen for 10 min) PFOS solution was irradiated for 4–6 h and the solution (2 mL) was sampled on an hourly basis using a syringe, while a longer irradiation time (2–11 d) was adopted in our preliminary experiments. Although the reaction solutions were hot in most of the tests the evaporation loss was minimal (≤5%) due to the semi-closed system. According to the experimental design, O$_2$ or N$_2$O was pumped into the reactor from the bottom of the reaction solution at 20 mL/min. Phosphate (6.0 mM) was employed as the pH buffer to eliminate the impact of varying pH, and the initial pH of the solution was adjusted using 10 M KOH (for pH ≤ 4, using 6.0 mM H$_2$PO$_4$ and KOH; for 5 ≤ pH ≤ 11, KH$_2$PO$_4$ and KOH; for pH = 11.8, K$_2$PO$_4$ only). In case of H$_2$O$_2$ or t-BuOH addition, these chemicals were added into the solution prior to pH adjustment.

Analysis. PFOS concentration was measured using a high performance liquid chromatograph (HPLC, 2695, Waters Inc., USA) coupled with a mass spectrometer (MS, LCQ Advantage MAX. Thermo Fisher Scientific Inc., USA). Prior to the measurement, the sample was diluted with methanol to ensure a PFOS concentration of less than 2.5 μM. In addition, PFOS standard solutions of 0.2 and 2.5 μM were also analyzed in each sample sequence in accordance with the order from low to high concentrations. A Phenomenex Luna 5 μ C18(2) 100A separation column (4.6 mm i.d. × 150 mm, 5 μm particles) was used for the analysis. The column temperature was set at 40°C. A mixture of eluent A (10 mM
Table 1 | Comparison of this study with reported methods for PFOS degradation

| Method | Conditions | \(k^{(h^{-1})}\) | \(E_{\text{CO}}^{\text{h}}(10^3 \text{kWh/m}^3/\text{order})\) | Reference |
|--------|------------|-----------------|-----------------|-----------|
| Direct UV | [PFOS]: 40 \(\mu\)M 750 mL 36–46 C LPML: 32 W | 0.0054 | 18.19 | Yamamoto, et al. 10 |
| UV in iso-propanol | [PFOS]: 40 \(\mu\)M [NaOH]: 68 mM 750 mL iso-propanol 38–50 C LPML: 32 W | 0.039 | 2.52 | Yamamoto, et al. 10 |
| UV/KI | [PFOS]: 20 \(\mu\)M [KI]: 10 mM 30 mL ambient temperature UV: 8 W | 0.18 | 3.41 | Park, et al. 19 |
| UV/K\(_2\)S\(_2\)O\(_8\) | [PFOS]: 20 \(\mu\)M [K\(_2\)S\(_2\)O\(_8\)]: 10 mM 30 mL ambient temperature UV: 8 W | 0.24 | 2.56 | Park, et al. 19 |
| UV/FeCl\(_3\) | [PFOS]: 20 \(\mu\)M [FeCl\(_3\)]: 100 \(\mu\)M 400 mL 25°C LPML: 23 W | 0.070 | 1.90 | Jin, et al. 13 |
| Sonolysis | [PFOS]: 20 \(\mu\)M 60 mL 20 C ultrasonic: 200 W, 200 kHz | 0.96 | 8.00 | Moriwaki, et al. 14 |
| Plasma bubble | [PFOS]: 100 \(\mu\)M 30 mL 25°C | 0.15 | 3.99 | Yasuoka, et al. 18 |
| UV with optimization of pH and temperature | [PFOS]: 37.2 \(\mu\)M PBS: 6.0 mM, pH 11.8 100°C 1000 mL MPMML: 500 W | 0.91 | 1.27 | this work |

\(^{a}\text{pseudo-first-order rate constants;}

\(^{b}\text{electrical energy per order, defined as the number of kilowatt-hours of electrical energy required to reduce the concentration of a pollutant by 1 order of magnitude in 1 m}^3\text{of contaminated water, proposed as a figure of merit for removal of pollutant at low concentrations by the Photochemistry Commission of the International Union of Pure and Applied Chemistry}^{4};\)

\(^{c}\text{low pressure mercury lamp;}

\(^{d}\text{medium pressure mercury lamp with a low UVC luminous efficiency, which also acted as the heat source.}

ammonium acetate in water) and B (methanol) was employed as the mobile phase, and the flow rate was maintained at 0.5 mL/min. The eluent gradient started with 40% B for 1 min and then was linearly increased to 100% B within 6 min and held at that gradient for 5 min, and eventually returned to the starting conditions within 1 min and held for 2 min for equilibrium during the injection interval. The MS instrument parameters were adopted: nitrogen sheath gas flow rate, 25 arbitrary units; aux/sweep gas flow rate, 3 arbitrary units; spray voltage, 4.5 kV; heated capillary temperature, 350°C; capillary voltage, −4 V; and tube lens offset, 10 V.

The fluoride and sulfate ions were measured using an ion chromatograph (ICS-2000, Dionex Co., USA), which consisted of a degasser, a guard column (IonPac AG11-HC, 4 × 50 mm), a separation column (IonPac AS11-HC, 4 × 250 mm), a column heater (30°C), and a conductivity detector with a suppressor. An online generated KOH solution (30 mM), with a flow rate of 1.5 mL/min, was used as the mobile phase. The suppressor current was set at 112 mA. The aqueous standard solutions containing both fluoride (0–1000 \(\mu\)M) and sulfate (0–100 \(\mu\)M) were prepared to produce the external calibration curves. Blank and all the standard solutions were analyzed in the beginning of each sample sequence. The solution pH was measured with a pH meter (Delta 320, Mettler Toledo Co., USA) at ambient temperature (20°C).

Calculations. The PFOS decomposition rate constants were calculated assuming that the photodegradation followed pseudo-first-order decay kinetics (Eq. 8)\(^a\):\)

\[
\frac{[\text{PFOS}]}{[\text{PFOS}]_0} = \exp(-kt) \tag{8}
\]

where \([\text{PFOS}]_0\) and \([\text{PFOS}]\) are the PFOS concentrations at the start of the reaction and at the irradiation time \(t\), respectively, and \(k\) is the PFOS decomposition rate constant. Although pseudo-first-order kinetics might not be very suitable for some cases with significantly varied pH, our data show that one of the reactants (i.e., hydrated electrons) remained a constant concentration during the reaction process, suggesting that it is appropriate and acceptable to adopting the pseudo-first-order kinetic constant for a quantitative evaluation of the PFOS decomposition in this study.

In addition, the degree of the PFOS decomposition can be reflected by the defluorination ratio, which is defined as (Eq. 9):

\[
\text{Defluorination ratio} = \frac{([F^-]_i) - ([F^-])}{([PFOS]_i) - ([PFOS])} \times 17 \tag{9}
\]

where \([F^-]_i\) and \([F^-]\) refer to the initial concentration of fluoride ions and their concentration at time \(t\), respectively.

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