



PHOTOLYSIS OF AQUEOUS PERFLUOROOCTANOATE AND PERFLUOROOCTANE SULFONATE**

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Perfluorinated chemicals (PFCs), as represented by perfluorooctanoate (PFOA: $C_7F_{15}CO_2^-$) and perfluorooctane sulfonate (PFOS: $C_8F_{17}SO_3^-$) have been widely used and detected over the globe. Their chemical inertness makes them highly resistant toward not only conventional treatments but also advanced oxidation processes. In this study, the hydrated electron-mediated reductive degradation of PFOX (X = A for PFOA and S for PFOS) was explored in an aqueous humic acid solution in which UV light is irradiated to excite humic acid, thereby ejecting electrons to the aqueous PFOX. The PFOX degradation was monitored with MS/MS and was further confirmed by quantifying fluorides. The quantum yield for the PFOX degradation was estimated to be as low as 10^{-4} . The F-index, the degree of defluorination ($[F^-]_{\text{produced}} / [PFOX]_{\text{degraded}}$), was 0.7 and 2.3 for PFOA and PFOS, respectively, indicating they were partially degraded. In addition, it was determined that an electron-donating ethylenediaminetetraacetic acid (EDTA) is essentially required to inhibit the recombination between the oxidized humic acid and the hydrated electron; yet it appears to interfere with the one-electron-reduced PFOX behavior at a different degree depending on the varying ionic headgroups (carboxylate vs. sulfonate).

INTRODUCTION

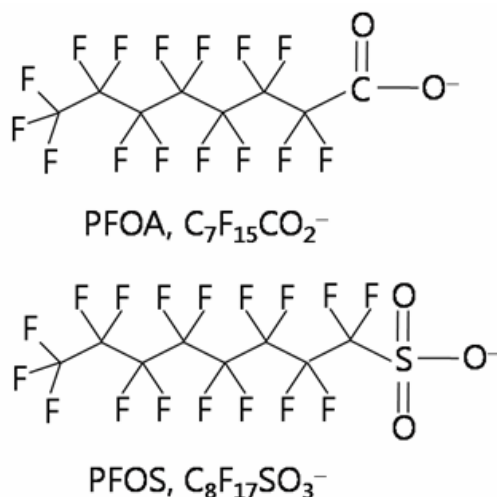
Perfluorinated chemicals (PFCs) that are represented by perfluorooctanoate (PFOA: $C_7F_{15}CO_2^-$) and perfluorooctane sulfonate (PFOS: $C_8F_{17}SO_3^-$) have been widely (see Scheme 1) used primarily in the production of durable polymers (e.g., Teflon), hydrophobic textiles, aqueous film-forming foams (AFFFs), etc.^{1,2} Their wide usage and discharge to the environment causes them to be detected globally such as in surface water, wastewater, vacuum cleaners, house dust, food, animals, and humans likely due to atmospheric and oceanic circulation process.^{3,4} Locations that were remote from PFOA and PFOS production sites (e.g., South Korea) also were reported to have multiple PFC contamination sites at concentration

levels ranging from 0.04 to 730 ppb and from 0.24 to 320 ppb for PFOS and PFOA, respectively.^{5,6} Of note is that certain locations have 10 – 100-fold higher PFC concentration levels.

PFCs have low vapor pressure, low acid dissociation constants (pK_a), and very high thermochemical stability due to their relatively strong bond strengths (413.0 kJ/mol for F_3C-CF_3 vs. 530.5 kJ/mol for $F-C_2F_5$). This stability makes them highly persistent and resistant to conventional wastewater treatments.⁷⁻¹¹ A variety of alternative treatment technologies have been studied, including direct photolysis,¹² persulfate photolysis,^{13,14} polyoxometalate photolysis,^{15,16} TiO_2 photocatalysis,^{17,18} iodide photolysis,¹⁹ Fe^0 at sub- and supercritical conditions,^{20,21} and sonolysis.²²⁻²⁵

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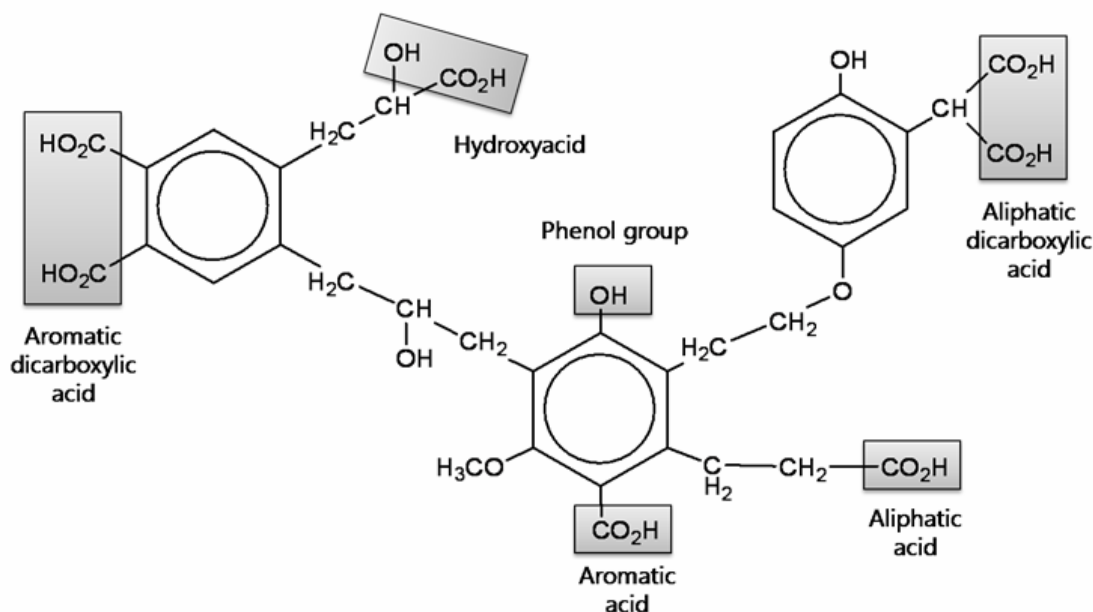
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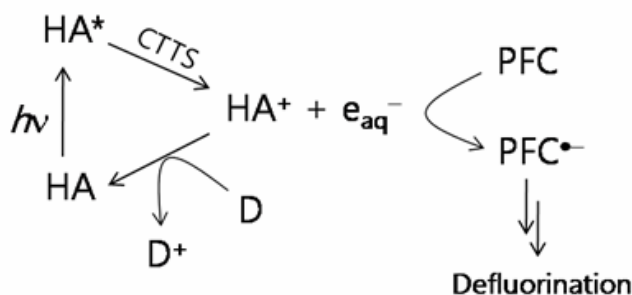
Scheme 1 – Structure of perfluorinated octanoate (PFOA, protonated) and pefluorinated octanesulfonate (PFOS, protonated).

Advanced oxidation processes (AOPs) that are utilizing hydroxyl radical ($\cdot OH$) as a primary oxidant (e.g., TiO_2 photocatalysis, UV/ H_2O_2 , Fenton, ozonation, etc) were found to be less effective despite the high reduction potential of $\cdot OH$ ($E^\circ = 2.73$ V).^{26,27} This might be attributed to the absence of hydrogen atoms at the PFOX for $\cdot OH$ to abstract. In fact, the bimolecular rate constants (k) of $\cdot OH$ with PFOA and PFOS were estimated to be far lower than $\sim 10^7$ $M^{-1} s^{-1}$. These rates are two orders of magnitude smaller than those of hydrocarbon analogues (e.g., 5.6×10^9 $M^{-1} s^{-1}$ for $C_7H_{15}COO^-$ vs. 3×10^7 $M^{-1} s^{-1}$ for $C_7F_{15}COO^-$).²⁸⁻³⁰

The reductive degradation of the PFCs has also been demonstrated to be technically viable as well. The high electronegativity of fluorines makes the PFCs reducible by electron donors. A number of reductive defluorinations of fluorinated chemicals (FCs) by chemical and electrochemical methods have been reported. However, most studies have been conducted either in non-aqueous solvents or for unsaturated FCs^{31,32} since C-F bonds of linear PFCs are very difficult to reduce due to their low reduction potentials ($E < -2.7$ V).²⁶ For example, Hori *et al.* attempted to degrade PFOX by using elemental iron, Fe^0 ($E = -0.447$ V), in water under highly severe conditions (i.e., 20 MPa, 350 °C).²¹



Scheme 2 – Proposed structure of humic acid.



Scheme 3 – Proposed PFC defluorination mechanism by photosensitized humic acid in water.

In this study, the reductive degradation of perfluorooctane sulfonate (PFOS: $C_8F_{17}SO_3^-$) and perfluorooctanoate (PFOA: $C_7F_{15}CO_2^-$) have been explored for the first time in photosensitized humic acid solution in water (see Scheme 2 for the structure of humic acid and Scheme 3 for the proposed defluorination in the humic acid solution) and compared with that of the UV/KI system. It has been known that polyhydroxy aromatic compounds and aromatic carboxylic acids, primary components of humic acid in soils or natural waters, produce hydrated electrons when they absorb UV or near-UV light.³³⁻³⁵ As compared to the technologies of subcritical Fe^0 ,²¹ vitamin $B_{12}/Ti(III)$ -citrate³⁶ and UV/KI,¹⁹ the photosensitized humic acid is more environmentally oriented and applicable since humic acid, a natural organic matter (NOM), is found in natural environments in the range of 10 ppm.

EXPERIMENTAL

1. Materials and Reagents

Perfluorooctane sulfonate potassium salt (PFOS: $C_8F_{17}SO_3^-K^+$) and perfluorooctanoate ammonium salt (PFOA: $C_7F_{15}CO_2^-NH_4^+$) were provided by 3M. Potassium iodide (KI, Fisher), humic acid sodium salt (Aldrich), and ethylenediaminetetraacetic acid (EDTA) sodium salt (Junsei, 98%) were used as received. PFOS and PFOA stock solutions were prepared at 500 mg/L, and the pH was adjusted to between 6 and 8 with HCl and NH_4OH . 1 mol/L KI and 100 mg/L humic acid stock solutions were prepared and the pH was adjusted to the circum-neutral pH ranges.

2. Photolysis

PFOX (X = S for PFOS and A for PFOA) and humic acid (or potassium iodide) stock solutions were diluted with distilled water (resistivity > 18.0 $\Omega \cdot cm$) to the desired concentrations and the final reaction volume was fixed at 30 mL in a Pyrex glass reactor with a quartz window. A monochromatic wavelength among $\lambda = 254, 302,$ and 365 nm from an 8 W-light source (UVP) was selected for irradiation to the reaction solution through the quartz window. Argon was

continuously purged through the aqueous solution. A 0.3-mL sample aliquot was taken at different time points during photolysis and diluted prior to analysis. The incident photon flux for the UV 254 nm was determined to be 5.17×10^{-5} mol/L/min by iodide/iodate actinometry with high precision.

3. Analysis

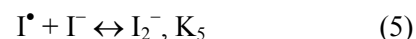
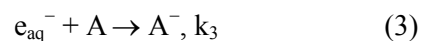
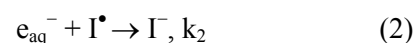
The analysis of PFOX was completed following the method described elsewhere.¹⁹ In brief, PFOX and its possible intermediates were analyzed by high-performance liquid chromatography/mass spectrometry (HPLC-MS, Agilent 1100 LC and Agilent Ion Trap) with a Bestasil C18 column. The eluent was composed of 2 mM aqueous ammonia acetate and methanol with a gradient mode at a flow rate of 0.3 mL/min. The samples were analyzed by the MS/MS (Agilent, MSD Trap) in negative mode monitoring for the molecular ions of PFOS ($m/z = 499$) and decarboxylated PFOA ($m/z = 369$).

The amount of fluoride was analyzed by ion chromatography (IC, Dionex DX-120) equipped with a Dionex IonPac AS 14 column and a conductivity detector. Aliquots (0.3 mL) that were filtered through a 0.45- μm PTFE filter (Millipore) to remove the possible flocculated humic acids were injected to the IC. The eluent was composed of 3.5 mM Na_2CO_3 and 1 mM $NaHCO_3$, and the flow rate was 1 mL/min.

RESULTS AND DISCUSSION

1. Iodide Photolysis vs. Humic acid Photolysis

Fig. 1 shows the time profiles of the aqueous PFOX degradation in the UV254 nm-irradiated iodide and humic acid solutions. In the iodide photolysis, the initial PFOS degradation is faster than that of PFOA and becomes increasingly similar as the photolysis proceeds. Iodide photochemistry for the production of the hydrated electron is well-established as follows.



where CTTS and A refer to a charge-transfer-to-solvent and electron acceptor (*e.g.*, O₂ and N₂O), respectively. At photo-stationary state where [e_{aq}⁻] becomes constant, the PFOX degradation rate could be expressed as the following:

$$-d[\text{PFOX}]/dt = k_4[e_{\text{aq}}^-] \times [\text{PFOX}] = k_4'[\text{PFOX}] \quad (6)$$

$$[\text{PFOX}]_t = [\text{PFOX}]_0 \exp(-k_4' \cdot t) \quad (7)$$

where $k_4' = k_4[e_{\text{aq}}^-]$. The dissolved oxygen molecule has been shown to be a strong electron quencher ($k_3 = 1.9 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$); thus PFOX is not degraded at all in the presence of oxygen.¹⁹ Note that UV254 nm is not able to excite PFOX

molecules since PFOX (*e.g.*, PFOA) only absorbs wavelengths shorter than *ca.* 240 nm.¹⁴

Humic acid photolysis (eqs. 8 – 10) has a significantly different effect on the PFOX degradation. As presented in Fig. 1, tiny amount of PFOA (~10%) was degraded, of which the degradation rate constant is approximately one-sixth of that of the iodide photolysis. On the other hand, the PFOS degradation rate constant in the HA solution is much higher than that of the iodide solution by a factor of 1.7 (Table 1).

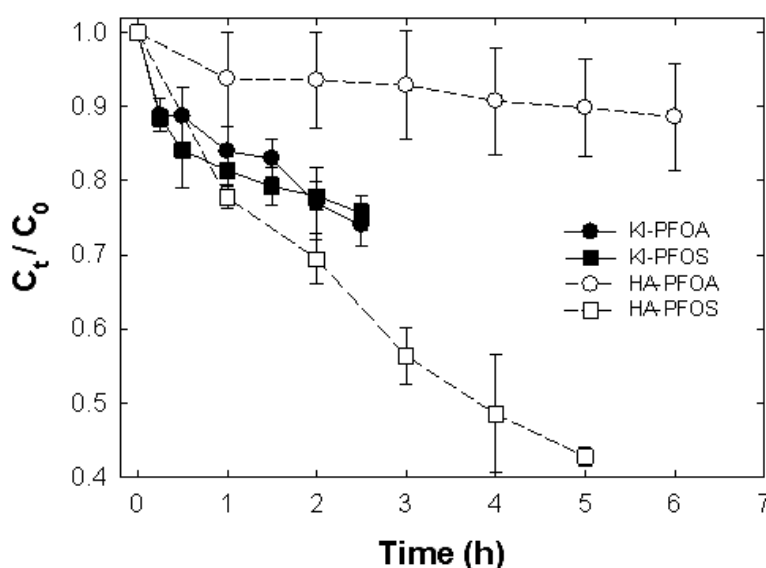


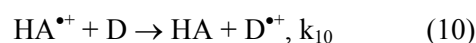
Fig. 1 – Time profiles of aqueous PFOX degradation in UV 254 nm-irradiated iodide and humic acid solutions. X refers to S for PFOS and A for PFOA. [PFOS] = 1 ppm (2.0 μM); [PFOA] = 1 ppm (2.4 μM); [KI] = 10 mM; [HA] = 50 ppm; [EDTA] = 1 mM for HA solution. Ar-purged continuously.

Table 1

Degradation rate constants ($\times 10^{-3} \text{ h}^{-1}$) of PFOA and PFOS

#	Experimental conditions ^a	PFOA			PFOS		
		UV 254	UV 302	UV 365	UV 254	UV 302	UV 365
1	HA 50ppm; PFOX 1ppm; D 1mM	17.4	16.4	9.28	174	134	105
2	HA 10ppm; PFOX 1ppm; D 1mM		12.4			55.9	
3	HA 50ppm; PFOX 1ppm; D 0.1 mM		9.78			18.4	
4	HA 50ppm; PFOX 1ppm; D 0 mM		3.77			4.20	
5	HA 50ppm; PFOX 5ppm; D1 mM					73.5	
6	HA 50ppm; PFOX 10ppm; D 1mM					25.9	
7	KI 10mM; PFOX 1 ppm	105			102		

a. HA and D refer to humic acid and electron donor (EDTA), respectively, and PFOX refers to PFOA (X = A) or PFOS (X = S).



A unique difference between the iodide and the humic acid photochemistry is that the HA system

basically requires the electron donor (D; discussed below), whereas the iodide does not necessarily require the externally added donor due to the rapid quenching of the iodine radical (I^\bullet) by the surrounding iodide (I^-) (eq. 5; $K_5 = k_5/k_{-5} > 1.2 \times 10^4$), therefore inhibiting the recombination.

2. Effects of Reaction Parameters

Fig. 2 shows the effects of UV wavelengths ($\lambda = 254, 302,$ and 365 nm) on the photodegradation of PFOX in the humic acid solution. It is obvious that the PFOS degradation rates become greater as the incident wavelengths are shorter (Fig. 2a). Humic acid has no specific light absorption band; instead, its absorptivity (*i.e.*, absorption coefficient) increases at the shorter wavelengths (Fig. 2b). This implies that more photons might be available for generating the hydrated electrons, likely leading to enhancing the PFOX degradation. However, it does not necessarily indicate the quantum yield (ϕ_e) for the production of the hydrated electron grows as the incident wavelength shortens because ϕ_e is influenced by other conditions such as photosensitizer, light intensity,

etc. For instance, Zepp *et al.*³⁵ determined ϕ_e in a 355 nm-laser flash photolysis for various natural organic matters, ranging from 1.7×10^{-3} to 7.6×10^{-3} . Wang *et al.*³³ compared the low and high intensity irradiations of the same wavelength and found that ϕ_e in natural sunlight decreased by a factor of 100, as compared to that of a highly intensive laser flash photolysis. Furthermore, Thomas-Smith and Blough³⁴ observed that ϕ_e of colored dissolved organic matters decreased with increasing wavelength (*e.g.*, $1.2 \times 10^{-4} \leq \phi_{e,296 \text{ nm}} \leq 2.7 \times 10^{-4}$; $2.1 \times 10^{-5} \leq \phi_{e,355 \text{ nm}} \leq 9.0 \times 10^{-5}$). In this study, $\phi_{e,254 \text{ nm}}$ for the PFOS and PFOA degradation were determined to be 1.7×10^{-4} and 1.3×10^{-5} , respectively, which are approximately one order of magnitude lower than that of the reported laser flash photolysis data. Note that the ϕ_e of this study does not refer to the number of e_{aq}^- produced per incident photon (eq. 8); instead, it was obtained based on the PFOX degradation rates (eq. 4), which inevitably lowered the quantum yield. ϕ_e s at the other wavelengths (302 and 365 nm) were not determined; yet they are expected to be lower than $\phi_{e,254 \text{ nm}}$.

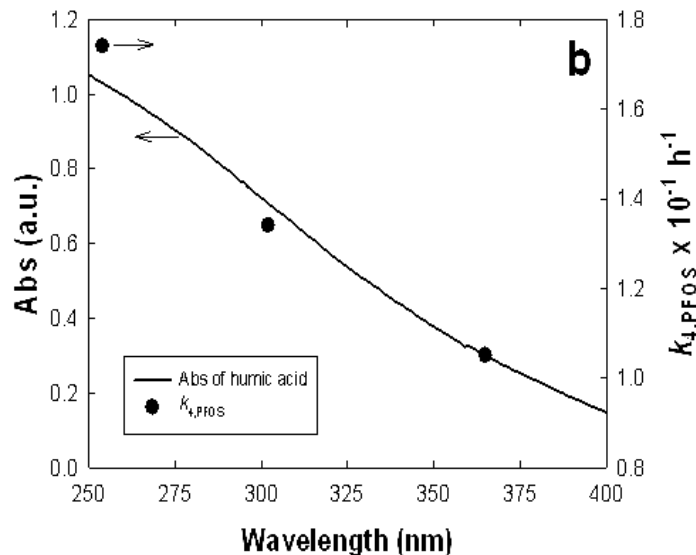


Fig. 2 – (a) Effects of UV wavelength on the photolytic degradation of PFOX in humic acid solution (b) Dependence of the degradation rates and quantum yields of PFOS on the incident wavelengths. [PFOS] = 1 ppm (2.0 μM); [PFOA] = 1 ppm (2.4 μM); [HA] = 50 ppm; [EDTA] = 1 mM; Ar-purged continuously.

The effects of the concentrations of HA and EDTA were investigated as well. As compared in Fig. 3, the PFOX degradations were enhanced as the HA concentration increased likely due to the greater degree of photo-sensitization and thereby

the larger production of the hydrated electrons. The effect of the EDTA concentration is more pronounced. In the absence of EDTA, PFOX was negligibly degraded (Fig. 3); yet the growing concentration significantly increases the PFOX

degradation rates (Table 1). Since EDTA has been usually employed as an electron donor in photosensitization systems, the role of EDTA would be similar in this HA/PFOX system. In other words, without EDTA, the HA radical (HA^\bullet) is very rapidly recombined with the hydrated electron (eq. 9), thereby effectively inhibiting the reaction of the hydrated electron and PFOX (eq. 4). However, in the presence of EDTA, the HA^\bullet can be regenerated to the HA^- by electrons transferred from EDTA (eq. 10), and this regeneration should be competitive to the recombination (eq. 9). In this regard, other studies on the comparison of electron transfer kinetics between the recombination and

the regeneration are very necessary for full understanding of this photochemistry.

The PFOS concentration also affects its degradation rates. As shown in Fig. 4, as the initial PFOS concentration increases the degradation rate decreases ($k_{4,\text{PFOS}} = 0.134, 0.0735, \text{ and } 0.0259 \text{ h}^{-1}$ at $[\text{PFOS}] = 1, 5, \text{ and } 10 \text{ ppm}$, respectively. 1 ppm PFOS equals $2.0 \times 10^{-6} \text{ M}$). However, when comparing their respective absolute amounts that were degraded for the same period of photolysis, the order of efficiency changes. For example, 6 h-photolysis leads to the degradation of 48.2, 132, and $93.2 \times 10^{-9} \text{ mol}$ of 1, 5, and 10 ppm PFOS, respectively, indicating that the photolysis is most efficient at 5 ppm.

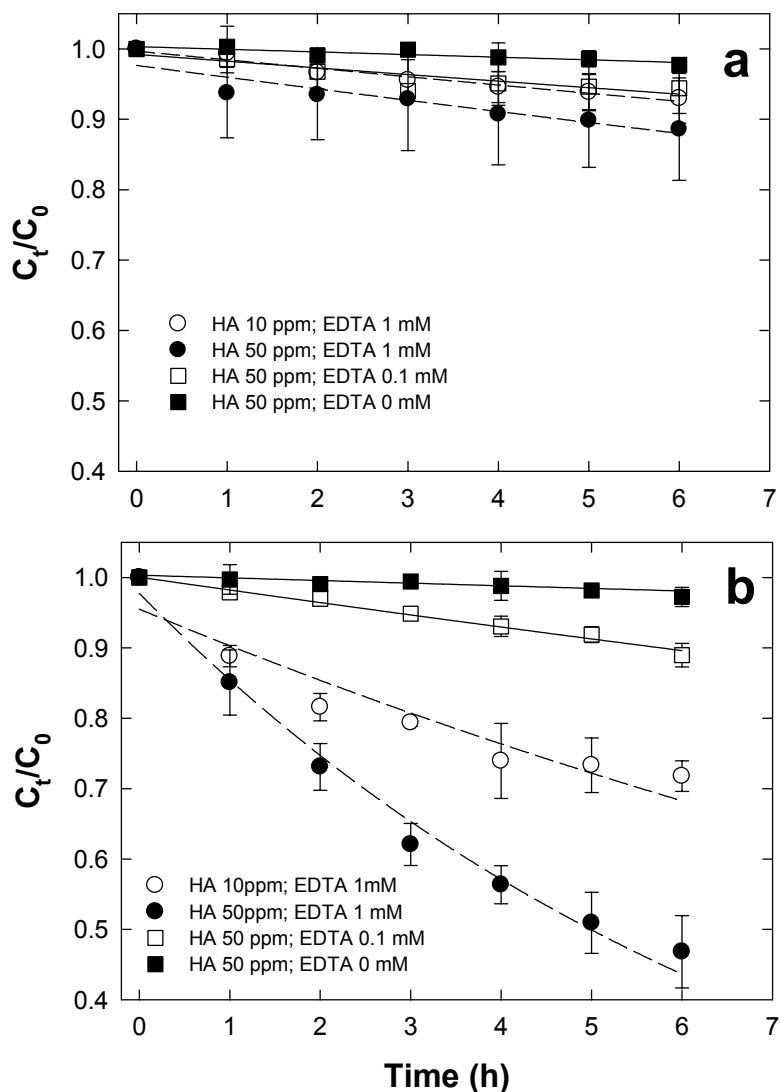


Fig. 3 – Effects of humic acid and EDTA concentrations on the degradation of (a) PFOA and (b) PFOS in UV302 nm-irradiated humic acid solution. $[\text{PFOS}] = 1 \text{ ppm}$ ($2.0 \mu\text{M}$); $[\text{PFOA}] = 1 \text{ ppm}$ ($2.4 \mu\text{M}$); Ar-purged continuously.

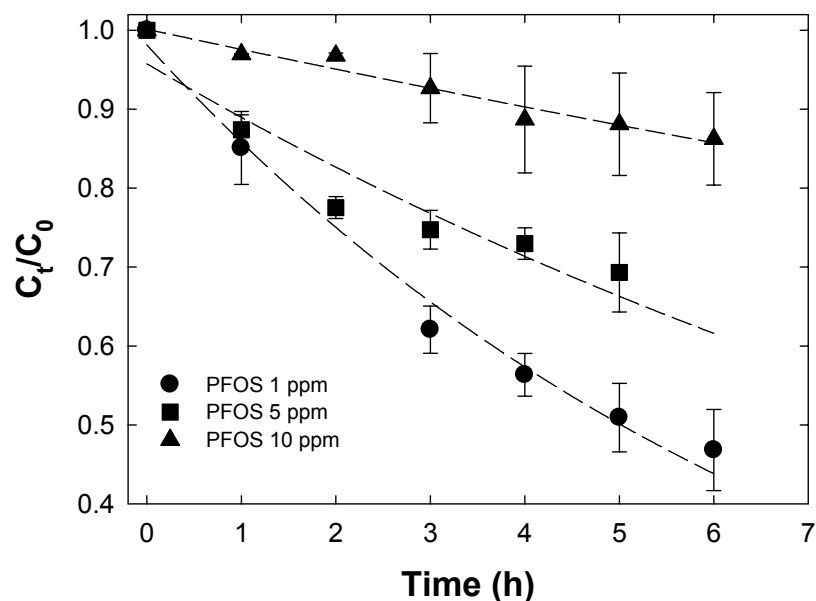


Fig. 4 – Effects of initial PFOS concentration on their degradation in UV302 nm-irradiated humic acid solution. [HA] = 50 ppm; [EDTA] = 1 mM; Ar-purged continuously.

3. Defluorination and Its Implication

The PFOX reaction with hydrated electrons eventually produces fluoride (F^-), of which the measurements would enable the exploration of the PFOX photochemistry.¹⁹ Reductive fluoride elimination is affected by the C-F bonding character, F and C electron densities, reduction/oxidation potential, anion radical stability upon accepting electrons, ionic headgroup, C-F chain length, and electron-

donating reagent strength. Iodide photolysis has been demonstrated to be capable of eliminating PFOX fluorines by their reaction with hydrated electrons. In agreement with the previous report, the PFOX photolysis eliminates fluorines of approximately 2.4 and 7.3 μM from PFOA and PFOS, respectively, in the UV-irradiated humic acid solutions for 6 hours (Fig. 5). The greater amount of fluoride liberation from PFOS is consistent with the higher PFOS reaction rate.

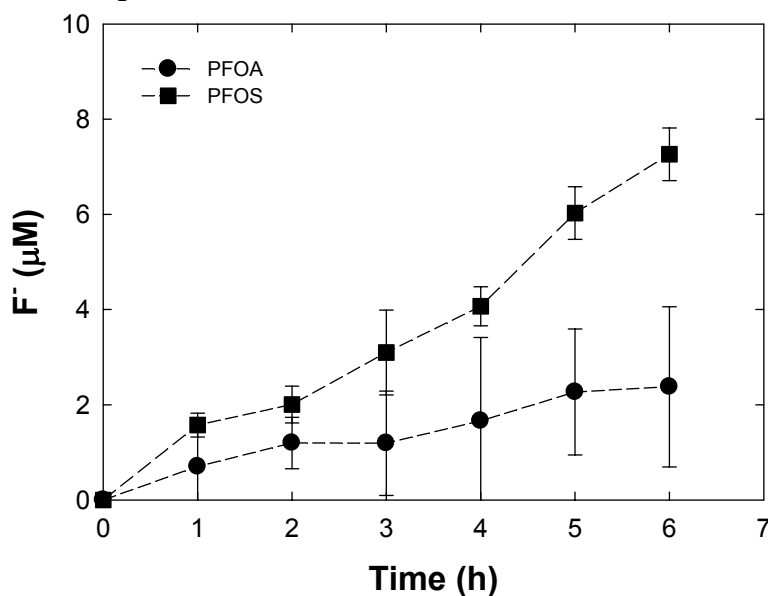


Fig. 5 – Time profiles of fluoride production during the photolytic degradation of PFOX in UV302nm-irradiated humic acid solution. [PFOS] = 1 ppm (2.0 μM); [PFOA] = 1 ppm (2.4 μM); [HA] = 50 ppm; [EDTA] = 1 mM; Ar-purged continuously.

The F-index, defined by the amount of fluoride produced per unit amount of degraded PFOX (*i.e.*, $[F^-]_{\text{produced}} / [PFOX]_{\text{degraded}}$), was also estimated. As shown in Fig. 6, the plots of $[PFOX]_{\text{degraded}}$ vs. $[F^-]_{\text{produced}}$ have slopes of 0.68 for PFOA ($R^2 = 0.85$) and 2.34 for PFOS ($R^2 = 0.93$), indicating that approximately 0.7 and 2.3 fluoride molecules are liberated as the PFOX unit molecules are degraded. The greater PFOS F-index is also observed in the iodide photolysis, suggesting that the PFOS reactivity with the hydrated electron is always higher than that of the PFOA irrespective of the UV-irradiated iodide solution and the humic acid solution. However, the humic acid photolysis should be discerned from the iodide as follows. First, the F-index values (*i.e.*, slopes) are much

smaller in the humic acid. The F-indexes of PFOS and PFOA in the iodide solution are around 9 and 2, respectively, which are *ca.* 3.8 and 2.4 times higher than those in the humic acid, respectively, despite similar degradation rates (in particular for PFOS). This suggests the existence of unknown PFOX degradation pathways that hinder the PFOX defluorination, such as the recombination among defluorinated PFOX, oxidized humic acid (or monomers), and oxidized EDTA. Second, the PFOS-to-PFOA F-index ratio of the iodide photolysis is estimated to be approximately 4.5, while that of the humic acid is approximately 3.5. This difference would arise from the much lower reactivity of PFOA in the humic acid solution.

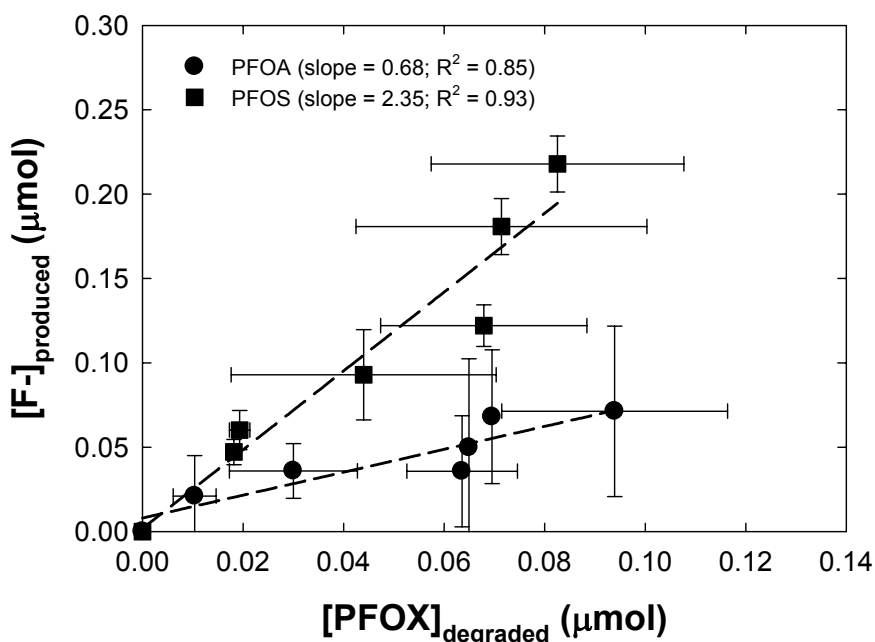


Fig. 6 – Relationships between degraded PFOX concentrations and produced fluoride concentrations. [PFOS] = 1 ppm (2.0 μM); [PFOA] = 1 ppm (2.4 μM); [HA] = 50 ppm; [EDTA] = 1 mM; UV 302 nm-irradiated; Ar-purged continuously.

The low F-index values further imply that PFOX is not completely degraded and that some partially degraded PFOX exists as ionic molecules in the solution and/or as gaseous molecules in the headspace. In the previous iodide photolysis, a number of gas-phase intermediates were identified as the iodinated and non-iodinated hydrofluorocarbons of C1 – C8, while the PFOS has a much more diverse sets of intermediates. In this study, 2 or 3 fluorides were eliminated from the PFOS, and the extent of defluorination is quite similar to that of the iodide-PFOA system which is

approximately 2. The analysis of gaseous intermediates was attempted by trapping head-space gases in a typical PFOX photolysis condition ([PFOX] = 1 ppm; [HA] = 50 ppm; [EDTA] = 1 mM; UV302 nm-irradiated for 6 hours in the presence of argon) and no gases other than background carbon dioxide were detected. This indicates that either the photolysis did not proceed sufficiently to produce the gaseous intermediates or the intermediates, if produced, remained in the aqueous phase by forming a kind of complex with the humic acid. For the latter case, the liquid phase

analysis was attempted as well, and a number of interfering molecules associated with the humic acid were observed, therefore causing difficulties in the intermediate analysis.

CONCLUSIONS

This study has demonstrated that the photosensitized humic acid can reductively degrade PFOA and PFOS in water. The degradation of the PFOA and PFOS accompanied the elimination of fluorides from the substrates with low F indexes, implying an incomplete reaction. In addition, continued photolysis would cause the degradation of humic acid and produce a number of intermediates, leading to a more complicated reactions. This would alter the degradation mechanism as well. Despite the limited condition, however, this photolysis has a significant implication that recalcitrant perfluorinated compounds could be degraded through a natural process in conjunction with sunlight and natural organic matters. The latter, primarily composed of humic acid, are commonly found at 10 ppm in drinking water and at much elevated concentrations in natural water. In addition, EDTA also has been found at 10–100 nM and sometimes at ~ μ M ranges in natural waters.³⁷

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