Effect of pH and Coexisting Species on the Photochemical Decomposition of Perfluorooctanoic Acid by Iron (III) Sulphate


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ABSTRACT
Perfluorinated compounds including perfluorooctanoic acid (PFOA), which have been detected globally in the environment and in wildlife, have recently received a great deal of attention as environmental contaminants because they are ubiquitous in the environment. In this study, the effect of pH and coexisting ions on the decomposition of PFOA was evaluated under a combined treatment of ferric ion and ultraviolet radiation. The defluorination ratio at pH 2.0 after 72 hr was 101% of the initial PFOA concentration (48 μM). The defluorination rate constant of PFOA during the initial 4 hr at pH 2.0 was 56 × 10^-3 hr^-1. Furthermore, SO₄²⁻ ions might have interfered with the complexation of PFOA with Fe³⁺. Moreover, hydroxyl radical was detected in the sample solution of pH 2.0, 3.0, and 3.5 using electron spin resonance spectroscopy. The hydroxyl radical oxidized Fe²⁺ to Fe³⁺, which was reduced by the PFOA decomposition. The strongest absorbance at 250 nm was observed at the sample solution at pH 2.0. Consequently, the photochemical decomposition for PFOA was more efficient at pH 2.0 due to the strong UV absorbance and the influence of the hydroxyl radical.

Keywords: decomposition, ferric ion, hydroxyl radical, perfluorooctanoic acid, ultraviolet

INTRODUCTION
Perfluorinated compounds have been widely used in industries as products or raw materials for surface treatment in photolithography, emulsifier in polymer synthesis, paper coatings, waxes, fire-fighting foams, and polishes because of their specific characteristics such as high interfacial activity, high thermal and chemical stability, and high light transparency (Schultz et al., 2003). These compounds have been detected globally in the environment, in wastewater treatment plants, in wildlife, and in humans (Giesy and Kannan, 2001; Sinclair and Kannan, 2006; Tanaka et al., 2008; Jin et al., 2009; Vassiliadou et al., 2010). They have recently received a great deal of attention as ubiquitous environmental contaminants (Giesy and Kannan, 2002; Schultz et al., 2003; Houde et al., 2006). In the compounds they produced including various analogues, the perfluorinated carboxylates of 3,200 - 7,200 t were exhausted globally during 1951 - 2004. Especially, perfluorooctanoic acid (PFOA) was estimated to constitute 80% of the emission amount in 2000 (Prevedouros et al., 2006). In fact, PFOA also has high water solubility compared to perfluorooctanesulfonic acid (Kauck and Diesslin, 1951; Arp et al., 2006; Harino et al., 2009).

In Japan in 2002, PFOA was designated as a Type II Monitoring Chemical Substance under the Chemical Substances Control Law. In January 2006, the United States Environmental Protection Agency (US EPA) launched a global stewardship program to
reduce PFOA emissions and its presence in products by 95% by 2010, intending its complete elimination by 2015 (U.S. EPA., 2006). However, conventional methods for treatment of wastewater such as H$_2$O$_2$ + UV light irradiation, use of Fenton’s reagent (Fe$^{2+}$ + H$_2$O$_2$), and use of TiO$_2$ photocatalyst are not applicable because hydroxyl radicals in aqueous solutions are only slightly reactive toward PFOA (Hori et al., 2004; Moriwaki et al., 2005; Tanaka et al., 2008). Therefore, an efficient removal method for PFOA is necessary to protect the water environment and improve the drinking water quality. Recently, various decomposition treatments for PFOA were examined. A combined treatment using ferric ion with ultraviolet was evaluated for the decomposition ability of PFOA wherein 78.9% of PFOA was decomposed after 4 hr using this method (Wang et al., 2008). However, the effects of pH and other factors such as coexisting ion species on the PFOA decomposition were only slightly examined. Moreover, the decomposition mechanism of PFOA has not yet been clarified. Furthermore, the iron species were examined using electron spin resonance spectroscopy (ESR) and UV/Vis absorption photometry (Hori et al., 2007). However, the effects of pH on these spectra were not examined as well as the reacting species such as the hydroxyl radical.

The effects of pH and coexisting ions in water as well as the other factors related to the decomposition of PFOA were the focus of this study. The effect of pH in water on the decomposition of PFOA was evaluated for the combined treatment using ferric ion with ultraviolet light. The effect of the coexisting ion for the decomposition of PFOA was also examined because the ion species might affect the decomposition of PFOA (Hori et al., 2007). Moreover, the reacting species were also investigated to clarify the Fe$^{3+}$ regeneration cycle by the hydroxyl radical using ESR and to clarify the decomposition mechanism using UV/Vis absorption photometry.

**MATERIALS AND METHODS**

**Materials**

Perfluorooctanoic acid (C$_7$F$_{15}$COOH, purity 96%) was purchased from Sigma-Aldrich Corp., St. Louis, MO, analytical grade iron (III) sulfate n-hydrate (Fe$_2$(SO$_4$)$_3$·nH$_2$O ($n=6$-$9$)) was purchased from Wako Pure Chemical Industries Ltd., Osaka, Japan, and 5,5-Dimethyl-1-Pyrroline-N-Oxide (DMPO) was purchased from Labotec Ltd., Tokyo, Japan. Other reagents were purchased as analytical grade or extra pure grade materials (Wako Pure Chemical Industries Ltd., Osaka, Japan and Kanto Chemical Co. Inc., Tokyo, Japan). Purified water was prepared using a Milli-Q System Direct-Q (MilliPore Corp., Bedford, TX). Pure air (99.9%) was used as well. A 1.21 mmol/L PFOA aqueous stock solution was prepared from PFOA. A 5 mmol/L Fe(III) aqueous stock solution was prepared from Fe$_2$(SO$_4$)$_3$·nH$_2$O. The number of hydrates of Fe$_2$(SO$_4$)$_3$·nH$_2$O was confirmed by forming an anhydrous salt at 180°C, it was used as 7.00 ± 0.03 in these experiments.

**Experimental procedure for photochemical defluorination**

The photochemical reactor is illustrated in Fig. 1. The photochemical reactions were conducted in a two-layer glass tubular reactor with external diameter of 108 mm and internal diameter of 84 mm. A low-pressure mercury lamp (14 W, APUV-12; 3M Co., St. Paul, MN, USA) emitting 254 nm UV light was placed at the center of the reactor with
quartz tube protection (inner diameter 20 mm). To cool the reactor, tap water flowed into the jacket between the two-layer glass reactor. The sample solution was prepared from PFOA and Fe(III) stock solutions to a concentration of 48 μM PFOA and 50 μM of ferric ions and was filled into the reactor (Wang et al., 2008). The pH of the sample solution was initially adjusted to 2.0, 3.0, 3.5, 3.7, 5.0, and 7.0. However, only pH 3.7 was not controlled. The pH adjustment was conducted using HCl, H2SO4, and NaOH after NaCl and Na2SO4 had been added to exclude the effect of the ionic strength. Ultraviolet rays were irradiated to the pH-adjusted sample solution by the low-pressure mercury light while pure air was supplied. Pure air was supplied continuously into the reactor through a microporous glass plate with a flow rate of 100 mL/min during the reaction. The samples were collected at regular intervals until 72 hr. Controls of the pH of the sample solution were not conducted during the reaction. The pH values of the sample solutions adjusted with HCl decreased from 2.0, 3.0, 3.5, 3.7, 5.0 and 7.0 to 1.8, 2.9, 3.4, 3.6, 3.9 and 4.7, respectively, after 72 hr of reaction. The changes in pH were not apparent in the sample solution at pH 2.0 adjusted with H2SO4. The decreases in pH values appear to be caused by the production of formic acid based on the reaction mechanism reported previously by Wang et al. (2008).

**Fluoride ion measurement**

Fluoride ion (F−) was measured to evaluate the defluorination ratio of PFOA by ion-chromatography (DX-120; Dionex Corp., Sunnyvale, CA, USA) consisting of a manual sample injector (injection volume: 25 μl), a pump, a guard column (IonPac AG14A, 4.0 mm i.d., 50 mm length; Dionex Corp.), a separation column (IonPac AS14A, 4.0 mm i.d., 250 mm length; Dionex Corp.), a column oven, a self-regenerating suppressor (ASRS: Dionex Corp.), and a conductivity detector. The mobile phase, a solution containing Na2CO3 (8.0 mM) and NaHCO3 (1.0 mM), was pumped into the system with a flow rate of 1.0 mL/min. The limit of detection was 0.01 mg/L. Defluorination ratio (%) was calculated using equation (1):

\[
\text{Defluorination ratio} = \left( \frac{C_F}{C_0} \times 15 \right) \times 100
\]  

(1)
where $C_F$ denotes the measured F\(^{-}\) concentration (µM), and $C_0$ denotes the initial PFOA concentration (µM). The factor 15 corresponds to the number of fluorine atoms in the PFOA molecule.

The defluorination rate constant of PFOA, $k$ (hr\(^{-1}\)), during the initial 4 hr was calculated from the slope of the pseudo-first-order kinetic curve based on the method of Wang et al. (2008), and the defluorination rate constant of PFOA was also determined in the initial 4 hr since there was a linear relation for all experimental conditions in this study. It appears that the reaction mechanism and the reacting species such as Fe\(^{3+}\) are static. The PFOA concentration, $C_{PFOA}$ (µM), was calculated using equation (2):

$$C_{PFOA} = C_0 - \{C_0 \times \text{(defluorination ratio/100)}\}. \quad (2)$$

Identification of radical species for PFOA decomposition

The identification of radical species that is related to the decomposition of PFOA was determined using an ESR spectrometer (JES-FR30EX, JEOL, Tokyo, Japan) in the X-band (9.5 GHz) at 298 K, where the ESR signal was registered at a microwave power of 4.0 mW and amplitude modulation of 0.1 mT in the field range of 328 - 343 mT. For this purpose 180 µL of sample solution was irradiated with UV light for 1 hr and subsequently collected and 20 µL of DMPO was added rapidly to the sample collected. The mixture was stirred for 10 s. The radical species were measured 1 min after DMPO was added.

Confirmation of UV/vis absorption spectra

The UV-Vis absorption spectra (200 - 500 nm) of the sample solution adjusted to several pH values were monitored using a UV-Vis spectrophotometer (UVmini-1240; Shimadzu Corp., Kyoto, Japan).

RESULTS AND DISCUSSION

Decomposition efficiency and kinetics of PFOA

The defluorination ratios of PFOA in the sample solution adjusted at several pH values from 2.0 - 7.0 are depicted in Fig. 2. The defluorination ratios increased at every pH as the UV irradiation time increased. The solution used for pH adjustment, spiked salt, defluorination ratio, defluorination rate constant, and ion concentrations used in each experimental condition are listed in Table 1. The final defluorination ratio for pH 2.0 solution after 72 hr of UV irradiation was 101%, which was higher than those for solutions of pH 3.0, 3.7, 5.0, and 7.0 (71%, 43%, 36%, and 8.7%, respectively). The defluorination ratio decreased as the pH value in the sample solution increased. The defluorination ratios of PFOA for solutions of pH 2.0 and 3.7 were almost mutually identical during the initial 4 hr of UV irradiation, although those at pH 3.5 or lower were higher than that at pH 3.7 at 72 hr. The effect of coexisting ions on the defluorination ratios for pH 2.0 solutions are depicted in Fig. 3. The defluorination ratios in sample solution, except those containing H\(_2\)SO\(_4\) and no salt and those containing HCl, H\(_2\)SO\(_4\), and Na\(_2\)SO\(_4\) reached 100%.

The decomposition of PFOA in the sample solution during the initial 4 hr could be interpreted as pseudo-first-order reaction kinetics. The pseudo-first-order kinetic curves
of defluorination of PFOA for the sample solution adjusted at several pH values are depicted in Fig. 4. The defluorination rate constants of PFOA during the initial 4 hr for solutions of pH 2.0, 3.0, 3.7, 5.0, and 7.0 were $56 \times 10^{-3}$ hr$^{-1}$, $46 \times 10^{-3}$ hr$^{-1}$, $17 \times 10^{-3}$ hr$^{-1}$, $10 \times 10^{-3}$ hr$^{-1}$, and $5 \times 10^{-3}$ hr$^{-1}$, respectively.
hr⁻¹, 53 × 10⁻³ hr⁻¹, 6.5 × 10⁻³ hr⁻¹, and 1.0 × 10⁻³ hr⁻¹, respectively. Consequently, the defluorination rate constants for solutions where HCl and NaCl were used at pH 2.0 and 3.7 were respectively about 8 times and 50 times higher than those at pH 5.0 and 7.0. The effects of coexisting ions on the pseudo-first-order kinetic curves of defluorination of PFOA at pH 2.0 are depicted in Fig. 5. The defluorination rate constants of the sample solution with HCl were higher than those of the sample solution with H₂SO₄. On the sample solution with H₂SO₄, the defluorination rate constants for solutions without spiking salt during the initial 4 hr were 9.3 × 10⁻³ hr⁻¹ and 7.2 × 10⁻³ hr⁻¹ whereas those of the sample solution with spiking salt were 27 × 10⁻³ hr⁻¹ and 6.7 × 10⁻³ hr⁻¹. The defluorination rate constant on the sample solution containing HCl and NaCl was two times that of the sample solution containing H₂SO₄ and NaCl. Moreover, the defluorination rate constant on the sample solution containing SO₄⁻² ion and Cl⁻ ion (15 mM and 20 mM, respectively) was 17 × 10⁻³ hr⁻¹, whereas that on the sample solution containing SO₄⁻² ion and Cl⁻ ion (20 mM and 20 mM, respectively) was 7.7 × 10⁻³ hr⁻¹. The defluorination rate constant of the sample solution at the fixed Cl⁻ ion concentration decreased as SO₄⁻² ion concentration increased. The defluorination rate constant decreased after 4 hr.

**Decomposition mechanism for PFOA**

Identification of the reacting species related to the decomposition of PFOA was also conducted. The ESR spectra on the sample solution are depicted in Fig. 6. The hydroxyl

![Fig. 4 - Pseudo-first-order kinetic curve of the defluorination of PFOA.](image1)

![Fig. 5 - Effect of coexisting ions on the pseudo-first-order kinetic curve of defluorination of PFOA at pH 2.0.](image2)
radical identified at $g$ values 2.019 and 2.010 was detected in the sample solution of pH 2.0, 3.0, and 3.5. Moreover, the intensity of the hydroxyl radical spectra increased as the pH value of the sample solution decreased. The relation between the relative intensity of the hydroxyl radical and the Fe concentration in the sample solution of pH 2.0 is depicted in Fig. 7. Generation of the hydroxyl radical was significantly correlated ($p < 0.01$) with the Fe concentration ($r = 0.989$). Therefore, the hydroxyl radical appears to have been generated by the reaction of Fe ions and UV light. Moreover, Fe$^{3+}$ formed the complex with PFOA when PFOA is photolyzed by 254 nm UV light (Wang et al., 2008). During this process, Fe$^{3+}$ was used and reduced to Fe$^{2+}$. However, the hydroxyl radical oxidized Fe$^{2+}$ to Fe$^{3+}$, which was reduced by the decomposition of PFOA (Wang et al., 2008). The gradual defluorination of PFOA in sample solutions of pH 3.5 or less after 4 hr (Fig. 2) is apparently the result of the regeneration of Fe$^{3+}$, as described previously. The ratio of the defluorination ratio at 4 hr to the final defluorination ratio of pH 3.7 was 0.44, which was higher than those for pH 2.0, 3.0, or 3.5 (0.21, 0.24, and 0.12, respectively). The defluorination rate of PFOA in sample solution at pH 3.7 where the hydroxyl radical is not generated slowed down after 4 hr because the PFOA decomposition resulted from the initial Fe$^{3+}$ only. Therefore, this regeneration cycle of ferric ion is important for continuous PFOA decomposition.

Moreover, the coefficients related to SO$_4^{2-}$ ion and Cl$^-$ ion to the defluorination rate constants were calculated using bivariate analysis. Both of the coefficients related to SO$_4^{2-}$ ion and Cl$^-$ ion were negative (-0.96 and -0.056, respectively), and the ratio of contribution was $r^2 = 0.695$. Therefore, the contribution of SO$_4^{2-}$ ion was stronger than that of Cl$^-$ ion in the initial defluorination rate of PFOA. The relationship between the defluorination rate constants on the sample solution of pH 2.0 and SO$_4^{2-}$ ion concentration is depicted in Fig. 8. The defluorination rate constants decreased as SO$_4^{2-}$ ion concentration increased in the aqueous solution. Therefore, SO$_4^{2-}$ ions might have interfered with the complexation of PFOA with Fe$^{3+}$. However, the defluorination ratio
on the sample solution (containing H₂SO₄ and Na₂SO₄) increased to 100%. High reactivity of the SO₄⁻ radical anion against PFOA was observed, and caused the effective decomposition of PFOA (Hori et al., 2005, 2008; Lee et al., 2009). A SO₄⁻ radical anion formed under SO₄²⁻ ion existence, as expressed in equation (3) (Yu et al., 2004; Hori et al., 2005):

\[
\text{SO}_4^- + \text{H}_2\text{O} \leftrightarrow \text{HSO}_4^- + \text{OH}^- \leftrightarrow \text{SO}_4^{2-} + \text{H}^+ + \text{OH}^- \quad (3)
\]

The reactions of SO₄⁻ radical anions and PFOA are shown as equation (4) (Hori et al., 2005).

\[
\text{SO}_4^- + \text{PFOA} \rightarrow \text{SO}_4^{2-} + \text{PFOA}^{+} \quad (4)
\]

The mechanism of PFOA⁺ after an electron transfer with SO₄⁻ was proposed by Hori et al., (2005). Therefore, the SO₄⁻ radical anions that were generated from SO₄²⁻ ions such as equation (3) might also have caused the gradual decomposition of PFOA in this study.
Moreover, Cl\textsuperscript{-} ions can reportedly interfere with the complexation of short-chain (C\textsubscript{3}-C\textsubscript{5}) perfluorocarboxylic acids (PFPeA) with Fe\textsuperscript{3+} because the decomposition ratio using FeCl\textsubscript{3}·6H\textsubscript{2}O was lower than that of Fe\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}·7.5H\textsubscript{2}O on the photochemical decomposition of PFPeA (Hori \textit{et al.}, 2007). In this study, the relation between the defluorination rate constants and the increased Cl\textsuperscript{-} concentration was not clear for the aqueous solution with Fe\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}·nH\textsubscript{2}O (Table 1). However, the contribution of Cl\textsuperscript{-} ion by the bivariate analysis was much smaller than that of SO\textsubscript{4}\textsuperscript{2-} ion in the decomposition of PFOA. Therefore, the interference of the PFOA-Fe complexation by Cl\textsuperscript{-} ions appears to be affected by the chemical formula of the Fe compound used. Furthermore, because the defluorination ratio for pH 2.0 was also high, Cl\textsuperscript{-} generated by the reaction between Fe\textsuperscript{3+} and Cl\textsuperscript{-} with the UV irradiation (Moraes \textit{et al.}, 2004) might react also with PFOA as well as C\textsubscript{3}F\textsubscript{7}OCH\textsubscript{3} (Nohara \textit{et al.}, 2001), and might be related to the PFOA decomposition. However, Cl\textsuperscript{-} ion concentrations have not changed after the reaction; Cl\textsuperscript{-} ion concentrations in the sample solutions containing 20 mM SO\textsubscript{4}\textsuperscript{2-} ions were 19.5 - 19.8 mM during 0 - 72 hr. Therefore, the reported reactions by Moraes \textit{et al.} (2004) and Nohara \textit{et al.} (2001) might be apparent in this study. Chloride ion might be mainly related to the complexation of PFOA with Fe\textsuperscript{3+}, and affected the UV absorption.

The UV-Vis absorption spectra (200 - 500 nm) of the sample solution that had been adjusted to several pH values were also measured and are depicted in Fig. 9. Strong absorbance at 250 nm (main waveband of used UV lamp) was observed at pH 2.0. The absorbance at 300 nm was also observed at pH 3.0 and 3.7, and was not observed in pH 5.0 and 7.0. Therefore, the decomposition mechanism of PFOA might be different under pH 2.0, 3.0, 3.7, 5.0 and 7.0. Moreover, the UV absorption of PFOA decreased as the pH value increased. Reportedly, the solubility of PFOA in water is as high as 9,500 mg/L at 25°C (Kauck \textit{et al.}, 1951). Although the reactivity of PFOA decreased with the increase of SO\textsubscript{4}\textsuperscript{2-} ion under the same pH conditions (pH 2.0), it is not obvious that the decrease of the solubility of PFOA caused the decrease of its reactivity at pH 3.0 and 7.0. Furthermore, the colloid which is believed to be iron was observed under pH 7.0. The sample solution was colorless at pH 3.0 or less, and was changed to light-brown transparent due to iron as the pH value increased. The reactivity of PFOA might have decreased by the decrease of the solubility of iron in the higher pH regions. The effects of coexisting ions on the UV-Vis spectra of PFOA at pH 2.0 are depicted in Fig. 10. Strong absorbance at 250 nm was observed for every type of sample solution. Absorbance at 280 - 350 nm was not observed on the sample solution with Cl\textsuperscript{-} ions, but absorbance was observed for sample solution without Cl\textsuperscript{-} ions. The spike of HCl and NaCl appears to have caused the decrease of the UV-Vis absorbability of PFOA-Fe complex at 280 - 350 nm. Therefore, the photochemical decomposition of PFOA occurred more efficiently under pH 2.0 by the strong UV absorbance and the relation of the hydroxyl radical.
Fig. 9 - UV-vis spectra of PFOA.

Fig. 10 - Effect of coexisting ions on UV-vis spectra of PFOA at pH 2.0.
CONCLUSION
In this study, PFOA decomposition was examined under several pH conditions to ascertain the effects of pH of the sample solution. Decomposition was conducted by combined treatment using ferric ion with ultraviolet light. The final defluorination ratio at pH 2.0 was higher than those at pH 3.0, 3.5, 3.7, 5.0, and 7.0. The defluorination of PFOA on the sample solution of pH 3.7 was stopped 4 hr later, whereas that on the sample solution that was lower than pH 3.5 progressed gradually 4 hr later. The defluorination rate constant of PFOA during the initial 4 hr under pH 2.0 was $56 \times 10^{-3}$ hr$^{-1}$, which was about 8 times and 50 times higher than those at pH 5.0 and 7.0, respectively. Moreover, the defluorination rate constant was lower for higher SO$_4^{2-}$ ion concentrations in the aqueous solution. The SO$_4^{2-}$ ions might interfere with the complexation of PFOA with Fe$^{3+}$. The hydroxyl radical was detected mostly in the sample solution of pH 2.0. The hydroxyl radical was generated by the reaction of Fe ions and UV light. Decomposition of PFOA at pH values lower than 3.5 after 4 hr appears to have been caused by Fe$^{3+}$ regenerated by the hydroxyl radical. Strong absorbance at 250 nm was observed at pH 2.0. The PFOA photochemical decomposition occurred more efficiently under pH 2.0 because of the strong UV absorbance and the relation of the hydroxyl radical.

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