BEHAVIOR OF DISSOLVED IRON PHOTOCHEMICAL DECOMPOSITION OF PERFLUOROOCTANOIC ACID BY IRON (III) SULFATE

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Introduction

Perfluorocarboxylic acids (PFCAs) such as perfluorooctanoic acid ($C_7F_{15}COOH$, PFOA) have been used widely as products or raw materials for surfactants, surface treatment agents, and so forth because of their high interfacial activity, high thermal and chemical stability, and high light transparency[1,2].

Recently, perfluorinated-compound-related issues have changed. Along with particular efforts by one national agency (US EPA) in 2006, a global stewardship program was launched to reduce PFOA emissions and PFOA contents in products by 95% by 2010, with the aim of its complete elimination by 2015[3]. In Japan in 2002, PFOA was designated as a Type II Monitoring Chemical Substance under the Chemical Substances Control Law. However, because hydroxyl radicals in aqueous solution are only slightly reactive to PFOA, conventional methods of wastewater treatment, such as advanced oxidation processes, are not applicable[4–6]. Efforts to eliminate them from facility emissions and products began after it was demonstrated that PFCAs are persistent and that they bioaccumulate in the environment[3]. Now, an efficient PFOA removal method is being sought to protect water environments and drinking water quality. Various PFOA decomposition treatments have been examined[7–9]. A combined treatment using ferric ion with ultraviolet irradiation was evaluated for its PFOA decomposition capability. Reportedly, PFOA was decomposed 78.9% during 4 hr using the method[8]. We previously investigated the effects of pH, coexisting ions, and reacting species on a defluorination ratio and a defluorination rate constant for PFOA decomposition[10]. Results show that PFOA photochemical decomposition occurred more efficiently under pH 2.0 because of the strong UV absorbance and the hydroxyl radical. Reportedly, the hydroxyl radical is related to direct decomposition of PFOA, but only to a slight degree[4–6]. At low pH, the relation between strong generation of the hydroxyl radical and the continuous PFOA decomposition has not been clarified. The behavior of dissolved Fe ion has not been examined during the decomposition process. Furthermore, the behavior of PFCAs has not been clarified.

This study examined the behavior of dissolved Fe ion in water as a factor related to PFOA decomposition in addition to the effects of pH. The behavior and the effect of dissolved Fe ion in water under several pH conditions were examined to clarify the Fe^{3+} regeneration cycle. Moreover, the intermediate PFCA decomposed from PFOA as a starting material was investigated. Variations of the hydroxyl radical monitored using ESR were investigated under pH 2.0 and pH 3.7. Furthermore, the relation between the decomposition rate and the product of PFOA and Fe^{3+} concentrations was examined as a factor related to PFOA decomposition.

Materials and methods

Before filling into the reactors, sample solutions containing both 48 μM PFOA and 50 μM of ferric ions were prepared from PFOA and Fe(III) stock solutions[8,10]. Those pH values were adjusted initially to 2.0, 3.7, and 5.0. Ultraviolet irradiation of the pH-adjusted sample solution was conducted using a low-pressure mercury light while pure air was supplied. The samples, which were collected at regular intervals until 72 hr, were measured for concentration of fluoride ion (F^-), Fe ion, PFCAs, and intensity of radical species. The pH values of the sample solutions adjusted with HCl decreased from 2.0, 3.7, and 5.0 to 1.8, 3.6, and 3.9, respectively, after 72 hr of reaction. Decreased pH values appear to result from the production of formic acid based on the reaction mechanism reported previously by Wang et al. (2008).

Fluoride ion was measured using ion chromatography (DX-120; Dionex Corp., Sunnyvale, CA, USA) to evaluate the PFOA defluorination ratio. The defluorination ratio (%) was calculated using equation (1):

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

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.

To evaluate the PFOA decomposition ratio and to examine the decomposition behavior, PFOA and perfluoroheptanoic acid (PFHpA) were measured using HPLC (LC-10Avp; Shimadzu Corp., Kyoto, Japan) equipped with a UV-Vis absorbance detector (wavelength: 210 nm). The PFOA decomposition rate in each collected time of sample solution was calculated as the product of the decomposition rate constant in each time and the PFOA concentration. The PFOA defluorination rate (μM·h^{-1}) was calculated using the pseudo-first-order kinetic.

The identification of radical species that is related to PFOA decomposition 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 was subsequently collected. Then 20 μl of DMPO was added rapidly to the collected sample. The mixture was stirred for 10 s. The radical species were measured 1 min after DMPO was added.

Iron species such as Fe^{2+} and Fe^{3+} in sample solutions were determined using spectrometry with 1,10-phenanthroline based on Japanese Industrial Standard (JIS) K 0102 "Testing methods for industrial wastewater"[11].

Results and discussion
PFOA Decomposition efficiency

Defluorination ratios of PFOA in the sample solution adjusted at pH 2.0, 3.7, and 5.0 are depicted in Fig. 1. The defluorination ratios increased at every pH as the UV irradiation time increased. The final defluorination ratio at pH 2.0 after 72 hr irradiation was 99% of the initial PFOA (48 μM), which was higher than those at pH 3.7, and 5.0 (38%, and 39%, respectively). The defluorination ratio increased as the pH value in the sample solution decreased. Defluorination ratios of PFOA at pH 2.0 and 3.7 increased gradually after 24 hr, although that at pH 5.0 increased linearly until 48 hr. Increase of the defluorination ratio at pH 5.0 appears to result from the decrease in pH value with the production of formic acid on the PFOA decomposition process.

Effect of pH conditions for PFCA concentrations on PFOA decomposition are depicted in Fig. 2. The PFOA concentration decreased under every pH condition as the UV irradiation time increased, and those of PFHpA increased. The PFOA decomposition at pH 5.0 occurred only slightly during the initial 4 hr because Fe^{3+} was low, and it had started after 4 hr. The PFOA concentration decreased early more as the pH value decreased, and PFOA at pH 2.0 and pH 5.0 had been decomposed completely by 72 hr. However, the final PFOA defluorination ratios at pH 2.0, 3.7, and 5.0 were 99%, 38%, and 39%, respectively (Fig. 2). Moreover, the residual ratio of PFHpA, which is an intermediate produced during the decomposition process starting from PFOA, was 4.2% at pH 2.0 after 72 hr, which was lower than that of either pH 3.7 or pH 5.0 (26% and 24%, respectively). A similar trend might be confirmed in the decomposition of PFHpA. Therefore, the sample solution pH appears to affect the decomposition of intermediate PFCAs in the PFOA decomposition process.
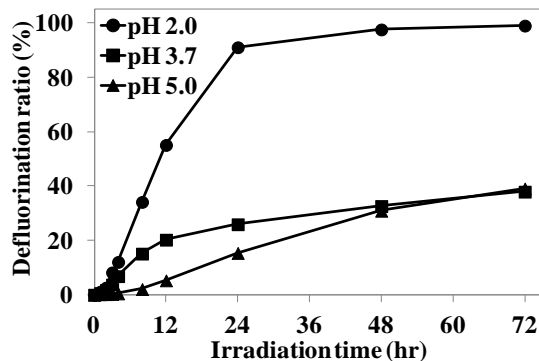

Fig. 1. Defluorination ratios for PFOA decomposition on ultraviolet irradiation.
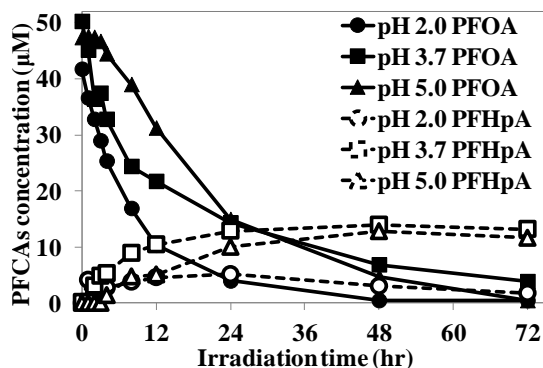
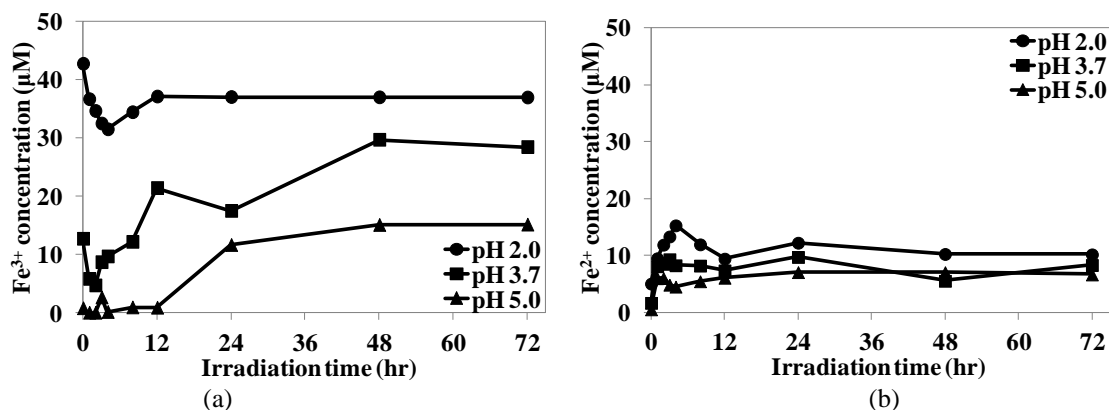Fig. 2. Effect of pH conditions for PFCAs concentrations on PFOA decomposition.

Fig. 3. Effect of pH conditions for dissolved Fe ion species on PFOA decomposition: (a) Fe^{3+} ion concentration and (b) Fe^{2+} ion concentration.

Redox behavior of dissolved Fe ion species and confirmation of Fe^{3+} regeneration

Effects of pH conditions for dissolved Fe ion species on PFOA decomposition are depicted in Fig. 3. The Fe^{3+} ion concentrations at every pH were decreased during the initial 2–4 hr. They increased after 4 hr. The Fe^{2+} ion concentrations at every pH were increased during the initial 2–4 hr, and decreased after 4 hr. The Fe^{2+} ion concentration changed continuously with the Fe^{3+} ion concentration. Reportedly, Fe^{3+} formed a complex with PFOA and PFOA is photolyzed by 254 nm UV light[8]. During this process, Fe^{3+} was used and reduced to Fe^{2+}. However, the hydroxyl radical suggested oxidizing Fe^{2+} to Fe^{3+}, which was reduced by the PFOA decomposition[8]. Results suggest that this regeneration cycle of ferric ion is important for continuous PFOA decomposition at lower pH, where the hydroxyl radical is generated[10]. Therefore, Fe^{3+} concentrations decreased as Fe^{2+} concentrations increased during the initial 4 hr because of Fe^{3+} was more reduced to Fe^{2+} by the active decomposition of PFOA, whereas Fe^{3+} concentrations increased as Fe^{2+} concentrations decreased after 4 hr because of the Fe^{3+} oxidization regeneration exceeded the Fe^{3+} reduction consumption by the gradual decomposition with the decrease of PFOA. A total dissolved Fe ion concentration at pH 2.0 changed only slightly during UV irradiation. The total dissolved Fe ion concentrations at pH 3.7 and pH 5.0 were low from 0 hr because of the solubility of iron. However, the concentrations appear to increase gradually because of the change of pH value in the solution by the production of formic acid during the reaction.

Effects of pH conditions for the relative intensity of the hydroxyl radical are depicted in Fig. 4. The relative intensity of the hydroxyl radical at pH 2.0 decreased as PFOA decomposed, whereas that at pH 3.7 increased. The radical was not detected at pH 5.0. The relative intensity at pH 2.0 decreased remarkably during the initial 4 hr. The hydroxyl radical appears to have reacted quickly with the increase of Fe^{2+} reduced with the PFOA decomposition (Fig. 3b). The hydroxyl radical is generated by the reaction of Fe ions and UV light, and also
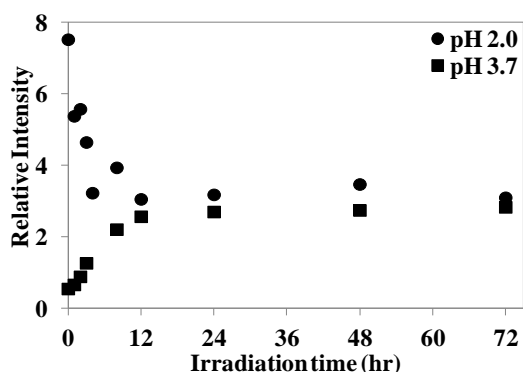

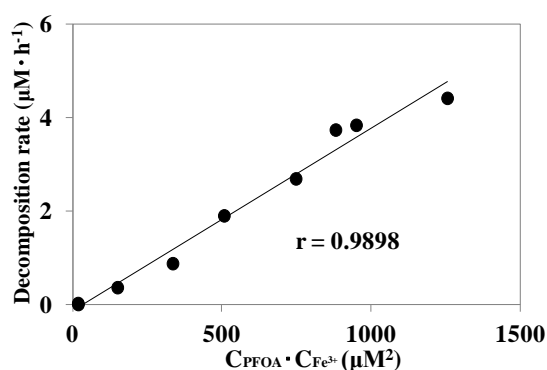Fig. 4. Effect of pH conditions for the relative intensity of the hydroxyl radical.

Fig. 5. Relation between PFOA decomposition rate at pH 2.0 and the product of PFOA and Fe^{3+} concentrations.

from the PFOA decomposition process[8]. Therefore, the relative intensities of the hydroxyl radical appear to have been constant because the PFOA decomposition became gradual and eventually ceased. Consequently, results clarified that the regeneration cycle of ferric ion is attributable to the hydroxyl radical. Moreover, we reported previously that the hydroxyl radical was not detected at pH 3.7, although it was detected at pH 3.5[10]. The increase of the relative intensity at pH 3.7 resulted from the slight change of pH value.

Factors related to PFOA decomposition

The relation between the PFOA decomposition rate at pH 2.0 at each collected time of sample solution and the product of PFOA and Fe^{3+} concentrations were examined to clarify factors related to PFOA decomposition. Both relations are depicted in Fig. 5. The PFOA decomposition rate was correlated significantly ($p < 0.01$) with the product of PFOA and Fe^{3+} concentrations ($r = 0.9898$) until 1–72 hr. Both relations fitted the second-order kinetics. The decomposition rate depended on the product of PFOA and Fe^{3+} concentration. Therefore, for the PFOA decomposition mechanism, results clarified that both the PFOA and Fe^{3+} concentrations are regulatory factors. Neither relation was observed at pH 3.7 or pH 5.0. For higher pH, the regulatory factor of the PFOA decomposition might differ from that at pH 2.0.

The intermediate PFCA, which are produced during decomposition from PFOA, was investigated. PFOA had mostly decomposed at every pH value by 72 hr, although PFHpA at pH 3.7 and pH 5.0 remained: 24–26%. The sample solution pH apparently affects the decomposition of intermediate PFCAs during PFOA decomposition. Moreover, at pH 2.0, Fe^{3+} concentrations decreased as Fe^{2+} concentrations increased during the initial 4 hr, although Fe^{3+} concentrations increased as Fe^{2+} concentrations decreased after 4 hr. Furthermore, the hydroxyl radical reacted quickly with the increase of Fe^{2+} reduced during the PFOA decomposition. Consequently, results clarified that the regeneration cycle of ferric ion is attributable to hydroxyl radical. The relation between the PFOA decomposition rate at pH 2.0 and the product of PFOA and Fe^{3+} concentrations was examined to clarify factors related to the PFOA decomposition. Both relations fitted the second-order kinetics, and the decomposition rate depended on the product of PFOA and Fe^{3+} concentration. Therefore, it was clarified for the PFOA decomposition mechanism that both the PFOA and Fe^{3+} concentration are regulatory factors.

Acknowledgements

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