

## Activation of persulfate by UV and Fe<sup>2+</sup> for the defluorination of perfluorooctanoic acid

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**Abstract.** Efficient defluorination of perfluorooctanoic acid (PFOA) was achieved by integrating UV irradiation and Fe<sup>2+</sup> activation of persulfate (S<sub>2</sub>O<sub>8</sub><sup>2-</sup>). It was found that the UV-Fe<sup>2+</sup>, Fe<sup>2+</sup>-S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, and UV-S<sub>2</sub>O<sub>8</sub><sup>2-</sup> processes caused defluorination efficiency of 6.4%, 1.6% and 23.2% for PFOA at pH 5.0 within 5 h, respectively, but a combined system of UV-Fe<sup>2+</sup>-S<sub>2</sub>O<sub>8</sub><sup>2-</sup> dramatically promoted the defluorination efficiency up to 63.3%. The beneficial synergistic behavior between Fe<sup>2+</sup>-S<sub>2</sub>O<sub>8</sub><sup>2-</sup> and UV-S<sub>2</sub>O<sub>8</sub><sup>2-</sup> was demonstrated to be dependent on Fe<sup>2+</sup> dosage, initial S<sub>2</sub>O<sub>8</sub><sup>2-</sup> concentration, and solution pH. The decomposition of PFOA resulted in generation of shorter-chain perfluorinated carboxylic acids (PFCAs), formic acid and fluoride ions. The generated PFCAs intermediates could be further defluorinated by adding supplementary Fe<sup>2+</sup> and S<sub>2</sub>O<sub>8</sub><sup>2-</sup> and re-adjusting solution pH in later reaction stage. The much enhanced PFOA defluorination in the UV-Fe<sup>2+</sup>-S<sub>2</sub>O<sub>8</sub><sup>2-</sup> system was attributed to the fact that the simultaneous employment of UV light and Fe<sup>2+</sup> not only greatly enhanced the activation of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> to form strong oxidizing sulfate radicals (SO<sub>4</sub><sup>•-</sup>), but also provided an additional decarboxylation pathway caused by electron transfer from PFOA to in situ generated Fe<sup>3+</sup>.

**Keywords:** perfluorooctanoic acid; synergism; persulfate; UV; ferrous ions

### 1. Introduction

Perfluorooctanoic acid (C<sub>7</sub>F<sub>15</sub>COOH, PFOA) is recognized as ubiquitous contaminants in water, wildlife and humans. Because the strong C-F bond (Vecitis *et al.* 2009), this compound shows high physical and chemical stability (Hurley *et al.* 2004). Its bioaccumulation and toxicity have adverse effect on human health and ecosystem (Melzer *et al.* 2010, Walters and Wallace 2010). Therefore, PFOA is recognized as a new kind of environmentally persistent organic pollutants (POPs) (Wang *et al.* 2009). It is urgent to develop effective methods to degrade this compound into harmless species.

Several advanced oxidation processes (AOPs) based on the generation of hydroxyl radicals (•OH) have been conducted to degrade perfluorinated compounds (PFCs). However, these systems

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were found not to be so effective (Hori *et al.* 2004, Schröder and Meesters 2005), possibly because that PFOA contains no hydrogen atoms available for the abstraction by  $\bullet\text{OH}$  (Li *et al.* 2012). It was reported that an extreme acidic condition (i.e.,  $\text{pH} < 2.0$ , perchloric acid) increased the reaction of perfluorocarboxylic anions with photogenerated holes in excited  $\text{TiO}_2$ , and improved the degradation of PFOA and shorter-chain PFCAs (Dillert *et al.* 2007, Panchangam *et al.* 2009b). Recently, we found that the UV-Fenton system could efficiently degraded PFOA, because the introduction of UV not only favored the production of abundant  $\bullet\text{OH}$ , but also enhanced C-F bond breakage (Tang *et al.* 2012). In comparison with  $\bullet\text{OH}$ , sulfate radical ( $\text{SO}_4^{\bullet-}$ ) was considered to be more effective in the PFOA degradation. Hori *et al.* (2005) found that PFOA was completely decomposed in the presence of  $\text{S}_2\text{O}_8^{2-}$  after 4 h of photo irradiation under oxygen atmosphere (0.48 MPa). The heated ( $80^\circ\text{C}$ )  $\text{O}_2$ -containing  $\text{S}_2\text{O}_8^{2-}$  system led to a defluorination efficiency of 77.5% for the added PFOA after 6 h of reaction (Hori *et al.* 2008). The combination of two or more AOPs was also investigated and such combined techniques were proven to be more effective than a single one (Lee *et al.* 2009, 2010, Panchangam *et al.* 2009a, Vecitis *et al.* 2010). Lee *et al.* (2009) reported the microwave-hydrothermal treatment with  $\text{S}_2\text{O}_8^{2-}$  could decompose 92.4% of PFOA within 1 h at  $130^\circ\text{C}$ . By adding trace amount of zero-valent iron (ZVI) to this system, the PFOA decomposition rate constant was increased from 0.48 to  $0.88 \text{ h}^{-1}$  at  $90^\circ\text{C}$  (Lee *et al.* 2010), because ZVI could decompose PFOA by itself (Hori *et al.* 2006). However, the above applications of persulfate oxidation to remediate PFOA contamination always coupled with an extreme reaction conditions such as elevated temperatures ( $80\text{-}130^\circ\text{C}$ ) and pressurization (0.48 MPa,  $\text{O}_2$ ). As a cost-effective and environmental-friendly alternative, a treatment method under mild conditions, close to those encountered at the atmospheric environment, is urgently needed. Since  $\text{Fe}^{2+}$  is an excellent activator to catalyze the formation of  $\text{SO}_4^{\bullet-}$  from  $\text{S}_2\text{O}_8^{2-}$ , an integration of  $\text{Fe}^{2+}$ - $\text{S}_2\text{O}_8^{2-}$  with other AOPs may improve the oxidation of PFOA under mild conditions. The main drawbacks of the  $\text{Fe}^{2+}$ - $\text{S}_2\text{O}_8^{2-}$  system were the slow regeneration of  $\text{Fe}^{2+}$  and the generation of  $\text{Fe}(\text{OH})_3$  sludge. It was worth noting that the  $\text{Fe}^{3+}$ -complex as  $\text{Fe}(\text{OH})^{2+}$  species can be excited under UV irradiation to re-generate  $\text{Fe}^{2+}$  and additional  $\bullet\text{OH}$  (Brillas *et al.* 2009). Moreover, the UV irradiation would induce an intramolecular oxidation-reduction caused by an electron transfer from PFCAs to  $\text{Fe}^{3+}$ , leading to the degradation of PFCAs and the regeneration of  $\text{Fe}^{2+}$  (Hori *et al.* 2007, Wang *et al.* 2008). In addition, the assistance of UV irradiation promotes the production of  $\text{SO}_4^{\bullet-}$  through decomposition  $\text{S}_2\text{O}_8^{2-}$  (Lau *et al.* 2007). Hence, the introduction of UV irradiation is expected to improve greatly the overall catalytic efficiency of  $\text{Fe}^{2+}$ - $\text{S}_2\text{O}_8^{2-}$  system toward the PFOA degradation. The present work is focused on the integration of UV irradiation and  $\text{Fe}^{2+}$  to activate  $\text{S}_2\text{O}_8^{2-}$  in the PFOA degradation at atmospheric environment, and aims at investigating the synergistic PFOA degradation in the UV- $\text{Fe}^{2+}$ - $\text{S}_2\text{O}_8^{2-}$  system. This proposed process may be considered as a photo-Fenton-like process, where persulfates are used instead of  $\text{H}_2\text{O}_2$ . The effect of several important operational parameters such as pH,  $\text{Fe}^{2+}$  and  $\text{S}_2\text{O}_8^{2-}$  concentrations were studied, and the catalytic mechanism was also exploited.

## 2. Materials and methods

### 2.1 Materials

PFOA ( $\text{C}_7\text{F}_{15}\text{COOH}$ , 96%), heptafluorobutyric acid (PFBA,  $\text{C}_3\text{F}_7\text{COOH}$ , 99%) and pentafluoropropionic acid (PFPrA,  $\text{C}_2\text{F}_5\text{COOH}$ , 97%) were purchased from Acros (New Jersey, y

wIUSA). Perfluoroheptanoic acid (PFHpA,  $C_6F_{13}COOH$ , 98%) was purchased from Alfa Aesar (Lancs, UK). Undecafluorohexanoic acid (PFHeA,  $C_5F_{11}COOH$ , 98%) and perfluoropentanoic acid (PFPeA,  $C_4F_9COOH$ , 98%) were purchased from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan). Ferrous sulfate, ferric sulfate, potassium peroxydisulfate, trisodium citrate, sodium nitrate were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All the chemicals were analytical grade and were used without further purification. Deionized water was used in the present work.

## 2.2 Degradation experiment

The experimental set-up was equipped with a cooling water-jacketed cylindrical quartz photoreactor and a 9 W low-pressure mercury (mainly emitting 254 nm UV light) as the light source located at the center of the reactor with a quartz tube protection. Cooling water was circulated to maintain the system at room temperature ( $25 \pm 1^\circ C$ ). In a typical experiment, a mixture solution (200 mL) containing PFOA ( $20.0 \text{ mol L}^{-1}$ ) and ferrous sulfate ( $1.0 \text{ mmol L}^{-1}$ ) was adjusted to pH 5.0 by using  $0.1 \text{ mol L}^{-1}$  NaOH. After  $S_2O_8^{2-}$  ( $30.0 \text{ mmol L}^{-1}$ ) was added into the solution, the degradation was immediately initiated by switching on the UV lamp. The reaction solution was magnetically stirred throughout the experiment run. At given time intervals, a liquid aliquot (1-2 mL) was sampled from the irradiated solution for analysis. All degradation experiments were conducted with duplicate and the averaged values were presented in the results.

## 2.3 Analytical methods

The concentrations of PFOA and the formed shorter-chain PFCAs were analyzed by HPLC (Agilent 1100, USA) coupled with a Trap-XCT ion-trap MS (Applied Biosystems, USA). HPLC separation was performed with a ZORBAX Eclipse XDB- $C_{18}$  ( $150 \text{ mm} \times 2.1 \text{ mm}$ , 5 m). The mobile phase was an aqueous solution containing methanol and  $5 \text{ mmol L}^{-1}$  ammonium acetate (pH 6.0) delivered with a flow rate of  $0.2 \text{ mL min}^{-1}$ . The operating gradient was achieved by increasing methanol from 40% to 80% in 10 min, holding on 5 min and then reverting to initial conditions within 2 min. The equilibration time was 8 min between two successive samples. The injected volume was 5  $\mu\text{L}$  and column temperature was kept at  $40^\circ C$ . The electro-spray ionization conditions in the negative ion mode were as follows: drying nitrogen gas flow rate of  $350 \text{ L h}^{-1}$  (40 psi), source temperature  $120^\circ C$ , capillary voltages 2.0 kV, the cone voltage 12V. Quantitative approach used multiple reactions monitoring (MRM), and quantization was monitored as corresponding [M-H]<sup>-</sup> for PFOA and its degradation products in the single MS mode and using external standard by peak area. External calibration curves for PFOA and other PFCAs were established from 1.0 to 20.0 and from 0.01 to 4.0  $\text{mol L}^{-1}$ , respectively. The detection limit of was  $0.001 \text{ mol L}^{-1}$  for these compounds.

The concentration of formic acid was determined by a DIONEX ion-chromatography system (ICS-3000) with a conductivity detector, IonPac AS15 (250 mm length  $\times$  4 mm i.d.) analytical column, IonPac AG15 (50 mm length  $\times$  4 mm i.d.) guard column, and anion ASRS electrolytic suppressor (ASRS 300, 4 mm, suppressor current of 134 mA). The mobile phase was KOH with a flow rate of  $1.2 \text{ mL min}^{-1}$  and the injection volume was 25  $\mu\text{L}$ . The operating gradient was conducted by increasing KOH from 5 to 45  $\text{mmol L}^{-1}$  in 18 min, holding on 12 min and then reverting to initial conditions within 6 min.

The quantification of  $Fe^{2+}$  ion was monitored with the 1,10-phenanthroline spectrophotometric method by measuring the absorbance at 510 nm according to GB/T 14427-2008. Persulfate was

determined with an iodometric method (Frigerio 1963). The formation of  $\bullet\text{OH}$  was evaluated by adding coumarin ( $0.2 \text{ mmol L}^{-1}$ ) as a fluorescence probe into the degradation systems, where coumarin readily reacts with  $\bullet\text{OH}$  to form highly fluorescent 7-hydroxycoumarin (Luo *et al.* 2010). The concentration of fluoride ion was determined with a fluoride ion selective electrode, where the limit of detection of fluoride ion was  $0.53 \text{ mol L}^{-1}$ . Defluorination efficiency (DE) was calculated as follows

$$DE = \frac{C_{F^-}}{C_0 \times 15} \times 100$$

where  $C_{F^-}$  is concentration of fluoride ion,  $\text{mol L}^{-1}$ ,  $C_0$  is initial concentration of PFOA, and the factor 15 corresponds to the number of fluorine atoms in one PFOA molecule.

### 3. Results and discussion

#### 3.1 Photochemical oxidation degradation of PFOA

Fig. 1(a) shows the chemical and photochemical defluorination of PFOA under different conditions. If the PFOA degradation was carried out in the solution of  $\text{S}_2\text{O}_8^{2-}$  activated by  $\text{Fe}^{2+}$ , the DE value was only 1.6% at 5 h. When the  $\text{S}_2\text{O}_8^{2-}$  was irradiated with 254 nm UV light, the DE value was up to 23.2% after 5 h reaction. However, when combining  $\text{Fe}^{2+}$  and UV irradiation to activate  $\text{S}_2\text{O}_8^{2-}$ , a DE value of 63.3% was achieved at the same reaction time. It was noting that PFOA in the UV- $\text{Fe}^{2+}$  system without  $\text{S}_2\text{O}_8^{2-}$  showed only 6.4% of DE within 5 h. These observations suggest that  $\text{SO}_4^{\bullet-}$  generated from  $\text{S}_2\text{O}_8^{2-}$  ions played an important role in the PFOA defluorination, and the integration of  $\text{Fe}^{2+}$  and UV greatly improved the PFOA defluorination.

In the UV- $\text{Fe}^{2+}$ - $\text{S}_2\text{O}_8^{2-}$  system, the concentration of PFOA was decreased from 20 to  $1.2 \text{ mol L}^{-1}$  after 5 h reaction, corresponding to a degradation removal of 93.9%, and the produced  $\text{F}^-$  ions was increased to  $189.9 \text{ mol L}^{-1}$ , corresponding to a DE value of 63.3% (Fig. 1(a)). By using LC/MS and IC, the major degradation intermediates were identified to be formic acid and six shorter-chain PFCAs. The time dependences of these intermediates were described in Fig. 1(c), where trifluoroacetic acid was not quantified due to its very low concentration. The concentrations of these intermediates were continuously increased in the reaction time window, and the PFCAs intermediates with longer carbon-chains showed higher concentrations at each reaction time. This implies that PFOA underwent a stepwise manner to remove the  $\text{CF}_2$  unit one by one and the difficulty in the defluorination of PFCAs was increased with increasing of carbon-chain length of the PFCAs intermediates. Moreover, the production of abundant formic acid indicates that one of the degradation pathways was mainly initiated on the breakage of C-C bond between  $\text{C}_n\text{F}_{2n+1}$  and  $\text{COOH}$  in  $\text{C}_n\text{F}_{2n+1}\text{-COOH}$  molecules (Wang *et al.* 2008). Apparent total organic carbon (TOC) was calculated by summing the residual PFOA, individual shorter-chain PFCAs intermediates and formic acid in the term of carbon atom. As shown in Fig. 1(b), the amount of TOC was decreased rapidly within the initial two hours and then decreased very slightly during the PFOA defluorination. The considerable loss of organic carbon during the degradation should be attributed to the generation of  $\text{CO}_2$  accompanying the mineralization of PFOA. The TOC removal was readily obtained by using the data of the calculated apparent TOC values. By comparing the time dependence of the PFOA defluorination with that of TOC removal (Fig. 1(d)), it was found that the rate of the PFOA defluorination was well matched with the rate of TOC decreasing. This hints

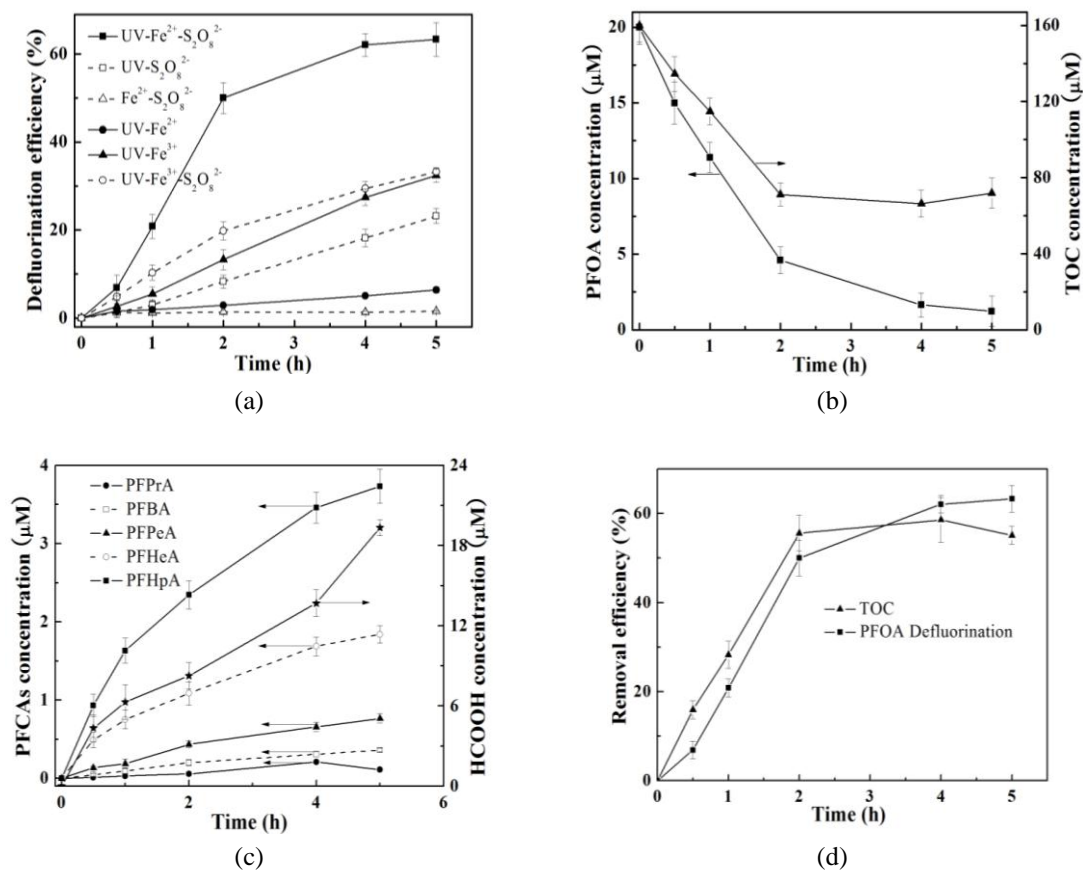


Fig. 1 (a) PFOA defluorination; (b) and (c) show the time profiles of the concentrations of PFOA, TOC and intermediates in the UV- $\text{Fe}^{2+}$ - $\text{S}_2\text{O}_8^{2-}$  system; (d) the comparison of PFOA defluorination efficiency with TOC removal in the UV- $\text{Fe}^{2+}$ - $\text{S}_2\text{O}_8^{2-}$  system. The reaction conditions were as follows: initial PFOA concentration, 20.0 mol  $\text{L}^{-1}$ ; initial  $\text{S}_2\text{O}_8^{2-}$  concentration, 30.0 mmol  $\text{L}^{-1}$ ; initial  $\text{Fe}^{2+}$  (or  $\text{Fe}^{3+}$ ) concentration, 1.0 mmol  $\text{L}^{-1}$ ; and initial solution pH, 5.0

that in the mechanism of the PFOA defluorination the path through the stepwise  $\text{CF}_2$  unit eliminating is more important than that involving the breakage of C-C bond.

### 3.2 Effect of major reaction conditions

The PFOA defluorination was influenced by the initial concentrations of  $\text{Fe}^{2+}$  and  $\text{S}_2\text{O}_8^{2-}$ , and solution pH. As the initial concentration of  $\text{Fe}^{2+}$  was increased from 0 to 1.0 mmol  $\text{L}^{-1}$ , the DE of PFOA at 5 h increased firstly from 23.2% to 63.3%, and then decreased gradually to 45.2% at 4.0 mmol  $\text{L}^{-1}$  (Fig. 2(a)). Higher  $\text{Fe}^{2+}$  concentrations can induce the formation of more  $\text{SO}_4^{\cdot-}$  (Eq. (1)), being benefit to the defluorination (Lee *et al.* 2010). However, excess  $\text{Fe}^{2+}$  ions themselves may consume  $\text{SO}_4^{\cdot-}$  (Eq. (2)), resulting in a low usage of  $\text{SO}_4^{\cdot-}$  available for the substrate oxidation.

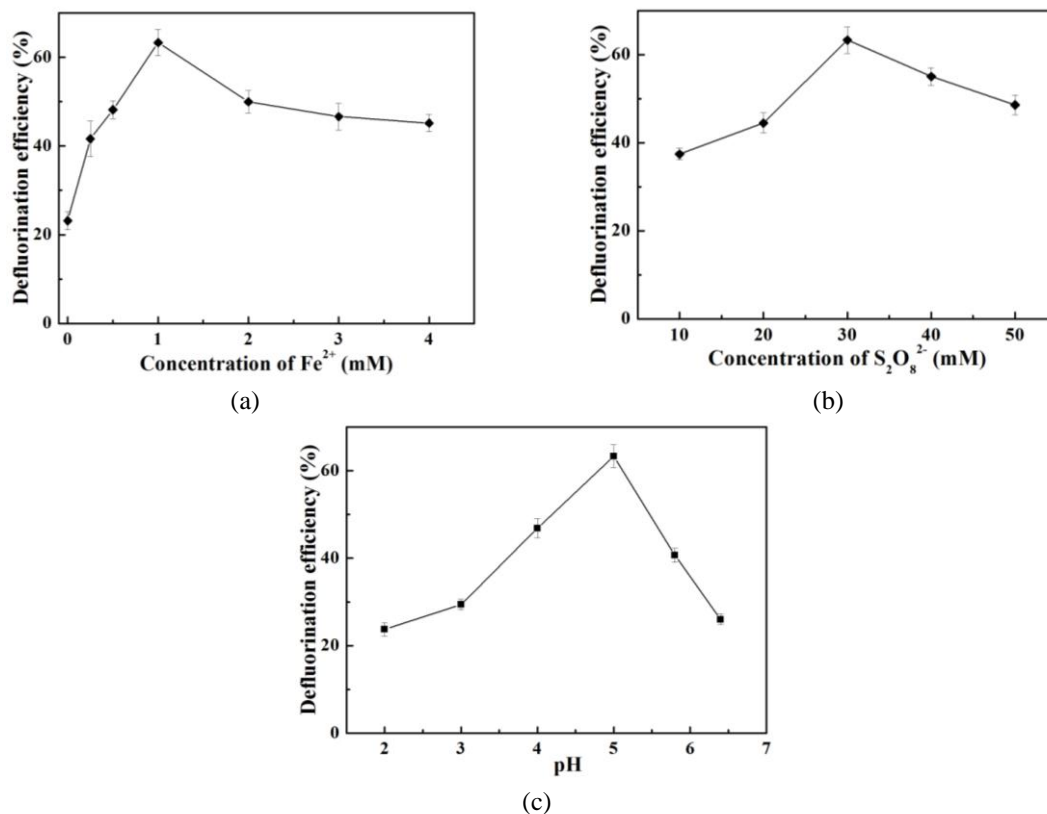
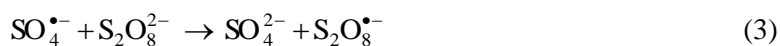


Fig. 2 Effects of (a) initial Fe<sup>2+</sup> concentration; (b) initial S<sub>2</sub>O<sub>8</sub><sup>2-</sup> concentration; and (c) pH on the defluorination of PFOA at 5 h reaction in the UV-Fe<sup>2+</sup>-S<sub>2</sub>O<sub>8</sub><sup>2-</sup> system



Fig. 2(b) illustrated the effect of initial S<sub>2</sub>O<sub>8</sub><sup>2-</sup> concentration on the PFOA defluorination. Greater addition of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> produces more SO<sub>4</sub><sup>•-</sup>, enhancing the PFOA defluorination. Nonetheless, excess S<sub>2</sub>O<sub>8</sub><sup>2-</sup> also acts as a SO<sub>4</sub><sup>•-</sup> scavenger (Eq. (3)), and higher SO<sub>4</sub><sup>•-</sup> concentration may induce self-quenching (Eq. (4)) (Huie and Clifton 1989), both of which are unfavorable to the PFOA defluorination. Thus, it was observed that increasing S<sub>2</sub>O<sub>8</sub><sup>2-</sup> dosage increased the DE value firstly, but then decreased it beyond 30.0 mmol L<sup>-1</sup> of S<sub>2</sub>O<sub>8</sub><sup>2-</sup>.

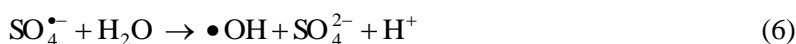
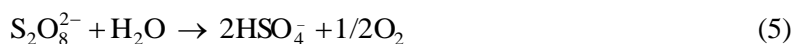


The influence of solution pH on PFOA defluorination was shown in Fig. 2(c). The DE at 5 h

was firstly increased from 23.7% to 63.3%, and then dramatically decreased to 26.0% as the pH increased from 2.0 to 5.0, and then to 6.4, respectively. The pH effect on the PFOA defluorination can be explained by the following reasons. Firstly, in acidic conditions ( $\leq$  pH 3.0), S<sub>2</sub>O<sub>8</sub><sup>2-</sup> exists mainly as ineffectual anions or weaker oxidants such as HS<sub>2</sub>O<sub>8</sub><sup>-</sup>, H<sub>2</sub>SO<sub>5</sub>, sulfur tetraoxide (SO<sub>4</sub>), and bisulfate (HSO<sub>4</sub><sup>-</sup>), being unfavorable to the formation of SO<sub>4</sub><sup>•-</sup> (Lau *et al.* 2007). Secondly, at pH > 5.0, the added Fe<sup>2+</sup> is easily oxidized to Fe<sup>3+</sup> by dissolved oxygen, leading to its precipitation as Fe(OH)<sub>3</sub>. This remarkably reduces the available concentrations of Fe<sup>2+</sup> for the activation of S<sub>2</sub>O<sub>8</sub><sup>2-</sup>. Thirdly, the increased Fe(OH)<sub>3</sub> precipitates at high pH values are suspended in the reaction solution, and reduce the photo permeability of UV light. Besides, under alkaline conditions, SO<sub>4</sub><sup>•-</sup> may react with OH<sup>-</sup> to form more hydroxyl radicals. When the pH is above 7, a conversion of SO<sub>4</sub><sup>•-</sup> to •OH makes it the dominant radical specie (Norman *et al.* 1970). The •OH species have a very low reactivity with PFOA in aqueous solutions. A combination of H<sub>2</sub>O<sub>2</sub> and UV irradiation has been applied to degrade PFOA, but degradation efficiency was lower than that in direct UV photolysis (Hori *et al.* 2004). Thus, a weak acidic solution favors the PFOA defluorination in the UV-Fe<sup>2+</sup>-S<sub>2</sub>O<sub>8</sub><sup>2-</sup> system, where an optimum pH was observed at pH 5.0.

### 3.3 Enhance PFOA degradation by the addition of Fe<sup>2+</sup> and S<sub>2</sub>O<sub>8</sub><sup>2-</sup> in several times and pH re-rejustment

It was noted that the formation of both organic intermediates and F<sup>-</sup> ions became much slower in the later reaction stage. This may be related to the great consumption of the added Fe<sup>2+</sup> and S<sub>2</sub>O<sub>8</sub><sup>2-</sup> in the reaction system. After 5 h reaction, only 0.8% and 63.7% of the added Fe<sup>2+</sup> and S<sub>2</sub>O<sub>8</sub><sup>2-</sup> were detected in the solution, respectively (curves in Figs. 3(a) and (b)), and the pH was decreased to 1.8. The decrease of pH was mainly due to the generation of formic acid and the release of H<sup>+</sup> during the reaction of persulfate and SO<sub>4</sub><sup>•-</sup> with H<sub>2</sub>O (Pennington and Haim 1968, Eldik and Harris 1980). The results were in agreement with the degradation of PFOA by persulfate using microwave activated (Lee *et al.* 2012). The reactions were listed below



As stated in Section 3.2, the low concentrations of activator and oxidant and low solution pH were harmful to the PFOA defluorination. To further confirm this, several interruptions such as pH re-adjustment, additional supply of reaction components were carried out at reaction time of 4 h. The pH re-adjustment to 3.0 could increase the PFOA defluorination to 66.2% after further 1 h reaction, being higher than that (63.3%) in the system without any interruption. By simultaneously re-adjusting pH to 3.0 and adding 10 mmol L<sup>-1</sup> S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, the PFOA defluorination was increased to 69.4% at the same reaction time, and if further supplying 1.0 mmol L<sup>-1</sup> Fe<sup>2+</sup> into the above interrupted system, the PFOA defluorination was increased up to 71.1%. Therefore, it can be anticipated that a complete defluorination of PFOA could achieve if maintaining the suitable reaction conditions.

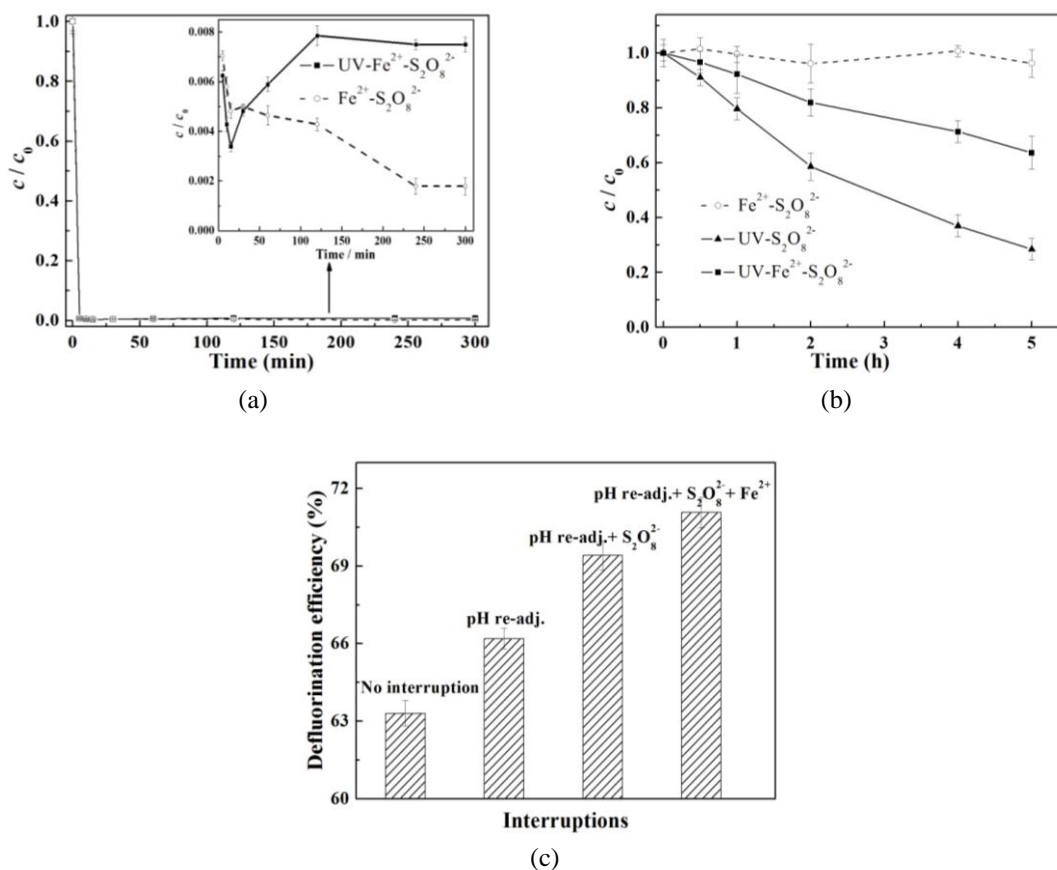


Fig. 3 Concentration changes of (a)  $\text{Fe}^{2+}$  and (b)  $\text{S}_2\text{O}_8^{2-}$ ; (c) PFOA defluorination in the UV- $\text{Fe}^{2+}$ - $\text{S}_2\text{O}_8^{2-}$  systems at 5 h without any interruption, and with re-adjusting pH to 3.0, adding 10 mmol  $\text{L}^{-1}$   $\text{S}_2\text{O}_8^{2-}$  and/or 1.0 mmol  $\text{L}^{-1}$   $\text{Fe}^{2+}$  at the reaction time of 4 h. The inset in (a) was amplification at reaction time from 5 to 300 min

### 3.4 Synergistic mechanism for the PFOA degradation in UV- $\text{Fe}^{2+}$ - $\text{S}_2\text{O}_8^{2-}$ system

The above discussion confirmed that the integration of UV irradiation and  $\text{Fe}^{2+}$  for the  $\text{S}_2\text{O}_8^{2-}$  activation was much more efficient than a single one alone for the PFOA defluorination. To clarify the synergistic effect of UV photochemical and  $\text{Fe}^{2+}$  chemical catalysis, the concentrations of two important reagents (i.e.,  $\text{Fe}^{2+}$  and  $\text{S}_2\text{O}_8^{2-}$ ) were monitored during the PFOA defluorination. As shown in Figs. 3(a) and (b), both the added  $\text{Fe}^{2+}$  and  $\text{S}_2\text{O}_8^{2-}$  disappeared gradually, suggesting a fast reaction between them (Eq. (1)). The introduction of UV irradiation greatly enhanced the consumption of  $\text{S}_2\text{O}_8^{2-}$ , for example, the residual  $\text{S}_2\text{O}_8^{2-}$  concentration was decreased from 28.9 mmol  $\text{L}^{-1}$  in the  $\text{Fe}^{2+}$ - $\text{S}_2\text{O}_8^{2-}$  system to 19.1 mmol  $\text{L}^{-1}$  in the UV- $\text{Fe}^{2+}$ - $\text{S}_2\text{O}_8^{2-}$  system after 5 h reaction. The more rapid consumption of  $\text{S}_2\text{O}_8^{2-}$  in the UV- $\text{Fe}^{2+}$ - $\text{S}_2\text{O}_8^{2-}$  system suggests that both UV and  $\text{Fe}^{2+}$  can activate  $\text{S}_2\text{O}_8^{2-}$  to produce  $\text{SO}_4^{\cdot-}$  (Eqs. (1) and (9)), and consequently accelerate the PFOA degradation.  $\text{SO}_4^{\cdot-}$  oxidize PFOA into perfluorinated alkyl radicals ( $\text{C}_7\text{F}_{15}\text{COOH}^{\cdot+}$ ),



which reacts rapidly with water to form unstable perfluorinated alcohol and then undergoes HF elimination and hydrolysis to form PFHpA, which has a carbon chain being loosed a  $CF_2$  unit in comparison with the original PFOA. A similar manner leads to produce other PFCAs (Eqs. (10)-(14)), as observed in Fig. 1(c).

The UV- $Fe^{2+}$ - $S_2O_8^{2-}$  system decomposed less  $S_2O_8^{2-}$  than UV alone at the same reaction time, whereas the PFOA defluorination in the former was much faster than that in the latter one (Fig. 1(a)). This indicates that besides  $SO_4^{\cdot-}$ , there is another factor making contribution to the PFOA degradation. As we know, UV irradiation is capable of converting a Fenton process to a photo-Fenton process, because the generated  $Fe^{3+}$  ions possess a characteristic absorption band around 300 nm (Fig. 4(a)). Once upon exposure to 254 nm UV light irradiation, the absorption of  $Fe^{3+}$  was decreased gradually, because  $Fe^{3+}$  complexes can be excited by UV light to convert to  $Fe^{2+}$  with no absorption at 250-500 nm, being accompanied by generation of  $\cdot OH$  (Eq. (15)). By using a fluorescence technique with coumarin as probe, the formation of  $\cdot OH$  was confirmed in the UV- $Fe^{3+}$  system and the generated  $\cdot OH$  were increased continuously as prolonging UV irradiation time (Fig. 4(c)). Besides, UV light has additional beneficial effect on the photolysis of  $Fe^{3+}$ -PFOA

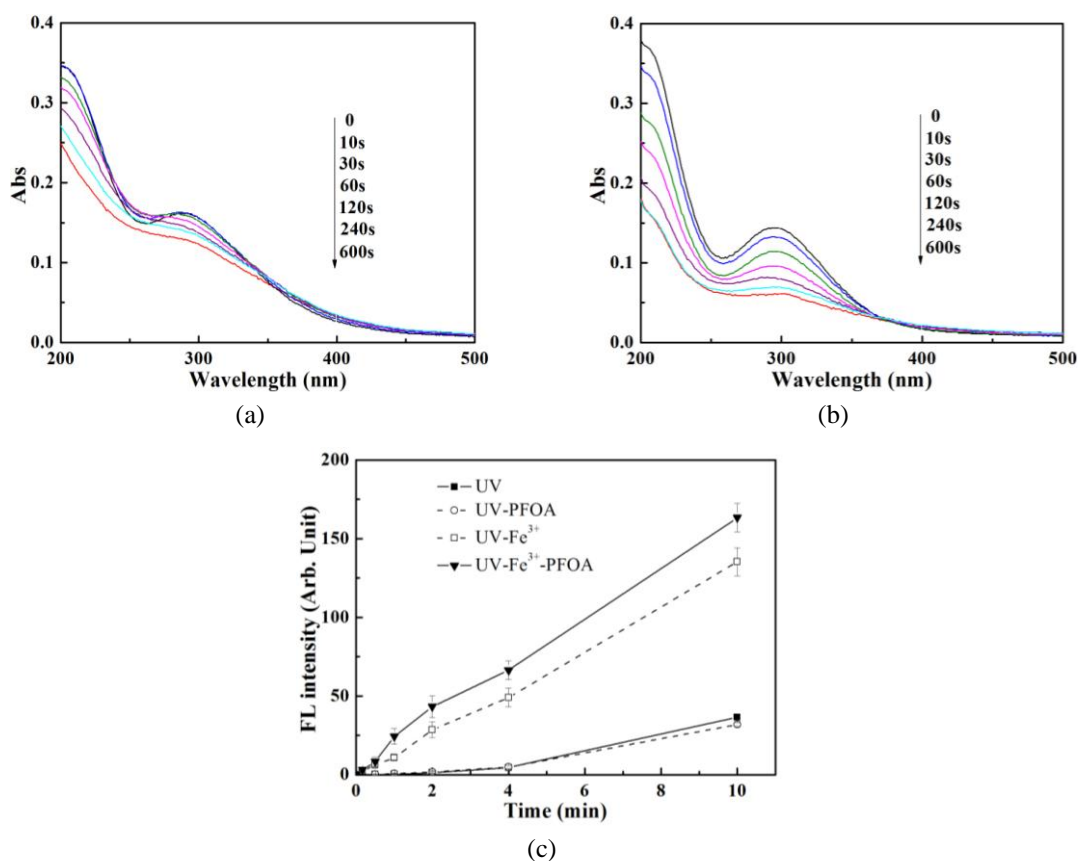
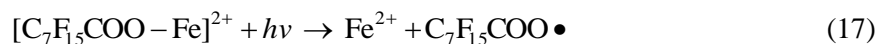
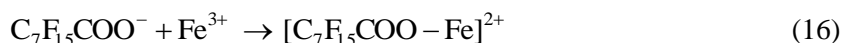
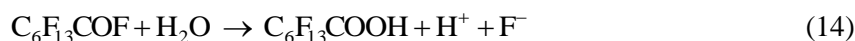
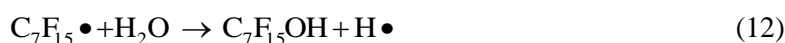
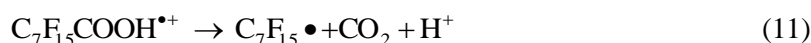
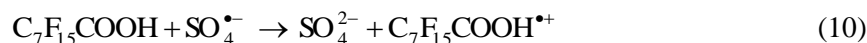


Fig. 4 UV-vis absorption spectra of  $Fe^{3+}$  solution (0.1 mmol L<sup>-1</sup>, pH 3.0) during UV irradiation (a) without and (b) with PFOA (0.1 mmol L<sup>-1</sup>); (c) Fluorescence intensity of the coumarin solution (0.2 mmol L<sup>-1</sup>, pH 3.4) in different systems

complexes. To confirm this proposal, the UV-Fe<sup>3+</sup> system was also conducted to degrade PFOA. As illustrated in Fig. 1(a), the PFOA defluorination as high as 32.5% was obtained after 5 h reaction. This is attributed to the electron transfer from PFOA to Fe<sup>3+</sup> in the excited Fe<sup>3+</sup>-PFOA complexes, leading to the regeneration of Fe<sup>2+</sup> and the formation of organic radicals which were further transformed into other products accompanying the formation of •OH (Eqs. (16)-(18)) (Wang *et al.* 2008). Thus, such intramolecular electron transfer process enhances the re-generation of Fe<sup>2+</sup> and generation of •OH. Accordingly, both the disappearance of Fe<sup>3+</sup> and the formation of •OH became faster in the co-existence of PFOA than that in the absence of PFOA under UV irradiation (Figs. 4(b) and (c)). Moreover, the slight increment of Fe<sup>2+</sup> concentration in the UV-Fe<sup>2+</sup>-S<sub>2</sub>O<sub>8</sub><sup>2-</sup> system in the reaction period of 15-120 min during the PFOA degradation supports that the introduction of UV irradiation enhanced the regeneration of Fe<sup>2+</sup> through the photolysis of Fe<sup>3+</sup>. These confirm that the Fe<sup>3+</sup>-mediated photochemical decarboxylation also makes great contribution to the PFOA degradation. As shown in Eqs. (16)-(18), the electron transfer between PFOA and Fe<sup>3+</sup> firstly generates unstable perfluorinated alkyl radicals, which reacts with water to form C<sub>6</sub>F<sub>13</sub>COOH, formic acid and fluoride ion. Then, short chain PFCA's are further degraded by reactions being similar to Eqs. (16)-(18). Although the UV-Fe<sup>3+</sup> system is more efficient than UV-Fe<sup>2+</sup> system in the PFOA defluorination, the PFOA defluorination is much lower in the UV-Fe<sup>3+</sup>-S<sub>2</sub>O<sub>8</sub><sup>2-</sup> system than in the UV-Fe<sup>2+</sup>-S<sub>2</sub>O<sub>8</sub><sup>2-</sup> system (Fig. 1(a)), because Fe<sup>2+</sup> can activate S<sub>2</sub>O<sub>8</sub><sup>2-</sup> to generate SO<sub>4</sub><sup>•-</sup>, but Fe<sup>3+</sup> cannot.



On the basis of the above discussions, it is concluded that the decomposition mechanism of PFOA in the UV-Fe<sup>2+</sup>-S<sub>2</sub>O<sub>8</sub><sup>2-</sup> system involves two important pathways. One is the direct attack of SO<sub>4</sub><sup>•-</sup> (Eqs. (10)-(14)), which were generated from the decomposition of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> by UV irradiation

and Fe<sup>2+</sup> activation, the other one is the UV-induced electron transfer from the excited PFOA to Fe<sup>3+</sup> (Eqs. (16)-(18)). The simultaneous use of UV irradiation and Fe<sup>2+</sup> greatly enhances the activation of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> to produce SO<sub>4</sub><sup>•-</sup>. The generated Fe<sup>3+</sup> can initiate the photochemical decarboxylation degradation of PFOA and additional photo-Fenton reaction under UV irradiation, accompanying its re-conversion to Fe<sup>2+</sup>, which further causes another reaction cycle. Thus, a markedly synergistic effect of UV irradiation and Fe<sup>2+</sup>-S<sub>2</sub>O<sub>8</sub><sup>2-</sup> catalysis is observed in the PFOA degradation.

#### 4. Conclusions

The PFOA defluorination was investigated by Fe<sup>2+</sup>-mediated activation of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> under UV irradiation.

- It was observed that the integration of UV and Fe<sup>2+</sup> activation was more efficient than the single one when using S<sub>2</sub>O<sub>8</sub><sup>2-</sup> as oxidant.
- The reaction parameters such as Fe<sup>2+</sup> concentration, S<sub>2</sub>O<sub>8</sub><sup>2-</sup> concentration and solution pH had great influences on PFOA degradation, and the optimal conditions were found to be as followed: 1.0 mmol L<sup>-1</sup> Fe<sup>2+</sup>, 30.0 mmol L<sup>-1</sup> S<sub>2</sub>O<sub>8</sub><sup>2-</sup> and initial solution pH 5.0.
- The PFOA decomposition proceeded in a stepwise manner, generating shorter-chain PFCAs, formic acid and fluorine ion.
- It was demonstrated that the PFOA defluorination in UV-Fe<sup>2+</sup>-S<sub>2</sub>O<sub>8</sub><sup>2-</sup> system involved two pathways. The formed SO<sub>4</sub><sup>•-</sup> from the decomposition of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> under the synergistic action of UV and Fe<sup>2+</sup> directly oxidize PFOA, and the generated Fe<sup>3+</sup> ions also initiated the photochemical decarboxylation degradation of PFOA through the electron transfer from PFOA (and its degradation intermediates) to Fe<sup>3+</sup>.
- The outcome of this study provides an efficient methods for the PFCAs treatment through simply integrating SO<sub>4</sub><sup>•-</sup>-involved AOPs under rather mild conditions.

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