Temperature effect on photolysis decomposing of perfluorooctanoic acid

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Abstract: Perfluorooctanoic acid (PFOA) is recalcitrant to degrade and mineralize. Here, the effect of temperature on the photolytic decomposition of PFOA was investigated. The decomposition of PFOA was enhanced from 34 to 99% in 60 min of exposure when the temperature was increased from 25 to 85 °C under UV light (201 - 600 nm). The limited degree of decomposition at 25 °C was due to low quantum yield, which was increased by a factor of 12 at 85 °C. Under the imposed conditions, the defluorination ratio increased from 8% at 25 °C to 50% at 85 °C in 60 min. Production of perfluorinated carboxylic acids (PFCAs, C7-C5), PFCAs (C4-C3) and TFA (C2) accelerated and attained a maximum within 30 to 90 min at 85 °C. However, these reactions did not occur at 25 °C despite extended irradiation to 180 min. PFOA was decomposed in a step-wise process by surrendering one CF_2 unit. In each cyclical process, increased temperature enhanced the quantum yields of irradiation and reactions between water molecules and intermediates radicals. The energy consumption for removing each μmol of PFOA was reduced from 82.5 kJ at 25°C to 10.9 kJ at 85 °C using photolysis. Photolysis coupled with heat achieved high rates of PFOA degradation and defluorination.

Key words: Perfluorooctanoic acid; PFOA; Photolysis; Temperature effect

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Introduction

Perfluorooctanoic acid (PFOA, $CF_3(CF_2)_6COOH$) is a member of the class of substances called perfluorinated chemicals (PFCs). PFOA has been produced and used in commercial products and industrial processes for over 60 years (Renner, 2004; Lindstrom et al., 2011). Interest and concern about PFOA is growing as more is learned about this anthropogenic chemical. PFOA is resistant to environmental degradation and has the potential for bioaccumulation (Post et al., 2012). PFOA enhances the health risks, including endocrine disrupting properties (White et al., 2011), immunotoxicity (DeWitt et al., 2012) and developmental effects (Fletcher et al., 2013) etc. PFOA is different from other persistent organic pollutants in its hydrotrope property and can; therefore, aggregate in the liver and

blood serum rather than in fatty tissues (Gebbink et al., 2009). Although the manufacture and use of PFOA are phasing out in some countries, PFOA has been frequently detected in drinking water (Post et al., 2009; Quinones and Snyder, 2009), biotas (Gebbink et al., 2009) and in people (Harada et al., 2007). However, PFOA is difficult to degrade using most conventional technologies (Vecitis et al., 2009). Thus, it is important and urgent to find an effective mineralization method.

Recently, a number of chemical technologies for PFOA decomposition have been reported. These methods cover various chemical process, including thermally-induced reduction (Krusic et al., 2005), microwave assisted oxidative decomposition (Lee et al., 2009; Lee et al., 2010), sonochemical pyrolysis (Vecitis et al., 2008; Cheng et al., 2010; Moriwaki et al., 2005), electrochemical degradation (Zhuo et al., 2011; Niu et al., 2012; Lin et al., 2012b) and photochemical decomposition (Wang et al., 2008; Wang et al., 2010; Wang and Zhang, 2011; Song et al., 2012). Among these reported methods, sonochemical, electrochemical and photochemical degradation are the most promising treatment alternatives to degrade PFOA efficiently. In the case of photochemical decomposition, there has been a number of attempts to promote the degradation of PFOA. Direct photolysis, as a clean technique, is limited by the low degradation efficiency and inadequate mineralization (Hori et al., 2004a). The indirect photoreactions have been developed to improve the efficiency of photo degradation. Some oxidants, such as ozone(Lin et al., 2012a), persulfate (Hori et al., 2005) and ferric ion (Hori et al., 2007), have been found to enhance the degradation and mineralization of PFOA. However, these methods require chemical compounds that are potential secondary pollutants. Photocatalysts have also been investigated for PFOA degradation. Titanium dioxide materials offer the advantage of generating hydroxyl radicals (HO•) in aqueous solution to help degrade most organic pollutant (Hoffmann et al., 1995), but HO• is not sufficiently effective to degrade PFOA ($k_{OH•+PFOA} \leq 10^5$ M^{-1} s^{-1}). The electronegative fluoride atoms in PFOA reduce the electron density of the terminal $-COO-$ group and are thus inimical to electron transfer between HO• and the $-COO-$ group (Vecitis et al., 2009). Indium oxide (In_2O_3) exhibits remarkable photocatalytic activity for PFOA decomposition. The tightly bidentate compound or the bridging configuration of PFOA molecule to the In_2O_3 surface enhances the direct decomposition of PFOA by photogenerated holes in In_2O_3 under UV irradiation (Li et al., 2012a). Nanostructured In_2O_3 with greater oxygen vacancy defects shows higher photocatalytic activity (Li et al., 2013; Li et al., 2012b). However, the mineralization is inadequate, because degradation products may deplete the

68 oxygen vacancy defects of the photocatalysts. As a result, it is essential to explore a more
69 efficient and clean method for the removal and mineralization of PFOA.

70   Water molecules involved in reacting with intermediates in the decomposition
71 processes of PFOA. The reaction temperature exhibits significant influence on the
72 decomposing efficiency (Lee et al., 2010; Xiao et al., 2011). The low solution temperature
73 (20 °C) in persulfate oxidation systems require 648 hours to degrade 81% of PFOA (Lee et al.,
74 2012), whereas hot water (80 °C) persulfate oxidative systems can completely degrade PFOA
75 in 6 hours (Hori et al., 2008). This acceleration is attributed to the abundant sulfate radicals
76 which were formed quickly at high temperature to degrade PFOA. In the electrochemical
77 degradation of PFOA by a boron-doped diamond (BDD) film electrode, the apparent reaction
78 rate constant increased from 0.108 h^{-1} to 0.444 h^{-1} as reaction temperature increased from
79 20 °C to 100 °C (Xiao et al., 2011). In the photolysis processes for decomposing PFOA,
80 intermediate reactions involved with the water molecules have been reported (Hori et al.,
81 2004a; Chen et al., 2007). However, there have been few reports concerning the temperature
82 effects on the PFOA photolysis degradation.

83   Photolysis, is a clean PFOA treatment approach. However, it is constrained by poor
84 efficiency and limited mineralization. There are two practical approaches to enhance the
85 photolysis efficiency of PFOA, which include application of deep ultraviolet light and the
86 promotion of quantum yields. PFOA has a strong absorption peak centered at 190 nm and a
87 general broad light absorption from 220 to 600 nm. The combination of 185 nm and 254 nm
88 could achieve higher degradation efficiency than 185 nm (Chen et al., 2007; Giri et al., 2011).
89 Therefore, compound light may achieve high PFOA degradation efficiency. The quantum
90 yield describes the ratio of the absorbed photons that transform the pollutant. This is
91 dependent on the probability of the excited-state achieved by absorbed photon and their
92 ability promote the reaction to products (Schwarzenbach et al., 2003). The promotion of the
93 quantum yield of the irradiated light will enhance the PFOA degradation. Nevertheless, there
94 have been few reports to investigate the temperature effect on the quantum yield and the
95 photolysis reaction for degrading PFOA up to now.

96   The main objective of this study is to explore the temperature effect on the photolytic
97 degradation of PFOA. The quantum yield of compound light at various temperatures were
98 calculated and discussed. The production of intermediates and fluoride ions were investigated.
99 The potential for temperature elevation to enhance the degradation or the mineralization of
100 PFOA by photolysis was explored.

1 Materials and Methods

1.1 Standards and Chemicals

Perfluorooctanoic acid (PFOA, sodium salt, 97%, CAS NO.: 335-67-1) was purchased from Aldrich Chemical Co. (New Jersey, USA). Methanol (HPLC grade) was purchased from Fisher Scientific (USA). Ammonium acetate (LC-MS Ultra, CAS NO.: 631-61-8) was purchased from Sigma-Aldrich Co. LLC. (Shanghai, China). All other chemicals used in this work were of analytical grade. An aqueous solution of PFOA was prepared using high purity water (18.2MΩ·cm) obtained from the Milli-Q Ultrapure Water Purification Systems (Millipore, USA).

1.2 Photolysis Experiments

The photolysis experiments were conducted in a tubular quartz reactor with an inner diameter of 55 mm and a length of 250 mm (Figure S1). A high-pressure mercury-vapor lamp (500 W, Beijing Lighting Research Institute) was used to provide UV illumination. The emission spectrum of the mercury-vapor lamp is shown in Figure S2. The lamp with a quartz envelope was placed in the center of the reactor. The reaction temperature was controlled by a thermal water jacket around the reactor (Figure S1).

The initial concentration of PFOA was set at 30 mg·L^{-1}. The reactor was filled with a volume of 500 mL PFOA aqueous solution. The temperature of photoreaction solution was controlled from 25 °C to 85 °C by circulating water in a bain-marie with a peristaltic pump. Two mL aliquots of the photoreaction solution were periodically collected for analysis of PFOA and intermediates at intervals of 0, 30, 60, 90, 120 and 180 min during the reaction. In addition, an additional 2 mL aliquot of the photoreaction solution was collected for determination of fluoride ions.

1.3 Analysis

An ultra-performance liquid chromatography-tandem mass spectrometry (UPLC–MS/MS) was used to determine the concentrations of PFOA and identify the photolysis intermediates. The UPLC system (Waters Corp., USA) was equipped with a C18 column (2.1 mm × 50 mm i.d., particle size 1.7 mm, Waters Corp., USA). The MS system was a Quattro Premier XE tandem quadrupole mass spectrometer (Waters Corp., USA) with an electrospray ionization source. The analytical method has been described previously (Zhou et al., 2013; Zhuo et al., 2012). The mobile phase was a binary mixture of solvent A (2 mmol·L^{-1} ammonium acetate in 5% methanol) and solvent B (2 mmol·L^{-1} ammonium acetate in 100% methanol) at a flow rate of 0.3 mL min^{-1}. The solvent gradient began with 25% A and 75% B, and was linearly ramped to 85% A and 15% B in 5 min, then ramped to 25% A and 75% B in

the following 2 min. The column was then allowed to equilibrate for 3 min and the total running time was 10 min. The injection volume of the samples was 10 μL. The tandem MS analysis was conducted in the multiple reaction monitoring (MRM) modes, and the cone voltage and collision energy were 30 V and 11 V, respectively. Standard solutions contained PFOA and some C2 - C7 shorter-chain PFCAs. Calibration standards were prepared in the range of 10 - 900 μg·L^{-1} POFA.

The concentration of fluoride ions (F$^-$) in aqueous solution were determined using an ion-chromatography system (ICS2000, Dionex, Sunnyvalley, USA) consisting of manual sample injector (sample injection volume: 25 μL), degasser, pump, separation column (250 mm length × 4 mm i.d., Dionex Ionpac AS11-HC, USA), column oven (30 °C) and conductivity detector with a suppressor device. The mobile phase consisted of a solution of KOH (30 mmol·L^{-1}) which was pumped into the system at a rate of 1.0 mL min^{-1}. The limit of detection (LOD) was 0.01 mg·L^{-1}. Defluorination ratio was calculated as follow (Eq. 1).

$$Defluorination\ ratio = \frac{C_{F^-}}{15 \times C_{PFOA}} \times 100\% \qquad (1)$$

Where C_{F^-} is the concentration of fluoride ion (mmol·L^{-1}), C_{PFOA} is initial concentration of PFOA (mmol·L^{-1}) and the constant 15 corresponds to the number of fluorine atoms in PFOA molecule.

2 Results

2.1 Degradation Kinetics of PFOA

The concentration of PFOA decreased with irradiation time, which was remarkably enhanced as temperature of the reaction system was increased (**Fig. 1**). The decrease in the concentration of PFOA in solution went from 39% at 25 °C to 100% at 85 °C within 60 min (**Fig.1a**). The decrease of PFOA followed first-order kinetics at the various temperatures (**Fig.1b, Table S1**). The reaction rate constants increased from 6.40 × 10^{-3} min^{-1} at 25 °C to 7.71 × 10^{-2} min^{-1} at 85 °C.

2.2 Defluorination

Fluoride ions were generated during the photolysis reaction, which increased as the temperature increased (**Fig. 2**). Defluorination ratio at 25 °C was 8%, which increased to 50% at 85 °C within 60 min (**Fig.2**). The defluorination ratio increased continuously to 77% at 85 °C from 60 min to 180 min.

2.3 Degradation Intermediates

The samples collected at different temperature were analyzed by UPLC-MS/MS chromatograms to identify intermediate products (**Fig.3 and S3**). According to the mass-charge ratio of the fragment ions, the intermediate products were identified as short chain PFCAs bearing C7-C2 perfluoroalkyl groups, including PFHpA ($C_6F_{13}COO^-$), PFHxA ($C_5F_{11}COO^-$), PFPeA ($C_4F_9COO^-$), PFBA ($C_3F_7COO^-$), PFPrA ($C_2F_5COO^-$) and TFA (CF_3COO^-) (Fig.3 and S3).

With the degradation of PFOA at 25 °C (**Fig.1a**), PFCAs (C7-C3) formation followed the order of chain length from PFHpA (C7) to TFA (C2). PFHpA (C7) was detected immediately. PFHxA (C6), PFPeA (C5), PFBA (C4) and PFPrA (C3) were detected at 30, 30, 60 and 180 min. TFA (C2) was not detected after 180 min of irradiation (**Fig.3a**).

The production of PFCAs accelerated as the temperature was increased (**Fig.3 and Table S3**). At 25 °C, PFCAs (C7-C2) were produced slowly and did not attain the maximum generation even after extended irradiation times to 180 min (**Fig.3a and Table S3**). At 85 °C, PFCAs (C7-C5), PFCAs (C4-C3) and TFA (C2) formed quickly and were at maximum concentration within 30, 60 and 90 min, respectively (**Fig.3d and Table S3**).

At high reaction temperatures, PFCAs (C7-C2) formation also followed the order of chain length from PFHpA (C7) to TFA (C2) (Fig.3b, c and d). PFHpA (C7), PFHxA (C6) and PFPeA (C5) formed first and achieved maximum concentration within 30 min. Following this, PFBA (C4) and PFPrA (C3) formed and achieved maximum concentration within 60 and 90 min, respectively. TFA (C2) generation did not achieve maximum concentration within 180 min (**Fig.3c**).

3 Discussion

3.1 The Effect of Temperature on PFOA Photolysis

It is well known that the efficiency of direct photolysis is limited by quantum efficiency and the intensity of the irradiating light, in which the intensity is increased at the cost of energy consumption (Hori et al., 2004a; Cao et al., 2010). The quantum yield is the number of degraded PFOA molecules divided by the number of photons absorbed by the system. The quantum yields at different temperatures were calculated according to equation S1. The quantum yields increased with temperature and obeyed equation 2 (**Fig.4**).

$$\Phi = 402.6 \times exp\left(\frac{-4424.6}{T + 273}\right) \qquad (2)$$

After the PFOA molecule absorbed a photon, it became unstable and underwent two competing processes in the experimental photoreaction system. These processes

included degradation or internal conversion to heat, which were initiated to return the molecule to a stable state (Zepp and Cline, 1977). High reaction temperatures inhibited the internal conversion to heat and favored the degradation process of PFOA. The promotion of quantum yield illustrates an increase in the proportion of PFOA molecules existing at an excited state that are involved in the degradation process. The quantum yield (1.72×10^{-3}) at 85 °C was twelve times higher than that (1.55×10^{-4}) at 25 °C (**Fig.4 and Table S1**). Temperature elevation promoted the quantum yields and thus enhanced the photolysis of PFOA.

3.2 Effect of Temperature on the Degradation of PFCAs Intermediates and Mineralization

The defluorination ratio increased by 50% when 99% PFOA was degraded in 60 min at 85 °C (**Fig.2 and 1a**), whereas the defluorination ratio continually increased to 77% (**Fig.2**) from 60 to 180 min (**Fig.3d**). The additional fluoride ions generated during the reaction from 60 to 180 min resulted from the degradation of PFCAs intermediates. Hydrogen ions were also simultaneously generated (**Fig.5**). The long chain PFCAs were degraded to fluoride ions, hydrogen ions and short chain PFCAs containing fewer CF_2 units (**Fig 2, 3 and 5**).

As the degradation of PFHpA (C7), PFHxA (C6) achieved their maximum concentration within 60 min at 45 °C (**Fig.3b**), but this process was observed within 30 min at 65 °C (**Fig.3c**). Obviously, the degradation of PFHpA (C7) was accelerated by increasing the temperature from 45 °C to 65 °C. Similarly, with the degradation of PFPeA (C5), PFBA (C4) occurred and achieved maximum concentration at 65 °C, but not at 45 °C (**Fig.3b and c**). This illustrated that the degradation of PFPeA (C5) was also enhanced as temperature was increased. These phenomena were also investigated in the other PFCAs intermediates (**Fig.3b, c, d and Table S3**). Higher reaction temperatures promoted the degradation of PFCAs into hydrogen ions, fluoride ions and short chain PFCAs.

The defluorination ratio was directly related to the degree of PFOA mineralization. The increase in the defluorination ratio suggested that PFOA was directly degraded to fluoride ions and carbon dioxide (Lee et al., 2012). Temperature elevation promoted the production of hydrogen ions and fluoride ions (**Fig.2 and 5**). The mineralization of PFOA by photolysis was promoted by increased reaction temperature.

3.3 Mechanism of PFOA Degradation

As illustrated above, as the PFOA was degraded, the defluorination ratio increased continually so that PFCAs intermediates were formed and decomposed, pH values decreased and these processes were enhanced as temperature increased (**Fig. 1, 2, 3 and 5**). The PFOA was decomposed into short chain PFCAs, fluoride ions and hydrogen ions at 85 °C with pattern similar to that at 25 °C, i.e. direct photolysis. Based on the results and direct photolysis, the mechanism of the temperature effects on photolysis to degrade PFOA is proposed.

The reaction temperatures (≤ 85 °C) are far below the thermolysis temperature (350 °C) and were not sufficient to degrade PFOA without irradiation (Krusic and Roe, 2004; Krusic et al., 2005). The C-C bond between C_7F_{15} and COOH is the weakest bond in the PFOA chemical structure because the fluorine atom has the strongest inductive electron withdrawal ability (Blondel et al., 1989). The light irradiation initially cleaves this weakest bond, which initiates the PFOA degradation. As a result, $C_7F_{15}\bullet$ radicals and carbon dioxide are generated in this step (eq. 3). The increasing reaction temperature promotes the quantum yield of the irradiating light and the population of PFOA molecules at excited state involved in degradation process is increased (**Fig.1,** eq. 2).
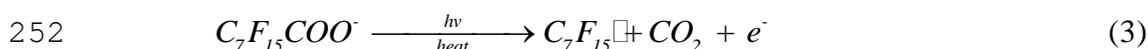
$$C_7F_{15}COO^- \xrightarrow[heat]{hv} C_7F_{15}\square + CO_2 + e^- \tag{3}$$

The end carbon atom of $C_7F_{15}\bullet$ radical possesses high electric charge intensity (Hori et al., 2004a; Chen et al., 2007), which prefers to react with electrophilic oxidants (Hori et al., 2003a; Hori et al., 2003b; Hori et al., 2004f; Dillert et al., 2007). For direct photolysis, the electrophilic oxidants are oxygen in the reaction solution or water molecules of the reaction solution (Niu et al., 2013; Gatto et al., 2015; Mitchell et al., 2013). The $C_6F_{13}C^{16}O^{18}O$ and $C_6F_{13}C^{18}O^{18}O$ are the main intermediates resulting from direct irradiation of PFOA in $H_2^{18}O$ solutions under high oxygen pressure (Hori et al., 2004a). This proves that the water molecule in solution is the main oxidative source. Consequently, primary perfluoroalcohols $C_7F_{15}OH$ are produced. $C_7F_{15}OH$ is thermodynamically unstable and generates acyl fluorides ($C_6F_{13}COF$) by releasing HF (eq. 4).

$$C_7F_{15}OH \xrightarrow{heat} C_6F_{13}COF + H^+ + F^- \tag{4}$$
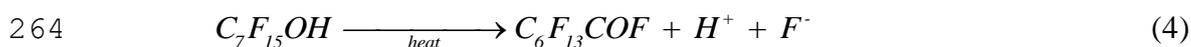
Hydrogen ions are continuously generated (**Fig.4**) and there was no other hydrogen source in the solution except the water molecule. In fact, $C_6F_{13}COF$ is immediately

hydrolyzed in water (eq. 5). By this process, PFHpA ($C_6F_{13}COO^-$), fluoride ions and hydrogen ions are formed.

$$C_6F_{13}COF + H_2O \xrightarrow{\text{heat}} C_6F_{13}COO^- + 2H^+ + F^- \tag{5}$$
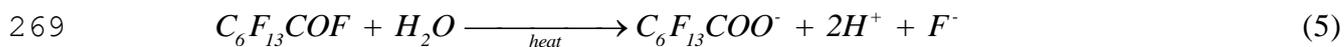
The generation of PFCAs intermediates in sequence from PFHpA (C7) to TFA (C2) (**Fig.3**) suggest that PFOA is degraded by losing CF_2 units in a step-by-step process. In the same way, the resulting PFCAs are decomposed into fluoride ions, carbon dioxide and the short chain PFCAs with less one CF_2 unit. In each cyclical process of losing one CF_2 unit, the increasing temperature promotes the quantum yield (eq. 2 and 3) and the hydrolysis reaction (eq. 4 and 5). Finally, PFOA is decomposed into fluoride ions and carbon dioxide.

3.4 Environmental Implications

Until recently, there has been little interest in the photolytic degradation of POFA, because of its low efficiency and inadequate mineralization capability. As presented in this study, the photolysis efficiency and mineralization of PFOA were enhanced by increasing the temperature of reaction solution (**Fig.1 and 2**). By increasing the reaction temperature increase to 85 °C, the total energy consumption is reduced. Furthermore, the photolysis technique requires no additional chemical regents.

The energy consumption was calculated based on the reaction conditions, initial concentrations and degradation kinetics (**Table 1**) (Vecitis et al., 2009). At the initial concentration 30 mg·L^{-1} (72.5 µmol•L^{-1}), the energy consumed to remove 15 mg•L^{-1} PFOA was 2997 kJ at 25 °C (**Table 1**), due mainly to light energy consumption, because the half-life was ca. 100 min (**Table 1**). Although the energy consumption (**Q in Table 1**) for elevating the solution temperature increased, the half-life was shortened and the required light energy was decreased, so that the total energy consumption was thus reduced. The energy consumption to remove a µmol PFOA was reduced from 82.5 kJ at 25 °C to 10.9 kJ at 85 °C (**Table 1**).

In addition to the lower energy consumption, photolysis, coupled with temperature, is a clean and green technique, which mitigates the adverse effects of secondary pollution, which are inevitable for numerous photochemical methods, especially those that demand photocatalysts or chemical reagents. This study supplies a clean and efficient approach to decompose PFOA.

4 Conclusions

The degradation of PFOA by photolysis coupled with temperature was investigated in this study. The photolysis of PFOA is accelerated due to the enhancement of quantum yield as the temperature is increased. PFOA is decomposed into fluoride ions, hydrogen ions and short chain PFCAs in sequence from PFHpA (C7) to TFA (C2). The mechanism for PFOA degradation begins with the loss of a CF_2 unit in a step-by-step process. In each cyclical degradation process from long chain PFCAs to short chain PFCAs with one less CF_2 unit, the quantum yields of irradiation light and the hydrolysis reaction are enhanced when the reaction temperature is increased. The promotional effect of temperature in each cyclically process of losing one CF_2 unit also strengthens the mineralization of the photolysis. The energy consumption for removing a μmol PFOA is reduced from 82.5 kJ at 25 °C to 10.9 kJ at 85 °C. This study provides an exploration on the application of thermal effects in the photolytic degradation of PFOA.

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at

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