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Temperature effect on photolysis decomposing of perfluorooctanoic acid

Tiliang Zhang, Gang Pan*, Qin Zhou

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China. E-mail: tiliangzhang@126.com

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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 (trifluoroacetic acid, 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 CF₂ 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.

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Introduction

Perfluorooctanoic acid (PFOA, CF₃(CF₂)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 are growing as more are 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). 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 (Gebblink 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 (Gebblink 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, 2010), sonochemical pyrolysis

* Corresponding author. E-mail: gpan6@yahoo.co.uk (Gang Pan).

(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, 2010; Wang and Zhang, 2011; Song et al., 2012). Among these reported methods, sonochemical, electrochemical and photochemical degradations are the most promising treatment alternatives to degrade PFOA efficiently. In the case of photochemical decomposition, there have 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 ($k_{\text{OH} + \text{PFOA}} \leq 10^5 \text{ (mol/L)}^{-1} \cdot \text{sec}^{-1}$). The electro-negative 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 (In₂O₃) exhibits remarkable photocatalytic activity for PFOA decomposition. The tightly bidentate compound or the bridging configuration of PFOA molecule to the In₂O₃ surface enhances the direct decomposition of PFOA by photogenerated holes in In₂O₃ under UV irradiation (Li et al., 2012a). Nanostructured In₂O₃ with greater oxygen vacancy defects shows higher photocatalytic activity (Li et al., 2012b, 2013). However, the mineralization is inadequate, because degradation products may deplete the oxygen vacancy defects of the photocatalysts. As a result, it is essential to explore a more efficient and clean method for the removal and mineralization of PFOA.

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

Photolysis is a clean PFOA treatment approach. However, it is constrained by poor efficiency and limited mineralization. There are two practical approaches to enhance the photolysis efficiency of PFOA, which include application of deep

ultraviolet light and the promotion of quantum yields. PFOA has a strong absorption peak centered at 190 nm and a general broad light absorption from 220 to 600 nm. The combination of 185 nm and 254 nm could achieve higher degradation efficiency than 185 nm (Chen et al., 2007; Giri et al., 2011). Therefore, compound light may achieve high PFOA degradation efficiency. The quantum yield describes the ratio of the absorbed photons that transform the pollutant. This is dependent on the probability of the excited-state achieved by absorbed photon and their ability promotes the reaction to products (Schwarzenbach et al., 2003). The promotion of the quantum yield of the irradiated light will enhance the PFOA degradation. Nevertheless, there have been few reports to investigate the temperature effect on the quantum yield and the photolysis reaction for degrading PFOA up to now.

The main objective of this study is to explore the temperature effect on the photolytic degradation of PFOA. The quantum yield of compound light at various temperatures was calculated and discussed. The production of intermediates and fluoride ions was investigated. The potential for temperature elevation to enhance the degradation or the mineralization of 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 (Pittsburgh, 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 (18.2 MΩ·cm) obtained from the Milli-Q Ultrapure Water Purification Systems (Millipore, Boston, 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 (Appendix A Fig. S1). A high-pressure mercury-vapor lamp (500 W, Beijing Lighting Research Institute, China) was used to provide UV illumination. The emission spectrum of the mercury-vapor lamp is shown in Appendix A Fig. S1. 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 (Appendix A Fig. S1).

The initial concentration of PFOA was set at 30 mg/L. The reactor was filled with a volume of 500 mL PFOA aqueous solution. The temperature of photoreaction solution was controlled from 25 to 85°C by circulating water in a bain-marie with a peristaltic pump. Two microliter 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.

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