



Efficient sonochemical degradation of perfluorooctanoic acid using periodate



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ABSTRACT

A rapid and efficient treatment method, using periodate (PI) for sonochemical oxidation of persistent and bioaccumulative perfluorooctanoic acid (PFOA) was developed. With an addition of 45 mM PI, 96.5% of PFOA was decomposed with a defluorination efficiency of 95.7% after 120 min of ultrasound (US). The removals of PFOA were augmented with an increase in PI doses. In all the PI + US experimental runs, decomposition efficiencies were essentially similar to those of defluorination, indicating that PFOA was decomposed and mineralized into fluoride ions. Lower solution pHs resulted in an increase in decomposition and defluorination efficiencies of PFOA due to acid-catalyzed. Dissolved oxygen increased the amount of IO_4 radicals produced, which consumed the more effective IO_3 radicals. Consequently, presence of oxygen inhibited the destruction of PFOA. The PFOA degradation rates with different gases sparging are in the following order: nitrogen > air > oxygen. Effects of anions follow the Hofmeister effects on PFOA degradation (i.e., $\text{Br}^- > \text{none} \geq \text{Cl}^- > \text{SO}_4^{2-}$). Br^- could react with $\cdot\text{OH}$ to yield radical anion Br_2^- that enhances the PFOA degradation. A reaction pathway was also proposed to describe the PI oxidation of PFOA under US irradiation.

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1. Introduction

Perfluorocarboxylic acids (PFCAs) including perfluorooctanoic acid ($\text{C}_7\text{F}_{15}\text{COOH}$, PFOA) have attracted increasing concerns because their undesirable presence in ubiquitous environment [1–3]. PFOA is one of the most widely used perfluorinated chemicals (PFCs) in semiconductor manufacturing and is contained in a wide variety of household products, including carpets, leather, paper, food containers, fabrics, and firefighting foams. Because of the high stability of C–F bond (C–F, 127 kcal/mol), PFOA and PFCs are extremely stable to chemical and thermal destruction, and are considered un-degradable in nature [4]. With the widespread use of these chemicals and a marked resistance to metabolic or environmental degradation, detectable levels of PFCs have now been documented in wastewater [5], surface water [6], tap water [7], wildlife [8–10] as well as in human blood serum [11], seminal plasma [12], and breast milk [6]. However, most of the advanced oxidation processes (AOPs) included ozone/hydroxyl radical oxidation are ineffective to destruct PFCAs due to the strong electro-

negativity of fluorine and the carbon–fluorine bonds [13]. Therefore, development of lowly energy-consuming and highly efficient decomposition methods to degrade PFOA is challenging and of great needs.

Several treatment methods have been developed to decompose aqueous PFOA, including ultrasonic irradiation [14], direct UV photolysis, UV-periodate oxidation [15], thermal-activated persulfate oxidation, UV- or microwave-activated persulfate oxidation [16,17], and UV-iodide reduction [18]. Ultrasound can effectively degrade PFCs (such as PFOA) via pyrolytic cleavages under transient high temperatures at the bubble–water interface. Cavitation phenomenon not only produces hotspots in water, which can degrade molecules by pyrolysis, but also produces free radicals species to react with the pollutants. US has been shown capable of yielding fast and complete mineralization of PFOA even in wastewater under the interferences of matrix inorganics [19]. Sonochemical degradation of PFOA could be enhanced by addition of additives such as sulfate ions [20–22], carbonate ions [23], TiO_2 [24], and persulfate [25].

Periodate (IO_4^- , PI), a well-known oxidant, whose reduction potential was reported to be +1.60 V, can be decomposed to the highly reactive intermediates by photolysis or sonolysis, such as IO_4^- , IO_3^- , $\cdot\text{OH}$, and O^- (as show in Eqs. (1)–(3)) [26]. The main free

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radical (IO_3^-) can effectively decompose PFOA by pathways including abstraction of fluorine (F) or electron (e^-) from PFOA [15].



The objectives of this study were to: (1) evaluate the effectiveness of periodate-sonochemical treatment for PFOA decomposition, (2) compare the efficiencies of degradation and defluorination with various periodate (PI) doses (0–45 mM), presence of specific ions (SO_4^{2-} , Cl^- and Br^-), sparging gases (N_2 , O_2 and air) and presence of radical inhibitors (such as *tert*-butyl alcohol, *t*-BuOH), and (3) explore the possible mechanism of PFOA decomposition.

2. Materials and methods

2.1. Materials

Perfluorooctanoic acid (PFOA, $\text{C}_7\text{F}_{15}\text{COOH}$, 96%) and sodium sulfate (Na_2SO_4 , 99%) were purchased from Aldrich. Potassium periodate (KIO_4 , 99%), perfluoroheptanoic acid (PFHpA, $\text{C}_6\text{F}_{13}\text{COOH}$, 98%), perfluoropentanoic acid (PFPeA, $\text{C}_4\text{F}_9\text{COOH}$, 97%), and heptafluorobutyric acid (PFBA, $\text{C}_3\text{F}_7\text{COOH}$, 99%) were purchased from Alfa Aesar. Undecafluorohexanoic acid (PFHeA, $\text{C}_5\text{F}_{11}\text{COOH}$, 97%), pentafluoropropionic acid (PFPrA, $\text{C}_2\text{F}_5\text{COOH}$, 97%) from Fluka, and trifluoroacetic acid (TFA, CF_3COOH), sodium chloride (NaCl , 99.8%), potassium bromide (KBr , 99%) from Riedel-deHaën were used in this study. *tert*-Butyl alcohol ($\text{C}_4\text{H}_9\text{OH}$, 99%) was purchased from J.T. Baker. All these chemicals were of analytical grade. All solutions were prepared with Millipore Milli-Q distilled water.

2.2. Reaction procedures

Schematics of the experimental setup are shown in Fig. 1. Sonochemical treatment was carried out under various conditions using a constant solution volume of 300 mL and an ultrasonic probe (BRANSON 2000Lpt, 150 W, 40 kHz, USA). The temperature of the reaction solution was kept constant at $25 \pm 1^\circ\text{C}$ in a temperature-controlled water bath. The initial concentration of PFOA was $170.1 \mu\text{M}$. The initial pH of the PFOA solution was 3.9, and was adjusted to 7.1 or 11.0 by 0.1 N NaOH. Before the ultrasonication experiments, nitrogen, air or oxygen gas, as needed, was bubbled

into solution at a flow rate of 200 mL/min via a sparger ring ($D = 4 \text{ cm}$) located in the reactor bottom for 20 min. During ultrasonication, the gas continues to be bubbled into solution at the same rate. At pre-specified time intervals, samples were retrieved and analyzed for PFCAs and other parameters. In all sonochemical experiments, the sonication irradiation was applied for a period of 120 min and all the runs were conducted in triplicate.

2.3. Analytical procedures

PFCAs were analyzed by using a high-performance liquid chromatography (HPLC) (DIONEX, UltiMate 3000, USA) equipped with a conductivity detector and an anion self-regenerating suppressor (ASRS 300 2-mm, USA). The by-products, C4–C8 perfluoroalkyl groups, were extracted using a $150 \times 2.1 \text{ mm } 3.5 \mu\text{m}$ column (Acclaim® Polar Advantagell, C18, DIONEX, USA) maintained at 30°C . Solutions of 70:30 (v/v) acetonitrile/Milli-Q water (Solution A), Milli-Q water (Solution B), and 9 mM NaOH/100 mM H_3BO_4 (Solution C) were mixed and introduced at the flow rate of 0.3 mL/min as the mobile phase. The gradient mode was operated as follows: 20% solution A, 20% solution B and 40% solution C for the initial 5 min, 20–60% of solution A for the next 15 min (5–20 min), and 60% solution A for the period afterwards (after 20 min). The limits of detection (LODs) using 50- μL samples, experimented from a signal-to-noise (S/N) ratio of 3, were 0.13 mg/L for PFBA, 0.12 mg/L for PFPeA, 0.16 mg/L for PFHeA, 0.18 mg/L for PFHpA, and 0.21 mg/L for PFOA.

Concentrations of short-chain PFCAs (TFA and PFPrA) were measured with an ion-chromatograph system (DIONEX, ICS-3000) consisting of an automatic sample injector, a degasser, a guard column (Ion Pac AS4A Guard Column, DIONEX), a separation column (Ion Pac AS4A Analytical Column, DIONEX), and a conductivity detector. The mobile phase was an aqueous solution containing $\text{Na}_2\text{B}_4\text{O}_7$ (5 mM) with a flow rate of 2 mL/min. The LODs (S/N = 3, injected at 50 μL) were 0.059 and 0.081 mg/L for TFA and PFPrA, respectively. An ion-chromatograph system was used to measure concentrations of fluoride ions. The mobile phase was an aqueous solution containing NaHCO_3 (1.7 mM), Na_2CO_3 (1.8 mM), and the flow rate was kept at 2 mL/min. The LOD (S/N = 3, injected at 50 μL) was 0.028 mg/L for F^- .

3. Results and discussion

3.1. Degradation of PFOA

Before the experiments of PFOA sonodegradation, a control run on PI (45 mM) oxidation of PFOA was conducted ($T = 25^\circ\text{C}$, without US, and kept in dark). After 120 min, more than 98% PFOA still existed in the solution which implied that PFOA is inert to PI oxidation under the mild condition similar to the natural environment. Fig. 2 illustrated that the effect of PI doses (0, 2.25, 4.5 and 45 mM) on US degradation (120 W, 40 kHz) of PFOA ($170.1 \mu\text{M}$) under initial pH of 3.9 over a period of 120 min. With US only (without PI), 26.2% of PFOA were decomposed after 120 min and the concentration of fluoride was $165.9 \mu\text{M}$, which corresponds a defluorination efficiency of 6.5%. The defluorination efficiency, expressed as (moles of fluoride formed)/(moles of fluorine content in the original PFOA), is an indicator for the extent of PFOA mineralization. With 2.25 mM PI, 54.6% of PFOA was decomposed after 120 min with a defluorination efficiency of 53.7%. With an increase of PI dose to 45 mM, 96.5% of PFOA was decomposed after 120 min with a defluorination efficiency of 95.7%. Both decomposition and defluorination efficiencies increased with PI doses. The reaction intermediates of short-chain PFCAs were monitored throughout the entire reaction period. But almost all the concentrations of

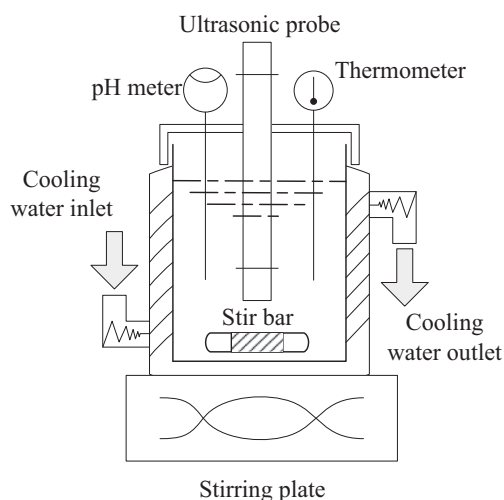


Fig. 1. Schematics of the experimental setup.

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