



Enhanced sonochemical degradation of perfluorooctanoic acid by sulfate ions



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ABSTRACT

This study investigated the effects of sulfate ions on the decomposition of perfluorooctanoic acid (PFOA) by ultrasonic (US) irradiation at various pHs, sulfate doses, powers and temperatures. The removal of PFOA was augmented with an increased sulfate ion concentration, with PFOA being almost completely decomposed in 90 min at 25 °C with a sulfate dose of 117 mM. The two major mechanisms in the sulfate-assisted sonochemical system are the direct destruction of PFOA by cavitation and the indirect destruction of PFOA by sulfate free radicals. The decomposition of PFOA followed pseudo-first-order kinetics and was not influenced by pH. The reaction rate constants decreased with increases in temperature due to decreases in the surface tension of the solution.

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1. Introduction

Perfluorooctanoic acid (C₇F₁₅COOH, PFOA) is widely used in industry. It is used as a surface treatment agent in photolithography, an emulsifying agent in polymer synthesis, a fire retardant, and is one component of paper coating. It is very stable in the natural environment due to its strong C–F bonds (110 kcal/mol) [1–3]. PFOA has been detected in aquatic environments and animals, and has been demonstrated to exhibit bioaccumulative and biomagnificative effects [4]. Therefore, there is interest in developing methods for PFOA removal.

It is currently known that PFOA can be degraded by photo-catalytic and Fenton oxidation [5], as well as by hydrothermal treatment. However, these treatment methods are largely inefficient, expensive and energy demanding. For example, hydrothermal treatment requires that the temperature be maintained at subcritical (100–350 °C) or supercritical (>350 °C) levels. While other methods exist to successfully remove other organic pollutants, such as conventional advanced oxidation processes (AOPs), they generally utilize relatively inactive hydroxyl radicals and are inefficient in the destruction of PFOA [6]. On the other hand, sonochemical treatment exploits pyrolytic cleavages to destroy

organic pollutants and is an emerging and effective method which can be used effectively to remove PFOA specifically [6–8].

Ultrasonic (US) treatment operates through cavitation, which not only produces plasma in water, thus degrading molecules by pyrolysis, but also produces free radicals and other reactive species that can enhance the number of collisions between free radicals and pollutants. US irradiation has been shown to enhance the degradation rate of various pollutants including phenol, dyes and pharmaceutical compounds [9–12]. Sonochemical degradation of organics can be further enhanced by the addition of additives such as photocatalytic compounds [5], exfoliated graphite [10], ozone [13], H₂O₂ [14], elemental iron [15], carbonate [11], persulfate [16] and sulfate [17].

Sulfate radical is strongly oxidizing ($E^0 = 2.43$ V) [18] and is highly effective in degrading organic pollutants in water [19]. In comparison to hydroxyl radicals ($E^0 = 2.8$ V), sulfate radicals have a higher selectivity and effectiveness in oxidizing target chemical compounds because of their more electrophilic nature [9].

Recent studies investigating the decomposition of organic pollutants by persulfate oxidation with microwave, ultrasound, photochemical and pulsed electrical discharge treatment have found sulfate radicals to be primarily responsible for the oxidation and destruction of those organic pollutants [5,20–22].

Therefore, on account of the need for a more time and energy efficient method of PFOA removal, this study explored the effect

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of the presence of sulfate radicals on the decomposition rate of PFOA undergoing US treatment. The effects of sulfate dose, US power, pH, temperature and surface tension were investigated.

2. Materials and methods

2.1. Materials

The perfluorooctanoic acid (PFOA, $C_7F_{15}COOH$, 96% purity) used in this study was purchased from Aldrich. The perfluoroheptanoic acid (PFHpA, $C_6F_{13}COOH$, 98%), perfluoropentanoic acid (PFPeA, C_4F_9COOH , 97%), and heptafluorobutyric acid (PFBA, C_3F_7COOH , 99%) were purchased from Alfa Aesar. The undecafluorohexanoic acid (PFHeA, $C_5F_{11}COOH$, 97%), pentafluoropropionic acid (PFPrA, C_2F_5COOH , 97%) were purchased from Fluka, and the trifluoroacetic acid (TFA, CF_3COOH) was purchased from Riedel-deHaen. The sodium sulfate (Na_2SO_4) 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 presented 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, 35 or 45 ± 1 °C in a temperature-controlled water bath. When sulfate was added, the initial pH of the solution was 4.3. For the experiments investigating pH, 1N H_2SO_4 and 1N NaOH were used to adjust the pH to 7.3 and 11.1. US irradiation was applied for 120 min. Samples were withdrawn at pre-specified time intervals and filtered before analysis.

2.3. Analytical procedures

PFCs (perfluorocarbons) were analyzed using a high-performance liquid chromatography (HPLC) (Dionex, Ultimate 3000, USA) equipped with a conductivity detector and an anion self-regenerating suppressor (Asrs 300, USA). The mobile phase was

70% acetonitrile and 30% 9 mM NaOH and 100 mM H_3BO_4 . The flow rate was 0.3 mL/min and the injection volume was 50 μ l [21].

Fluoride and sulfate ion concentrations were measured with an ion chromatograph unit (ICS-3000, Dionex) which consisted of an automatic sample injector, a degasser, a pump, a guard column (Ion Pac As4a Guard Column, Dionex), a separation column (Ion Pac As4a Analytical Column, HPLC system, Dionex), and a conductivity detector with a suppressor device. The mobile phase was an aqueous solution containing $NaHCO_3$ (1.7 mM) and Na_2CO_3 (1.8 mM). The flow rate was 2 mL/min. The defluorination ratio (R) was calculated as follows:

$$R = \frac{C_{F^-}}{C_0 \times 15} \times 100 \quad (1)$$

where C_{F^-} is the concentration of fluoride in mM, C_0 is the initial concentration of PFOA in mM, and the value of 15 represents the number of fluorine atoms contained in one PFOA molecule. The limit of detection (LODs) using 50 mL samples, based on a signal-to-noise (S/N) ratio of 3, was 1 mg/L for perfluorocarboxylic acids (PFCAs).

Changes in surface tension of the sample solutions accompanying temperature changes of 15–60 °C were determined by a ring/plate tensiometer (LAUDA, TD1C, Germany) following the standard method.

3. Results and discussion

3.1. Degradation of PFOA

US degradation (150 W, 40 kHz) of 0.12 mM PFOA with sulfate (25 mM) and without sulfate at 25 °C and a pH of 4.3 was conducted for 120 min. The results are shown in Fig. 2. The percentage of PFOA removed was calculated by

$$\text{PFOA removal}(\%) = \frac{(C_0 - C)}{C_0} \times 100 \quad (2)$$

where C_0 is the initial PFOA concentration in mM and C is the PFOA concentration in mM. As shown in Fig. 2, sulfate addition to the US

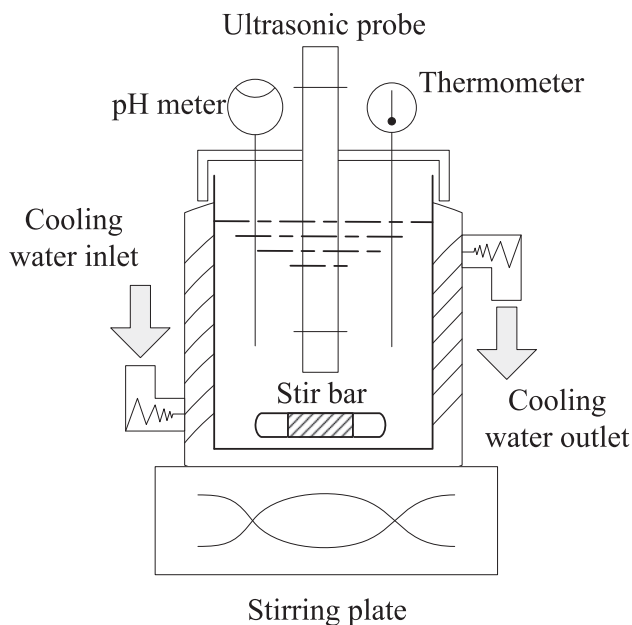


Fig. 1. Experimental setup schematic.

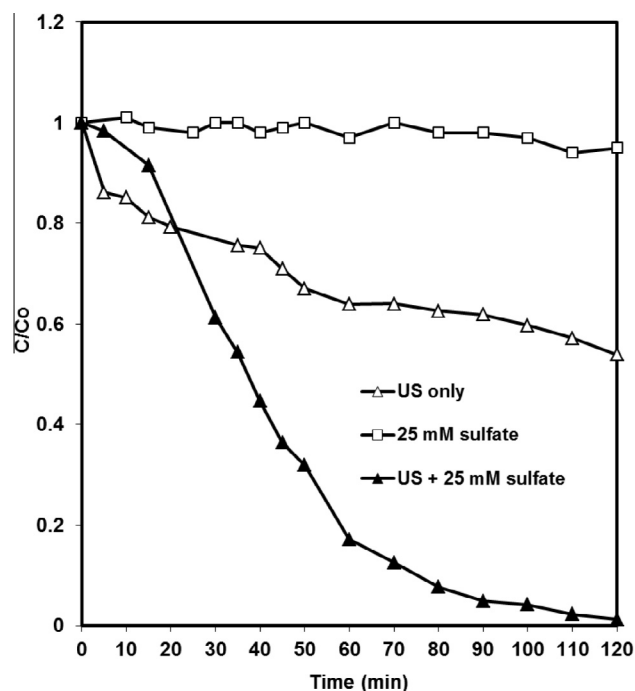


Fig. 2. Effects of sulfate addition on PFOA removal ($[PFOA]_0 = 0.12$ mM; $[sulfate]_0 = 0$ mM, 25 mM; initial pH = 4.3; $T = 25$ °C; power = 150 W).

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