



Effect of surfactants on the degradation of perfluorooctanoic acid (PFOA) by ultrasonic (US) treatment



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ABSTRACT

Perfluorooctanoic acid ($C_7F_{15}COOH$, PFOA) is an aqueous anionic surfactant and a persistent organic pollutant. It can be easily adsorbed onto the bubble-water interface and both mineralized and degraded by ultrasonic (US) cavitation at room temperature. The aim of this study is to investigate whether the effect of US on the degradation of PFOA in solution can be enhanced by the addition of surfactant. To achieve this aim, we first investigated the addition of a cationic (hexadecyl trimethyl ammonium bromide, CTAB), a nonionic (octyl phenol ethoxylate, TritonX-100), and an anionic (sodium dodecyl sulfate, SDS) surfactant. We found the addition of CTAB to have increased the degradation rate the most, followed by TritonX-100. SDS inhibited the degradation rate. We then conducted further experiments characterizing the removal efficiency of CTAB at varying surfactant concentrations and solution pHs. The removal efficiency of PFOA increased with CTAB concentration, with the efficiency reaching 79% after 120 min at 25 °C with a 0.12 mM CTAB dose.

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1. Introduction

Perfluorooctanoic acid ($C_7F_{15}COOH$, PFOA) is widely used in industry 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 difficult to decompose in the natural environment due to its strong C–F bonds (110 kcal/mol) [1,2]. Moreover, it exhibits bioaccumulative and biomagnificative effects [3–5] and has been found in aquatic environments, animals, and humans [6–8]. Therefore, an effective method of PFOA removal should be developed. There are several commonly-used methods of PFOA degradation, including hydrothermal treatment [9,10], as well as advanced oxidation processes (AOPs), such as photo-catalytic and Fenton oxidation [11–15]. However, some of these treatment methods are expensive or energy demanding. This is because the high temperatures, high pressures and long degradation times they require lead to high energy consumption. Some of these methods additionally utilize hydroxyl radicals to remove pollutants, which have been noted in the literature to be largely inefficient at degrading PFOA due to their relative inactivity [16,17]. Ultrasonic (US) treatment produces micro-plasma via the cavitation phenomenon and is an effective method of destroying organic pollutants and

removing PFOA specifically [16,18–20]. This method does not only produce high temperature micro-plasma due to the collapse of tiny vapor bubbles produced by ultrasound, but also leads to in situ pyrolytic reactions in the vapor and interfacial regions of each collapsing bubble resulting in the breakdown of water producing radicals, such as hydroxyl radicals, oxygen atoms and hydrogen atoms [21–23]. These transient radicals react rapidly with compounds in the bubble gas phase and at the bubble interface. US is more effective than traditional AOPs because the concentration of the PFOA is much higher on the bubble interface than in the bulk solution at the high temperatures engendered by the cavitation process [24,25].

Organic contaminants, such as PFOA, are commonly present in industrial wastewater [26]. These compounds can evade the treatment process and enter the environment [27]. Surfactants have a significant influence on the fate and transportation of numerous organic contaminants [28–30] and can be used to increase the solubility of hydrophobic organic contaminants in water to a point below the critical micelle concentration (CMC), thus facilitating their removal [31]. The addition of surfactant may therefore improve the energy efficiency of PFOA removal by US treatment. This study explored the addition of surfactant on the decomposition rate of PFOA undergoing US treatment. The effects of surfactant type, concentration, and pH were investigated.

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2. Materials and methods

2.1. Materials

Hexadecyl trimethyl ammonium bromide (CTAB) was purchased from Fluka. Sodium dodecyl sulfate (SDS) was purchased from Merck, and octyl phenol ethoxylate (TritonX-100) was purchased from J.T. Baker. The PFOA (96% purity) used in this study was purchased from Aldrich. The perfluoroheptanoic acid (PFHpA, C₆F₁₃COOH, 98%), perfluoropentanoic acid (PFPeA, C₄-F₉COOH, 97%), and heptafluorobutyric acid (PFBA, C₃F₇COOH, 99%) were purchased from Alfa Aesar. The undecafluorohexanoic acid (PFHxA, C₅F₁₁COOH, 97%) and pentafluoropropionic acid (PFPrA, C₂F₅-COOH, 97%) were purchased from Fluka, and the trifluoroacetic acid (TFA, CF₃COOH) was purchased from Riedel-deHaen. All these chemicals were of analytical grade. All solutions were prepared with Millipore Milli-Q distilled water.

2.2. Experimental procedures

The schematics for the experimental setup are presented in Fig. 1 US treatment was performed using an ultrasonic probe (BRANSON 2000LPt, 150 W, 40 kHz, USA) with a constant solution volume of 300 mL in a temperature-controlled water bath kept at 25 ± 1 °C for 120 min. Samples were taken at pre-specified time intervals and filtered before analysis.

The pH of the solution was 4.0 following addition of the surfactant and was adjusted to 7.3 and 11.1 through the addition of 1 N H₂SO₄ and 1 N NaOH in the experiments investigating the effect of pH.

The surface tension of the sample solutions at various concentrations was determined with a ring/plate tensiometer (LAUDA, TD1C, Germany) following the methods detailed in previous studies [32,33].

2.3. Analysis

PFCs (perfluorocarbons) were detected using a high-performance liquid chromatography (HPLC) system (Dionex, Ultimate 3000, USA) equipped with a conductivity detector and an anion self-regenerating suppressor (Asrs 300, USA). The mobile phase was 70% acetonitrile with the remaining 30% being made up by a 9 mM NaOH and 100 mM H₃BO₄ solution. The flow rate was

0.3 mL/min and the injection volume was 50 μl [34]. Fluoride ion concentrations were measured with an ion chromatography unit (IC) (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, Dionex), and a conductivity detector with a suppressor device. The mobile phase was an aqueous solution containing NaHCO₃ (1.7 mM) and Na₂CO₃ (1.8 mM). The flow rate was 2 mL/min. The defluorination ratio (*R*) was calculated as follows [19]:

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

where *C_F⁻* is the concentration of fluoride in mM, *C₀* 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).

2.4. Energy consumption (*G*₅₀) calculation

The energy consumption calculated in terms of *G*₅₀ yield value is the amount of pollutant converted (50% of the initial total pollutant) divided by the energy input required to degrade that much pollutant (50% of the initial total pollutant) [35]:

$$G_{50} = \frac{1.8 \times 10^6 C_0 V_0 M}{P t_{50}} \quad (2)$$

C₀ is the initial concentration of the pollutant, *V₀* is the volume of treated solution in liters, *M* is the molecular weight of the pollutant, *P* is the power of the reactor in watts, and *t*₅₀ is the time in seconds required for 50% conversion. *G*₅₀ is expressed in grams/kilowatt-hour (g/kWh).

3. Results and discussion

3.1. Effect of surfactant type

Fig. 2 presents the variation in PFOA degradation with the addition of different types of surfactants during the US process over time. Adding cationic (CTAB) and nonionic surfactants (Triton-X100) improved the removal of PFOA with the

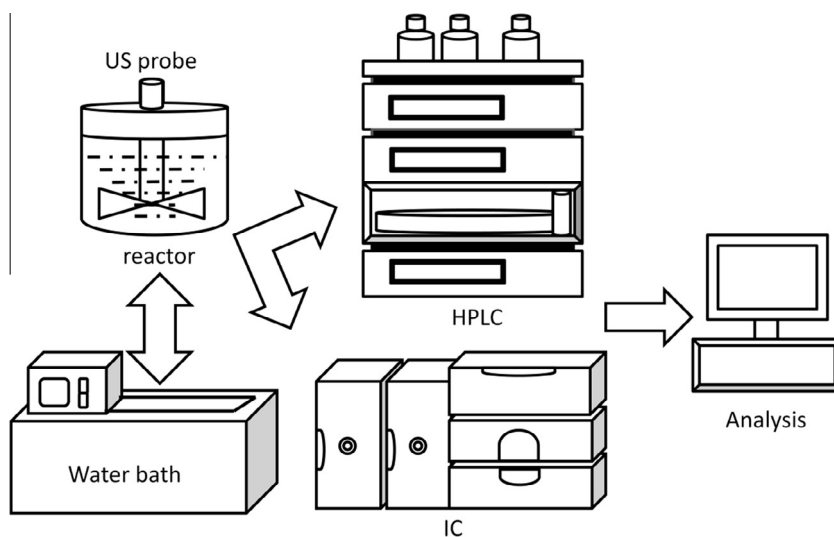


Fig. 1. Schematic of the experimental setup.

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