Sonochemical degradation of perfluorinated surfactants: Power and multiple frequency effects ☆

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ABSTRACT

Perfluorosulfonates and carboxylates, C_4 to C_8 surfactants, are sonolytically degraded primarily at the vapor–water interface of cavitation bubbles. The observed pseudo first-order rate constants for the elimination of the perfluorosurfactants indicate that rates should be proportional to the degree of interfacial bubble–water partitioning. In fact, the sonochemical degradation rates of the more soluble and less hydrophobic perfluorobutane sulfonate, PFBS, and perfluorobutanoate, PFBA, were found to be slower than longer chain analogs due to their greater water solubility compared to the C_8 counter parts. The observed degradation rate constants are found to increase with increasing power density. Enhanced degradation rates were observed for the C_8 surfactants, PFOS (∼12%) and PFOA (∼23%) under simultaneous irradiation at 20 kHz and 202 kHz at a power combined power density of 250 W L^{-1}.

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1. Introduction

The fate of perfluorinated organic compounds in the aquatic environment is of great concern because of their persistence, bioaccumulation [1], and toxicity [2,3]. Perfluorination yields unique physical properties such as chemical inertness, minimal coefficients of friction, and low polarizabilities, which makes them desirable for a wide variety of commercial applications [4]. Fluorochemicals (FCs), which include perfluoroalkylsulfonates and perfluorocarboxylates, have been used in many commercial products. They have been detected globally in the atmosphere, hydrosphere and biosphere. Their stability arises from their high bond strength (450–530 kJ mol^{-1}) and low polarizabilities [5]. Current remediation strategies are slow or ineffective toward perfluorinated contaminants due to their oxidative stability. Therefore, it is of importance to develop effective remediation processes to address the environmental issue of widespread perfluorochemical contamination and persistence.

The efficient decomposition of organic compounds using ultrasound irradiation is a viable technology in the remediation of environmentally persistent and recalcitrant compounds such as perfluorinated chemicals (PFCs). Ultrasound irradiation produces high energy chemistry in a very short timescale (∼nanoseconds). During irradiation a population of newly formed gas bubbles are excited to a resonant radius via rectified diffusion. This is followed by the absorption of energy during the rarefaction cycle of the ultrasonic waves causing their growth to a maximum size followed by an adiabatic collapse. The intense collapse generates average vapor temperatures near 5000 K [6,7] and pressures on the order of several hundred atmospheres [8]. These high temperature and pressure conditions are sufficient enough to pyrolyze perfluorinated surfactants which are localized at the interfacial region of the cavitation bubble, to their inorganic substituents [9].

Herein, we explore the effects of power density, single frequency, and dual frequency irradiation for the sonochemical treatment or remediation of perfluorochemicals. An increase in power density leads to a linear increase in the sonochemical degradation kinetics of perfluorinated surfactants. However, the intensity and energy efficiency in the acoustic field is dependent on the frequency value and on the presence of either dual or single frequency exposure.

2. Materials and methods

Perfluorobutyric acid (PFBA), perfluorohexanoic acid (PFHA), and perfluorooctanoate (PFOA) were purchased from Sigma Aldrich. Potassium perfluorobutane-1-sulfonate (PFBS), potassium

perfluorohexane-1-sulfonate (PFHS), and potassium perfluoro-octane-1-sulfonate (PFOS) were provided by 3 M. Ammonium acetate (>99%) and methanol (HR-GC > 99.99%) were obtained from EMD Chemicals Inc. Aqueous solutions were prepared with purified water using a Milli-Q system (18.2 mΩ cm resistivity). Acid solutions were brought to a pH of 7 by addition of ammonium hydroxide.

Sonication at single frequencies of 202, 358 and 610 kHz were performed at power densities of 83, 167, 250, and 333 W L^{-1} using an Allied Signal – Elac Nautik ultrasonic transducer with the solution contained in a 600 mL jacketed glass reactor. Dual frequency exposures at 20 + 202 and 20 + 610 kHz under an applied power density of 250 W L^{-1} were carried out using a 20 kHz horned transducer placed perpendicular to an Allied Signal – Elac Nautik ultrasonic transducer with the solution contained in a 600 mL jacketed glass reactor. The temperature was modulated with a Haake A80 refrigerated bath maintained at 10 °C. All reactions were sparged with argon for at least 30 min prior to and during the reaction unless otherwise noted. PFBS and PFBA were sonicated simultaneously at total initial concentrations of 300 and 470 nM, respectively. PFHS and PFHA were sonicated simultaneously at initial concentrations of 230 and 320 nM, respectively. Under varying power densities and single frequency exposures of either 358 or 610 kHz, PFOS and PFOA were sonicated simultaneously at initial concentrations of 200 and 240 nM, respectively. PFOS and PFOA concentrations were 200 and 240 nM, respectively, under dual frequency conditions.

PFBS, PFBA, PFHS, PFHA, PFOS and PFOA were analyzed using HPLC-MS. The samples were placed into 750 μL polypropylene auto-sampler vials and sealed with a PTFE septum crimp cap. 20 μL of collected or diluted sample was injected onto an Agilent 1100 LC for separation on a Betasil C18 column (Thermo-Electron) of dimensions 2.1 mm ID, 100 mm length and 5 μm particle size. A 2 mM aqueous ammonium acetate/methanol mobile phase at a flow rate of 0.75 mL min^{-1} was used with an initial 70:30 water/methanol composition. HPLC effluents were analyzed with an Agilent Ion Trap MS in the negative ion mode for the perfluorooctane-sulfonate molecular ion (m/z = 499), the perfluorohexanesulfonate molecular ion (m/z = 399), the perfluorobutane sulfonate molecular ion (m/z = 299), the decarboxylated perfluorooctanoate molecular ion (m/z = 369), the decarboxylated perfluorohexanoate molecular ion (m/z = 269) and the decarboxylated perfluorobutanoate molecular ion (m/z = 169). The nebulizer gas pressure was 40 PSI while the drying gas flow rate and temperature were 9 L min^{-1} and 325 °C, respectively. The capillary voltage was set at +3500 V and the skimmer voltage was – 15 V. Quantification was completed by first producing a calibration curve using 8 concentrations between 1 ppb and 200 ppb fitted to a quadratic with X^{-1} weighting.

3. Results

The rate of degradation of PFHX (where X = c(A)rboxylates or (S)ulfonates) and PFBX at 202 and 610 kHz were evaluated at power densities from 83 W L^{-1} to 330 W L^{-1}. PFOX rates were evaluated at the same power densities but at frequencies of 358 and 610 kHz. Plots of the pseudo-first-order rate constants, k, versus the input power density are shown in Fig. 1a–c for PFHX, PFBX, and PFOX, respectively. A gain in power density will amplify sonochemical effects. This is reflected in the measured rate constants which show linear increases with increasing power density. However, at 202 kHz, PFBA deviates from the trend in which the maximum rate constant is 0.035 min^{-1} at 250 W L^{-1} and subsequently decreases to ~0.032 min^{-1} at 330 W L^{-1} (Fig. 1a).

The effects of frequency and applied power density on the degradation rate of perfluorinated surfactants (C$_n$ > 5) were
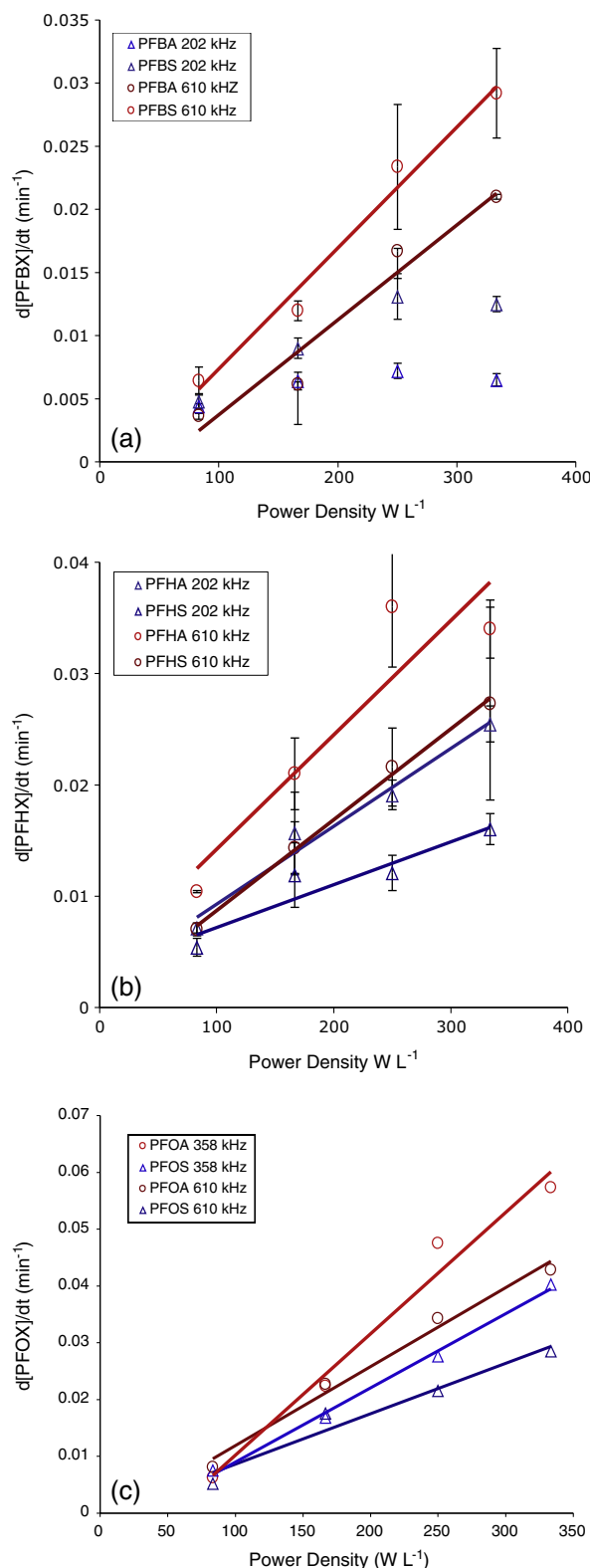

Fig. 1. Rate constant dependence on power densities 83, 166, 250, and 333 W L^{-1} at 202 and 610 kHz, 10 °C, Ar for (1a) PFHX, (1b) PFBX and (1c) PFOX.

explored in order to obtain optimal physical parameter conditions. The pseudo-first order rate constant, k, versus power density and frequency is shown in Fig. 2a and b. For each frequency, power was varied from 83 to 333 W L^{-1}. From the 3-D plot, the power density value of 333 W L^{-1} and ultrasonic frequencies of 358 kHz and 618 kHz for PFYA (where Y = (O)ctane or (H)exane) and PFYS,