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Sonochemical degradation of perfluorinated chemicals in aqueous film-forming foams

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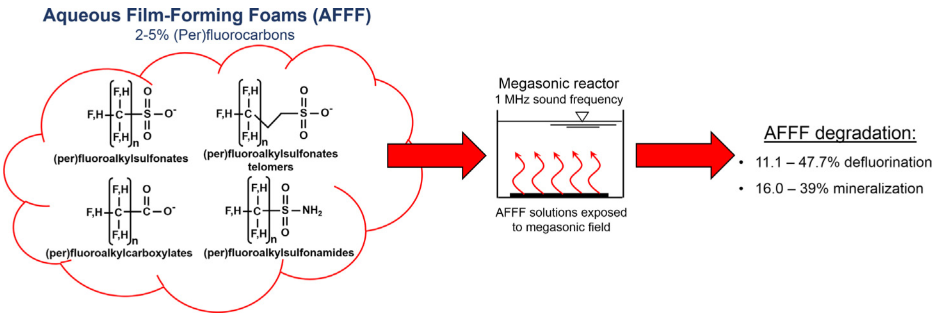
HIGHLIGHTS

- Acoustic treatment at 1 MHz was effective at degrading PFCs in AFFF formulations.
- Defluorination and mineralization rates were higher at 1 MHz compared to 500 kHz.
- Rate of defluorination increased with greater initial concentrations of TOF.

GRAPHICAL ABSTRACT



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ABSTRACT

Aqueous film-forming foams (AFFFs) are complex mixtures containing 1–5% w/w fluorocarbons (FCs). Here, we have investigated degradation of two commercial AFFF formulations, 3M and Ansul, using sound field at 500 kHz and 1 MHz, with varying initial concentrations ranging from 200 to 930× dilution. The foams were readily degraded by 1 MHz, with percentage of defluorination ranging from 11.1 ± 1.4% (200× dilution of 3M) to 47.1 ± 5.8% (500× dilution of Ansul). Removal of total organic carbon (TOC) ranged from 16.0 ± 1.4% (200× dilution Ansul) to 39.0 ± 7.2% (500× dilution Ansul). Degradation of AFFF was affected by sound frequency with rates of defluorination 10-fold greater when the frequency was 1 MHz than when it was 500 kHz. Mineralization of TOC was 1.5- to 3.0-fold greater under 1 MHz than 500 kHz. Rate of fluoride release was 60% greater for the greatest initial concentration of FC in Ansul compared to the least initial concentration. While the rate of mineralization of AFFF was directly proportional to the initial concentration of Ansul, that was not the case for 3M, where the rates of mineralization were approximately the same for all three initial concentrations. Results of the study demonstrate that sonolysis is a promising technology to effectively treat AFFFs.

1. Introduction

Aqueous film-forming foams (AFFFs) are complex mixtures whose major components include a solvent (typically a glycol ether), fluorochemical surfactants (perfluorinated anionic and par-

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tially fluorinated amphoteric), and hydrocarbon-based surfactants [1]. Fluorochemical (FC) surfactants represent 1–5% w/w of the AFFF composition and impart properties such as good spreadability, negligible fuel diffusion, and thermal stability to the foam [2]. AFFFs were produced from 1960s to 2001 as important chemical agents for extinguishing hydrocarbon-fuel fires; as of 2004, the US military still possesses almost 11 million liters of these across the country [2]. Continuous use of AFFFs for fire-fighting training and equipment maintenance in airports and former US military fire-fighting training sites [3] has caused groundwater contamination with FC concentrations ranging from 125 to 7090 $\mu g\,l^{-1}$ [1].

The same unique attributes that have made AFFF effective for fighting fires, especially those fueled by petroleum hydrocarbons, have also resulted in concern for these compounds in the environment. AFFFs are persistent in the environment. Concentrations of FCs and FC-precursors have been measured in groundwater, soil and sediments in a US Air Force Base where AFFFs were used until 1990 [4]. Forty to 100% of total initial concentrations of FC in AFFFs were FC-precursors at the site 20 years after use of AFFFs was discontinued. FCs, which were components of AFFFs, are known to be bio-accumulative and to cause toxicity [5–8]. The presence of FCs in mammals, birds, and fishes was first reported in 2001 [9,10]. Many studies have investigated the presence of FCs in human tissues and concluded that FCs accumulate in the human body during continuous exposure [11]. Due to the complexity of the AFFF mixture, there is limited information about toxicities of AFFFs [1]. Individual FCs can damage liver, affect the immune system, cause developmental and reproductive toxicology, and be carcinogenic to mammals [11].

Not only are FCs bio-accumulative and toxic, they are generally recalcitrant in the environment and resistant to natural degradation or chemical and biological treatment processes [12–14]. Effective degradation of individual FCs has been a challenge and often requires use of advanced oxidation processes at higher temperatures and/or pressures [14]. Use of ultrasonic and megasonic irradiation has been suggested as effective technologies to treat FCs [15–17]. When an acoustic field is applied to a liquid, the sound waves are transmitted with lower pressure (rarefaction) and higher pressure phases [18]. During low pressure cycles, in the bulk of the liquid containing dissolved gas or in some preexisting nuclei in the liquid, such as crevices or small solid particles, small cavities start to form [19]. The bubbles oscillate during several cycles (stable cavitation) and grow due to rectified diffusion until they become unstable and collapse during a higher pressure cycle (transient cavitation) [20]. The stable cavitation though milder can produce temperatures up to 2000 K [21], while collapsing events produce temperatures near 5000 K and pressures close to 1000 bar [19]. Such high temperatures and pressures produced during bubble oscillations or collapsing events will likely degrade FCs in solution, either by direct pyrolysis, or by reaction with hydroxyl radicals formed due to the homolytic decomposition of water under extreme conditions [19]. Sonochemical degradation of FCs would take place at the bubble-water interface, therefore adsorption of molecules on the bubbles is required prior to sonolysis.

When sonochemical degradation of 20 μM each of perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) was investigated at an acoustic frequency of 200 kHz, 60% degradation of PFOS and 85% degradation of PFOA was observed after sonication for 60 min [16]. Degradation of various FCs including perfluorobutanoic acid (PFBA), perfluorobutanesulfonic acid (PFBS), perfluorohexanoic acid (PFHxA) and perfluorohexanesulfonic acid (PFHxS) was observed at concentrations of 0.2–0.5 μM when a wide range of frequencies (202–1060 kHz) was applied [15]. The results of those studies suggested that the rate of sonochemical degradation of FCs was inversely proportional to length of the carbon chain. Since, different FCs would exhibit different degradation rates, sonochemical degradation of AFFF formulations depends on their specific compositions. PFOS (0.13–26.2 μM), PFHxS, PFBS and PFOA in the AFFF FC-600 were readily degraded under a 505 kHz frequency [22]. In a recent study, it was shown that sonochemical degradation of PFOS increased with the initial concentration until reaching a maximum (saturation concentration), and use higher sound frequencies increased the degradation rate but resulted in a less saturation concentration [23]. The main objective of the present study is to investigate sonochemical degradation of two AFFFs, 3M and Ansul, and effects of sound field and solution parameters such as the acoustic frequency (500–1000 kHz) and the initial FC concentration (200–930 times dilution) have on the efficiency of the process. Degradation of AFFFs was quantified by measuring the concentration of fluoride (F^-) and sulfate (SO_4^{2-}) released, as well as the total organic carbon (TOC) content and concentrations of selected FCs (PFBS, PFHxS and PFOS) with several durations of sonication.

2. Materials and methods

2.1. Materials

Samples of AFFF, representative of stockpiles of AFFFs present at various Air Force bases in the United States, were provided by Davis-Monthan Air Force base in Tucson (Arizona, USA). The manufacturers of these samples were 3M and ANSUL (USA). Total organic fluorine (TOF) of AFFF was measured at University of Saskatchewan, Canada. TOF was measured by use of combustion ion chromatography (CIC), following methods described by Codling et al. [24]. Undiluted TOF concentrations were 790 mM for 3M and 760 mM for Ansul. Sodium fluoride (99%) and total ionic strength adjustment buffer (TISAB II) used during F^- detection were purchased from Fisher Scientific Inc. (New Jersey, USA). Fluoride and SO_4^{2-} concentrations in the undiluted foams (without any degradation) were: 3M 8 mM F^- and 2 mM SO_4^{2-}; Ansul 0.8 mM F^- and 40 mM SO_4^{2-}.

Experiments were conducted in two different sonochemical reactors depending on the frequency. For experiments conducted at 500 kHz, the reactor was a 12 l, multi-frequency, cubical system custom made by Weber Ultrasonics (Clarkston, MI, USA) with transducers attached to the side walls. Experiments performed under 1 MHz sound frequency were conducted in a 4.5 l Minimeg® reactor from PCT systems Inc. (Fremont, CA, USA) with the transducer affixed to the bottom of the tank. The input power density to both transducers was fixed at ~ 8 W/cm^2. Pressure measurements in the experimental solutions (contained in the glass vessel and subjected to the sound field) were conducted using a calibrated hydrophone (HCT0310-1042, Onda Corp.) at a sampling rate of 20 million samples per second for 10 s. The measured values of root mean square (P_{RMS}) direct field pressures delivered to the solutions were 31.8 ± 1.2 kPa and 27.5 ± 4.9 kPa at 500 kHz and 1 MHz, respectively. The generation rate of hydroxyl radicals was measured by our research group [23], which increased with the sound frequency, being 4.1-fold higher rate at 1 MHz compared to 500 kHz.

2.2. Experimental set-up

Pictures of the experimental set-up are presented in Fig. S1 of the Supplementary Information (SI). Solutions of AFFF were prepared in ultrapure water obtained from a MilliQ Plus UV (18 MΩ-cm). A 200 ml aliquot of solution was placed into a glass reaction vessel situated at a fixed distance (1 cm) from the transducer and submersed in MilliQ water maintained at 30 °C by use of a cooling recirculating system. To avoid evaporation, solutions were covered with parafilm. Solutions were saturated with argon (polytropic index of

1.67) by bubbling them with argon for 20 min prior to the experiment and maintaining a blanket of this gas during the experiment. The experiments were monitored by measuring F^-, SO_4^{2-}, TOC, solution pH, and temperature as a function of time (0, 15, 30, 60, 90, 120, 150 and 180 min). Values reported are means from at least two independent experiments.

2.3. Analytical techniques

Concentrations of F^- was measured using a fluoride ion selective electrode (ISE) (Model 9609BNWP, Thermo Scientific Inc.). The ISE was calibrated using standards prepared with varying concentrations of sodium fluoride (10^{-6}–10^{-1} M). To ensure optimal ionic strength for potentiometric measurements TISAB II solution (5 ml) was added to samples (5 ml). Sulfate concentration was measured by suppressed conductivity ion chromatography with a Dionex IC-3000 system (Sunnyvale, CA, USA) fitted with a Dionex IonPac AS18 analytical column (4 × 250 mm) and AG18 guard column (4 × 50 mm). The concentration of the eluent (KOH) was 17 mM for 6 min. TOC analysis was performed using a Shimadzu total carbon analyzer V_{CSH} (Columbia, MD, USA). The samples were prepared using DI water and the pH adjusted to 2.0 using hydrochloric acid. The inorganic carbon was removed by sparging the samples with air. The remaining carbon was then combusted at 680 °C and analyzed. Selected samples were analyzed using an ultra-high performance liquid chromatograph (Ultimate 3000 UHP system) LC provided by Thermo Fisher Scientific Inc. (Barrington, IL, USA) and coupled to a quadrupole-time of flight mass spectrometer (TripleTOF 5600), from ABSciex (Concord, CA, USA), which provides high mass resolution.

3. Results and discussion

3.1. Sonochemical degradation of AFFFs (3M and Ansul) under a 1 MHz sound frequency

Sonochemical degradation of commercial AFFFs (3M and Ansul) was studied under an acoustic frequency of 1 MHz. The AFFFs were diluted ~930 times to an initial TOF concentration of 0.8 mM for 3M and 0.9 mM for Ansul. Concentrations of F^- ion increased as a function of duration of sonication, from zero to 0.27 ± 0.01 mM and 0.37 ± 0.03 mM for 3M and Ansul, respectively (Fig. 1A). The rate of defluorination of Ansul ($2.17 \pm 0.17\ \mu M\ F^-\ min^{-1}$) was 45% faster than that of 3M ($1.50 \pm 0.05\ \mu M\ F^-\ min^{-1}$), leading to a defluorination of $34.2 \pm 1.6\%$ in 3M and $45.4 \pm 3.5\%$ in Ansul (Fig. 1B). Mineralization of AFFF was quantified by measuring TOC of samples during the experiment (Fig. 1C). The initial concentration of TOC in 3M AFFF was 10.1 ± 0.4 mM and it decreased at a rate of $21.9 \pm 3.3\ \mu M$ TOC min^{-1} while in Ansul AFFF, the initial TOC concentration was 5.1 ± 0.5 mM, and rate of mineralization was $7.9 \pm 0.5\ \mu M$ TOC min^{-1}. The percentage of TOC removed or mineralization of AFFF was 32.3% greater for 3M ($39.0 \pm 7.2\%$) than for Ansul ($29.4 \pm 0.2\%$) (Fig. 1D).

Concentrations of SO_4^{2-} were measured as an indicator of degradation of perfluoroalkyl sulfonates (Fig. 1E). In the case of 3M AFFF, accumulation of SO_4^{2-} in solution during sonolysis increased quickly after the first hour of degradation, yielding a SO_4^{2-} concentration of $44.2 \pm 1.6\ \mu M$ corresponding to an average rate of generation of $2.09 \pm 0.01\ \mu M\ SO_4^{2-}\ min^{-1}$. By contrast, the rate of generation of SO_4^{2-} was not as significant when Ansul AFFF was degraded ($0.10 \pm 0.01\ \mu M\ SO_4^{2-}\ min^{-1}$) but the greater initial concentration of SO_4^{2-} in the foam led to a similar concentration of SO_4^{2-} ($49.8 \pm 4.7\ \mu M$) at the end of the experiment as that for 3M. The pH of the solution, which was very similar for both foams, changed from 6.4 (3M) or 5.9 (Ansul) to 4.2–4.0 during the first hour of the experiment, and then remained constant for the entire duration of the experiment (Fig. 1F).

Rates of degradation of AFFFs observed in our experiments were greater than those reported in the literature for other AFFFs. Mean rates of production of F^- and SO_4^{2-} during sonochemical degradation of FC-600, manufactured by 3M, at 505 KHz and with an initial PFOS concentration of 18.9 μM. were 0.80 and $0.19\ \mu M\ min^{-1}$ for F^- and SO_4^{2-}, respectively [22] In the present study, rates of production of F^- and SO_4^{2-} at 1 MHz for Ansul (0.9 mM TOF) were $2.17 \pm 0.17\ \mu M\ F^-\ min^{-1}$ and $0.10 \pm 0.01\ \mu M\ SO_4^{2-}\ min^{-1}$, respectively. In the case of 3M (0.8 mM TOF) under 1 MHz, mean rates of production of F^- and SO_4^{2-} were 1.50 ± 0.05 and $2.09 \pm 0.01\ \mu M\ min^{-1}$, for F^- and SO_4^{2-}, respectively. Thus, rates of production of F^- rates from Ansul and 3M were 2.7-fold and 1.5-fold greater, respectively, than production of F^- from FC-600 previously reported [22]. Similarly, the rate of production of SO_4^{2-} from Ansul was 2.0-fold less than that for FC-600, but 11.0-fold greater for 3M than for FC-600. These difference between previously reported rates [22] and those observed in the present study can be explained based on the different compositions of AFFFs and frequencies used in the two studies. Using the initial concentration of FC, Vecitis and coworkers calculated the total initial fluorine concentration to be 167 mM (TOF) for undiluted AFFF which is equivalent to ~0.7 mM after 250-fold dilution. Based on the defluorination rate reported, the time required to completely defluorinate AFFF would be 835 min. In the current study, the time for complete defluorination would be 535 and 370 min for 3M and Ansul, respectively. Thus, parameters such as type of AFFF, initial FC concentration, and sound frequency have a significant influence on sonochemical treatment of AFFFs.

Understanding chemical pathways during degradation of FCs by use of sonochemical treatment is both important and complex. Foam diluted ~930-fold and irradiated with a frequency of 1 MHz were analyzed using high resolution quadrupole time-of-flight (LC-qTOF) to monitor the degradation of FCs and identify their major degradation products of 3M (Fig. 2A) and Ansul (Fig. 2B). 3M was characterized by a greater diversity of FCs than Ansul, which contains perfluoroalkyl sulfonates, PFOA, and the 6:2 fluorotelomer thioether amido sulfonate, as well as perfluoroalkyl sulfonamides with carboxylic acid and amine functionalities, which is consistent with previously reported results [2,25], and material safety data sheets (MSDS) [26] that list amphoteric fluoroalkylamide derivatives. Alternatively, the primary components identified in Ansul AFFF were perfluoroalkyl sulfonates, accompanied by 8:2 fluorotelomer thioether amido sulfonate, 6:2 and 8:2 fluorotelomer thioether amido sulfonates [2], which are known components in other AFFFs [27,28]. However, the study by Place and Field [2] did not identify any of the perfluoroalkyl sulfonates detected in this study, although they are also listed as fluorosurfactants in the MSDS [29]. Formation of shorter chain FCs during 180 min of sonochemical degradation of foams was observed, as illustrated by formation or increases in relative intensities for compounds such as perfluoropropanesulfonic acid (PFPrS) and perfluoropentanesulfonic acid (PFPeS) in the case of 3M; and PFOS, perfluoroheptanesulfonic acid (PFHpS) and PFEtS, for the case of Ansul.

Concentrations of individual FCs (PFOS, PFHxS, PFBS and PFOA) in FC-600 diluted 5000-fold decreased continuously with sonication time under a frequency of 505 kHz [22]. However, formation of shorter chain perfluorocarboxylates was observed with sonication time during sonochemical degradation of PFOS and PFOA (0.20 mM PFOS and 0.24 mM PFOA) at 200 kHz [16]. Since AFFFs contain a mixture of FC, complexity during foam degradation would be expected to result in more mixtures due to some FCs being destroyed and fragmented, while others are formed through condensation reactions.

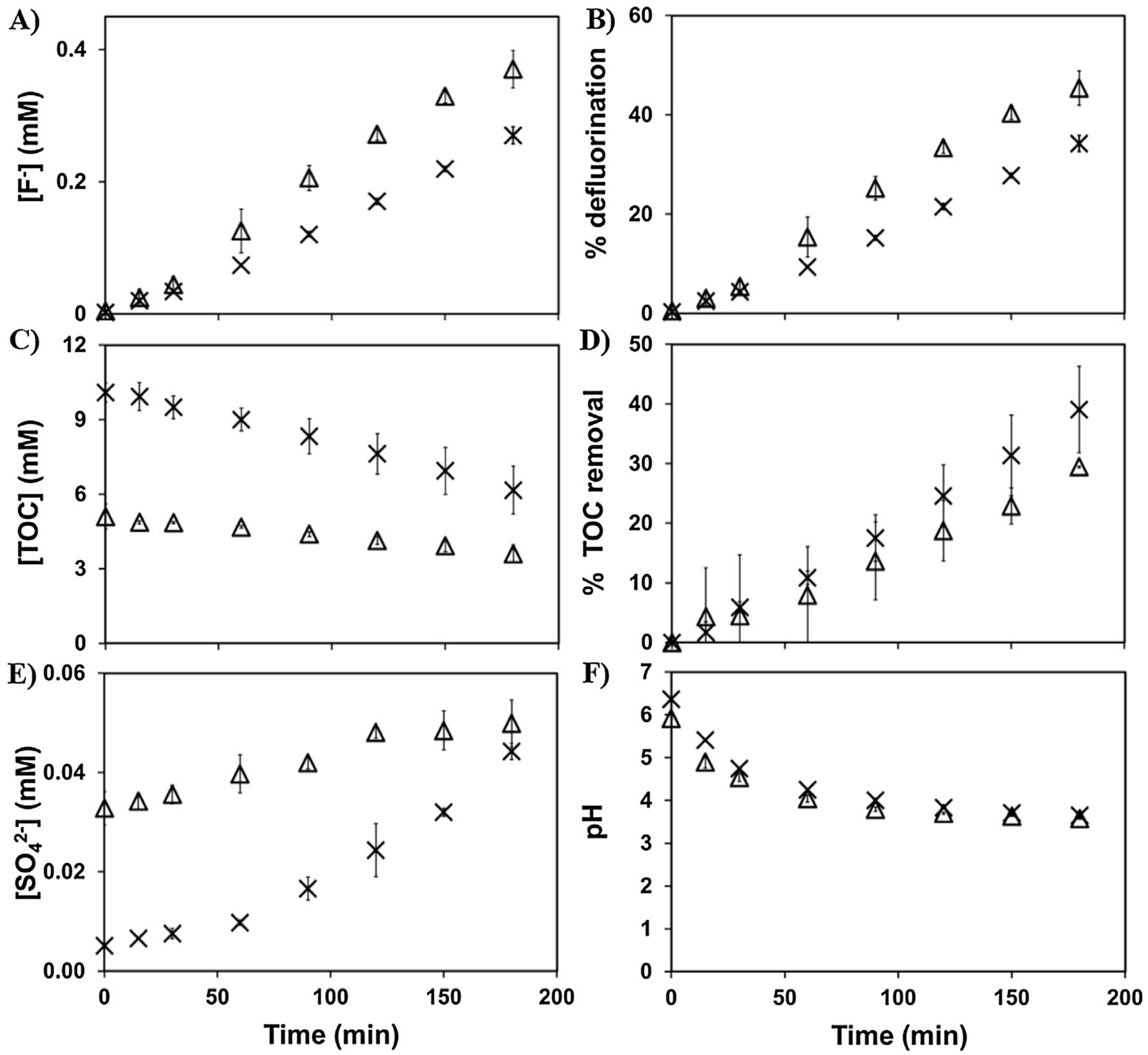

Fig. 1. Sonochemical degradation of 3M AFFF (0.8 mM TOF, ×), and Ansul AFFF (0.9 mM TOF, Δ) under a frequency of 1 MHz. This figure shows as a function of the sonication time (180 min): the release of fluoride (panel A); the percentage degradation calculated as the release of fluoride (panel B); the removal of total organic carbon (TOC) (panel C); the percentage of TOC removal (panel D); the release of sulfate (panel E); and, the change of the solution pH (panel F).

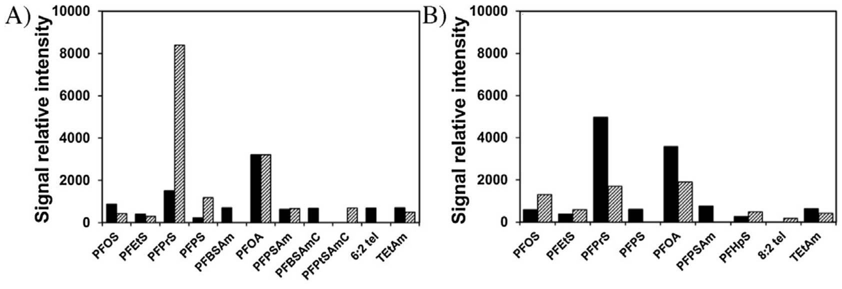

Fig. 2. Identification of the major FC present at the beginning of the experiment, $t = 0$ min (black bar), and after 180 min of sonication (inclined stripes bar) in a 929.4× diluted solution of AFFF 3M (panel A) and Ansul (panel B) when sonicated under a 1 MHz sound frequency. The abbreviations are: pefluorooctane-sulfonic acid (PFOS), perfluoroethane-sulfonic acid (PFEtS), perfluoropropane-sulfonic acid (PFPrS), perfluoropentane-sulfonic acid (PFPS), perfluoroheptane-sulfonic acid (PFHpS), perfluorooctanoic acid (PFOA), perfluorobutane-sulfonamide amine (PFBSAm), perfluoropentane-sulfonamide amine (PFPSAm), perfluorobutane-sulfonamide amine carboxylic acid (PFBSAmC), perfluorohexane-sulfonamide amine carboxylic acid (PFHxSAmC), 6:2 fluorotelomer (6:2 tel), 8:2 fluorotelomer (8:2 tel), and triethanolamine (TEtAm).

3.2. Role of the sound frequency on AFFF degradation

Effect of frequency of sound on sonochemical degradation of AFFF was studied for both 3M and Ansul, by comparing the results obtained under 500 kHz and 1 MHz, for an initial composition of 0.8 mM TOF 3M and 0.9 mM TOF Ansul (930 times dilution of the original AFFF). Concentrations of F^- and TOC at various sonication times for 3M and Ansul were investigated at two different frequencies of 500 kHz and 1 MHz (Fig. 3). Defluorination of FC was 10-fold greater when the solution was exposed to a frequency of 1 MHz than when exposed to 500 kHz. The concentration of F^- released from 3M after 180 min was only 0.09 ± 0.02 mM with 500 kHz cor-

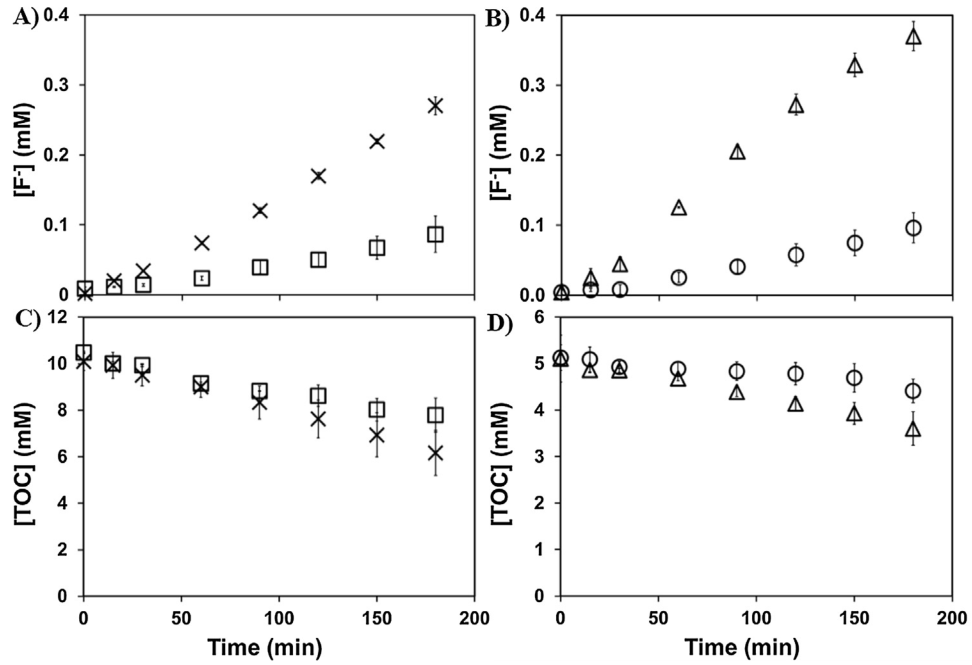

Fig. 3. Sound frequency effect on the sonochemical degradation of 929.4× dilution AFFF. This figure shows as a function of the sonication time (180 min) the release of fluoride when 3M (panel A) was sonicated under 500 kHz (□) or under 1 MHz (×); and when Ansul (panel B) was sonicated under 500 kHz (○) or under 1 MHz (Δ).

responding to a release rate of 0.43 ± 0.15 μM F^- min^{-1}, compared to 0.27 ± 0.01 mM (1.50 ± 0.05 μM F^- min^{-1}) when the frequency used was 1 MHz (Fig. 3A). Similarly, the concentration of F^- released from Ansul after 180 min of sonolysis under 500 kHz sound frequency was only 0.08 ± 0.02 mM (0.41 ± 0.13 μM F^- min^{-1}) versus 0.37 ± 0.03 mM with 1 MHz (2.17 ± 0.17 μM F^- min^{-1}) (Fig. 3B). In addition, mineralization of TOC was 1.5- to 3.0-fold greater when exposed to 1 MHz than 500 kHz. The concentration of TOC in 3M (Fig. 3C) decreased at a rate of 14.6 ± 4.3 μM TOC min^{-1} when sonicated under 500 kHz, which is 1.5-fold slower than if the frequency was 1 MHz (21.9 ± 3.3 μM TOC min^{-1}). In the case of Ansul (Fig. 3D), the difference in TOC mineralization at the two frequencies was even greater, with a 2.4-fold slower mineralization rate under 500 kHz (3.3 ± 0.3 μM TOC min^{-1}) than under 1 MHz (7.9 ± 0.5 μM TOC min^{-1}). The temperature values for these experiments are presented in Fig. S2 in the SI.

Sonochemical degradation of FC is considered to be mainly by direct pyrolysis [30], due to the high temperatures reached during stable bubble oscillations or collapsing transient bubbles [17,20]. Direct oxidation of FC by hydroxyl radicals formed due to the thermal decomposition of water and other species is thought to be a secondary degradation mechanism [17]. Because FC amphoteric nature and tendency to partition in the bubble-water interphase [31], rates of degradation of FCs depend on the number of available interfacial sites for adsorption of FC molecules, which is dictated by the frequency employed. The resonant radius of the cavities is inversely proportional with frequency. The resonant radius (R_0) can be calculated using Minnaert's equation [32] Eq. (1), assuming no interaction between bubbles:

$$R_0^2 = \frac{3 \times \gamma \times P_0}{\rho_0 \times \omega_0^2} \times 10^6\,(\mu m) \qquad (1)$$

ω_0 is the resonant frequency, $\omega_0 = 2 \times p \times f$ (rad s^{-1}), and f is the sound frequency (Hz); P_0 is the hydrostatic pressure (Pa); γ is the polytropic index (dimensionless) of the dissolved gas; and, ρ_0 is the density of the solution (kg m^{-3}). Assuming the same solution conditions and varying sound frequency, Eq. (1) can be rearranged to form Eq. (2).

$$R_0 = \frac{C}{f} \qquad (2)$$

where c is a constant grouping the conserving parameters for the same solution conditions. Therefore, the radius of a bubble formed under a 500 kHz sound field will be twice as long as that of a bubble formed under 1 MHz ($R_{0.500\,MHz} = 2 \times R_{1\,MHz}$). The ratio of available surface area to volume of a bubble (sphere) increases with decreasing radius (=$3 \times R_0{}^{-1}$). The larger ratio of surface area to volume and the greater number of cavitation events along with the greater number of bubbles formed per unit of time under higher frequencies [19] implies that more molecules can be adsorbed at the bubble-water interphase and, consequently, pyrolytically degraded when sonicated under higher frequencies for the same sonication time [15,19].

Greater rates of degradation at higher frequencies of sound have been reported previously in several studies. When carbon tetrachloride and hexachloroethane were sonochemical degraded at frequencies ranging from 20 to 1078 kHz; the rate of degradation increased until reaching a maximum at 618 kHz, after which the rate of degradation decreased with further increase in frequency [19]. Sonochemical degradation of chlorinated alkanes and alkenes was maximum at 618 kHz (205–1078 kHz) [33]. Similarly, the maximum rate of degradation of chlorinated compounds was at 300 kHz for a frequency range of 35–1000 kHz. [34] Additionally, sonochemical degradation of 0.23 μM PFHxS and 0.30 μM PFBS were maximum at 358 kHz and 610 kHz, respectively (frequency range from 202 to 1060 kHz)[15]. Sonochemical degradation of PFOS was directly proportional to frequency (25–1000 kHz) for lesser initial concentrations of PFOS (10 and 100 μM) without reaching a maximum [23]. However at a greater initial concentration of PFOS (460 μM) there was no significant difference between the rate of degradation at 500 kHz and 1 MHz (optimum frequency). The presence of optimum or maximum frequency, beyond which an increment in frequency will hinder rates of degradation, could be due to the balance between more cavitation events (number den-

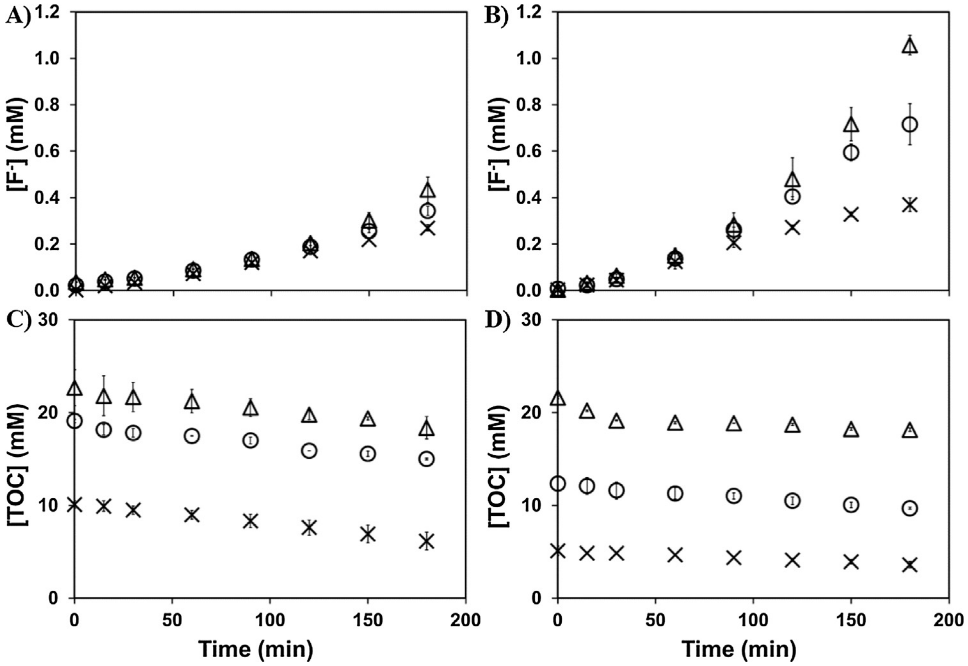

Fig. 4. Effect of the initial concentration on the sonochemical degradation of 3M AFFF and Ansul AFFF under a sound frequency of 1 MHz. The initial concentrations were 929.4× dilution (×), 500× dilution (●) and 200× dilution (△). These dilutions correspond to initial TOF concentration of 0.8 mM TOF in 3M and 0.9 mM TOF in Ansul, 1.5 mM in 3M and Ansul, and 3.7 mM in 3M and 3.8 mM in Ansul, from more to less dilution. This figure shows as a function of the sonication time (180 min): the release of fluoride in 3M (panel A); the release of fluoride in Ansul (panel B); the removal of total organic carbon (TOC) in 3M (panel C); and, the removal of total organic carbon (TOC) in Ansul (panel D).gr4

sity and frequency of oscillation or collapse of bubbles) and lesser cavitation intensity with increasing acoustic frequencies. The sonochemical degradation of AFFF was greater at 1 MHz than at 500 kHz suggesting the maximum or optimum frequency to be ≥1 MHz under the experimental conditions of this study. Based on these results, degradation of AFFF was investigated using a frequency of 1 MHz and different initial concentrations.

3.3. *Effect of the initial concentration on the extent and rate of sonochemical degradation of AFFFs*

The effect of concentration of FCs on rates of degradation of 3M and Ansul AFFF exposed to a frequency of 1 MHz with initial concentrations of TOF of 930× dilution (0.8 mM TOF 3M and 0.9 mM TOF Ansul), 500× dilution (1.5 mM TOF 3M and 1.5 mM TOF Ansul), and 200× dilution (3.7 mM TOF 3M and 3.8 mM TOF Ansul). Concentrations of F^- released and TOC consumed as a function of the sonication time for the different initial FC concentrations are shown in Fig. 4, and a summary of these results is presented in Table 1. Rates of sonochemical defluorination of AFFFs were directly proportional to initial concentration of FC. The amount of F^- released after 180 min of sonication of 3M AFFF accounted for degradation of 34.2 ± 1.6, 23.4 ± 1.3, and 11.1 ± 1.4% of initial concentrations of TOF in solutions containing 0.8, 1.5 and 3.7 mM TOF, respectively, (Fig. 4A). Similarly, F^- released from Ansul AFFF was 45.4 ± 3.4%, 47.1 ± 5.8%, and 27.8 ± 1.1% for initial TOFs of 0.9, 1.5 and 3.8 mM, respectively (Fig. 4B; Table 1). Concentrations of FC not only affected extent but also rate of defluorination AFFFs. Defluorination rate as a function of initial concentration of TOF is given for 3M and Ansul (Fig. 5A). Rate of degradation of Ansul was significantly affected by initial concentration, as indicated by rate of release of F^-, which was approximately 60% greater for the greatest initial TOF (3.8 mM) compared with the least initial concentration of TOF (0.9 mM). In the case of 3M AFFF, the effect is not as significant, since the difference in rate of release of F^- between the greatest and the least concentration of TOF was less (∼28%). Rates of degradation observed at greater concentrations of FC can be explained by greater availability of adsorbed FC molecules at the bubble-liquid interface and an increase in electrostatic repulsion between bubbles preventing them from coalescing, which enhances the number density of cavitating bubbles [35].

Mineralization of AFFF was not as greatly affected by initial concentration. Mineralization of 3M AFFF was independent of initial concentration with rates of mineralization of the order of 21.5 μM min^{-1} for all three concentrations (Fig. 4C). Rates of mineralization of Ansul AFFF were less than those of 3M AFFF and increased from 7.9 ± 0.5 μM min^{-1} to 14.4 ± 4.2 μM min^{-1} when concentrations of TOF increased from 0.9 to 1.5 mM. However, increase in FC concentration did not result in significantly greater rates of mineralization (14.8 ± 0.9 μM min^{-1} for 3.8 mM TOF) (Fig. 4D). Since adsorption of molecules is an important step prior to sonochemical degradation, rates of degradation at greater initial concentrations of FC are controlled by saturation kinetics which depends on availability of interfacial sites. Therefore, after reaching a maximum concentration degradation of AFFF will be independent of the initial concentration [16,17,33]. Since AFFF is a complex mixture of various chemicals, of which some are fluorinated, it is possible that the AFFF mineralization may be happening under saturation conditions, while defluorination occurs under sub-saturation conditions.

3.4. *AFFF defluorination kinetics*

Rate of defluorination of AFFF will be a function of the maximum rate of defluorination, r_{max}, which can be expressed by Eq. (3).

$$\frac{d[F^-]}{dt} r_{\max} \bullet \theta \qquad (3)$$

Table 1
Summary of the average rate constants calculated for the release of F⁻ and TOC degradation during the sonochemical degradation of Ansul and 3M under a 1 MHz sound frequency.

Formulation /[TOF] (mM)		Defluorination	TOC degradation	Defluorination (%)	TOC removed (%)
	Rate constant, k (μM min^{-1})	Rate constant, k (μM min^{-1})			
3M	0.8	1.5 ± 0.1	21.9 ± 3.3	34.2 ± 1.6	39.0 ± 7.2
	1.5	1.7 ± 0.1	21.1 ± 1.8	23.4 ± 1.3	21.3 ± 1.2
	3.7	2.1 ± 0.2	21.8 ± 8.0	11.1 ± 1.4	18.9 ± 1.7
Ansul	0.9	2.2 ± 0.2	7.9 ± 0.5	45.4 ± 3.4	29.4 ± 0.2
	1.5	4.1 ± 0.3	14.4 ± 4.2	47.1 ± 5.8	21.4 ± 3.6
	3.8	5.6 ± 0.4	14.8 ± 0.9	27.8 ± 1.1	16.0 ± 1.4

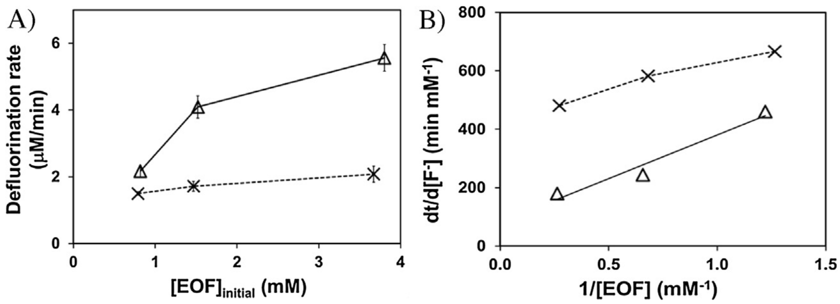

Fig. 5. Sonochemical degradation of 3M AFFF (×) and Ansul AFFF (Δ) under a frequency of 1 MHz. Panel A: Effect of the initial total organic fluorine (TOF) concentration (or initial PFC concentration) on the F⁻ release rate; and panel B: Linearization of rate of defluorination of AFFF as a function of initial organic F concentration. The inverse of rate of defluorination of AFFF ($dt/d[F^-]$) is plotted versus the inverse of the initial TOF concentration (1/[TOF]), as $dt/d[F^-] = 1/r_{\max} + 1/(r_{max}{\bullet}K_s){\bullet}1/[TOF]_0$. The dashed line is the linear fit for 3M AFFF: $1/r_{max} = 441$ min mM^{-1}, $1/(r_{max}{\bullet}K_s) = 184$ min, $R^2 = 0.976$. The black line is the linear fit for Ansul AFFF: $1/r_{max} = 82$ min mM^{-1}, $1/(r_{max}{\bullet}K_s) = 299$ min, $R^2 = 0.960$.

Table 2
Summary of the kinetics parameters calculated in this study for the sono chemical degradation of two AFFF, Ansul and 3M.

AFFF	r_{max}[a] (μM F⁻ min^{-1})	K_s[a] (M^{-1})	$[TOF]_{bubble}$[b] (mM)
3M	2.3	2397	41
Ansul	12.3	273	363

[a] $r_{\max}$ and K_s were obtained from the linear fitting of $dt/d[F^-]$ *vs.* 1/[TOF] (Fig. 5B), and applying Eq. (7).
[b] $[TOF]_{bubble}$ at was calculated using Eq. (6).

where θ is the fraction of occupied interfacial sites (dimensionless). θ is a function of the initial TOF concentration and the sonochemical partitioning coefficient, K_s, and it is calculated by use of Eq. (4).

$$\theta = \frac{K_s \bullet [\mathrm{TOF}]}{1 + K_s \bullet [\mathrm{TOF}]} \tag{4}$$

By substituting Eq. (4) into Eq. (3) the differential Eq. (5) is derived.

$$\frac{d\,[F^-]}{dt} = r_{\max} \bullet \frac{K_s \bullet [\mathrm{TOF}]}{1 + K_s \bullet [\mathrm{TOF}]} \tag{5}$$

The saturation concentration at the bubble surface, $[\mathrm{TOF}]_{\mathrm{bubble}}$, can be defined as the least concentration of FC that will provide the maximum rate of defluorination, or, the concentration at which θ becomes ≈ 1 Eq. (6).

$$[EOF]_{bubble} = \frac{\theta}{\left(1-\theta\right) \bullet K_s} = \frac{0.99}{0.01 \bullet K_s} \tag{6}$$

The kinetics parameters, $r_{\max}$ and K_s, for the AFFF degradation (under a given frequency), can be calculated by inverting Eq. (5) to form Eq. (7) [36]:

$$\frac{\mathrm{dt}}{d\,[F^-]} = \frac{1}{\mathrm{r_{max}}} + \frac{1}{\mathrm{r_{max}} \bullet K_s}\frac{1}{[\mathrm{TOF}]} \tag{7}$$

The data for 3M ($R^2 = 0.976$) and Ansul ($R^2 = 0.960$) AFFFs can be linearized by use of Eq. (7) (Fig. 5B; Table 2). Maximum rate of defluorination of AFFF exposed to 1 MHz, $r_{\max}$, was 2.3 μM F⁻ min^{-1} for 3M, and almost 4-fold greater for Ansul, 12.3 μM F⁻ min^{-1}. This result is indicative of the faster sonochemical degradation of Ansul in comparison with 3M. The K_s value was 2397 M^{-1} and 273 M^{-1}, for 3M and Ansul, respectively. Also, the saturation concentration at the bubble-liquid interface, $[\mathrm{TOF}]_{\mathrm{bubble}}$, was 8.7-fold greater for Ansul (363 mM) than for 3M (41 mM), which correlates well with the 10-fold lesser K_s value determined for Ansul. In comparison, the kinetic parameters reported previously [22] for sonochemical degradation of PFOS in FC-600 were $r_{\max} = 350$ nM min^{-1} and $K_s = 100{,}000$ M^{-1}.This result is consistent with the fact that the latter parameters were calculated for the disappearance of PFOS whereas the parameters presented in this study were obtained based on the fluoride released by the sonochemical degradation of a mixture of fluorinated reactants.

3.5. Energy requirement for the AFFF sonochemical degradation

The sonochemical degradation of AFFF has been proved as an effective and low energy method to treat persistent AFFF. The energy consumed to degrade 1 μmol TOC in the AFFF was estimated using the highest mineralization rate conditions (1 MHz and 200× dilution of the AFFF). The transducer intensity (W m^{-2}) was calculated using the following Eq. [5]:

$$\mathrm{I} = \frac{\mathrm{P}_{RMS}{}^2}{(\rho_0 \cdot \kappa)^{0.5}} \tag{8}$$

where P_{RMS} is 27.5 ± 4.9 kPa, the root mean square (RMS) direct field pressure delivered to the solution under 1 MHz frequency; ρ_0 is the fluid density (1000 kg m^{-3}); and, κ is the bulk modulus of the fluid (2.15×10^9 N m^{-2}). The calculated I was 515.8 W m^{-2}. The area of the 1 MHz transducer is 125 cm^2; therefore the power released to the solution is ~6.4 W. Knowing that the rate of mineralization is 21.8 μmol TOC min^{-1} for 3.7 mM TOF 3M and 14.8 μmol TOC min^{-1} for 3.8 mM TOF Ansul (Table 1), the energy required to degrade 1 μmol TOC in the foams is 17.7 J μmol^{-1} TOC^{-1} and 26.1 J μmol^{-1} TOC^{-1} for 3M and Ansul, respectively. For comparison with other technologies for PFOS degradation, the energy requirement was converted to J μmol^{-1} PFOS^{-1}, assuming that the foams are made exclusively of PFOS. With this wide assumption, the energy consumption is translated to 142.0 J μmol^{-1} PFOS^{-1} for 3M and 209.1 J μmol^{-1} PFOS^{-1} for Ansul. These numbers are lower than those reported for other higher energy techniques (*i.e.* 850 kJ μmol^{-1} PFOS^{-1} using UV photolysis) and sonolysis using lower sound frequencies (*i.e.* 95–4500 kJ μmol^{-1} PFOS^{-1} with 354 kHz) [14]. It is important to note the major weaknesses in the method described to calculate the energy requirements. First, it was assumed that the foams were made solely of PFOS. Secondly, the formation of secondary degradation products might slow the degradation rate over time. However, it can be concluded that the treatment of AFFF using megasonic frequencies is highly energy efficient compared with other current higher energy technologies.

4. Conclusions

Degradation of two AFFF formulations, 3M (0.8 mM TOF) and Ansul (0.9 mM TOF), under 1 MHz sound frequency resulted in 45.4% and 34.2% defluorination, respectively after 180 min of sonication. Under similar conditions, measurements of TOC showed 39.0% and 29.4% mineralization for 3M and Ansul, respectively. Due to an increase in the available interfacial sites for the molecules to adsorb and possible increase in the number of cavitation events with increasing acoustic frequency, greater defluorination and mineralization of AFFF were observed greater frequencies. The initial TOF concentration affected the rates of sonolysis kinetics with faster defluorination rates achieved when greater initial concentrations of TOF were used. However, AFFF mineralization was not significantly influenced by the initial TOF concentration. In conclusion, sonochemical treatment is a promising and energy efficient method for destruction of FCs in formulations of AFFF.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhazmat.2016.05.078.

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