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Sono-chemical treatment of per- and poly-fluoroalkyl compounds in aqueous film-forming foams by use of a large-scale multi-transducer dual-frequency based acoustic reactor

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ABSTRACT

Aqueous film-forming foams (AFFFs) contain a mixture of organic chemicals, including per- and poly-fluorinated, alkyl sulfonate substances (PFAS) (1–5%, w/w). Some longer-chain PFAS can be toxic, moderately bioaccumulative and persistent in the environment. In the present work, decomposition of PFAS present in two commercially available AFFFs (ANSUL- and 3M-) was investigated using a sono-chemical reactor of volume 91 L. The reactor consists of 12 transducers with operating frequencies of 1 MHz or 500 kHz and total input power of 12 kW. Degradation of PFASs performed using various dilutions of AFFF revealed that release of F^- and SO_4^{2-} ions was inversely proportional to initial pH of up to 4. Defluorination of ANSUL-AFFF resulted in an increase in the concentration of F^- released from $55.6 \pm 0.3 \mu M$ (500× dilution) to 58.6 ± 0.6 (25× dilution), while for 3M AFFF it increased from $19.9 \pm 0.7 \mu M$ (500× dilution) to $217.1 \pm 2.4 \mu M$ (25× dilution). Though amounts of F^- released were less for ANSUL-AFFF than for 3M-AFFF, there was a considerable increase in removal of TOC and release of SO_4^{2-} present in ANSUL-AFFF. Approximately 90.5% and 26.6% reduction of perfluoroalkyl sulfonates (PFSA) and perfluoroalkyl carboxylates (PFCA) in 3M, respectively, and 38.4% reduction of fluorotelomer sulfonates in ANSUL-AFFF were achieved in 13 h. Estimated costs of energy for the treatment of ANSUL-AFFF and 3M-AFFF at a 500× dilution were $\$0.015 \pm 0.0001/L$ and $\$0.019 \pm 0.0002/L$, respectively.

1. Introduction

Fluorinated aqueous film-forming foams (AFFFs) have extensive uses for controlling petroleum-based fires at airports, especially Air Force stations, naval facilities, oil refineries and automotive races. AFFFs is a mixture of hydrocarbons and per-fluorochemical surfactants (1–5% w/w) [1,2]. Per- and poly-fluoroalkyl substances (PFASs) have unique amphiphilic properties that impart the foam with properties, such as high spreadability, on hydrocarbon fuel that allow AFFFs to separate fuel from oxygen in the air and thus quench the fire [3]. PFAS-based surfactants are amphiphilic and resistant to combustion and thermally stable, which are properties that impart advantages over hydrocarbon surfactants. This is due in part to the non-polar group of perfluorocarbon tail of hydrophobic and oleophobic properties [4–6].

Large quantities of AFFFs that have been used at U.S. Air Force

bases for training and routine operations have resulted in widespread contaminated of groundwater with PFASs [7]. Groundwater in areas surrounding some airports, especially at Air Force bases, is contaminated with PFAS [8]. As much as 40–100% of PFAS released remains in groundwater even 20 years after being released to the environment [1,2]. Due to growing environmental concerns associated with releases of PFASs, uses of AFFFs containing longer-chain PFASs, such as perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) have been discontinued for military operations [9]. It is estimated that approximately 11 million liters of AFFFs are left untreated at various air-force stations across the USA. Several studies have been directed towards the treatment of PFASs in AFFFs [8,9]. Recently (May 2016), the United States Environmental Protection Agency (US-EPA) set a new lifetime health advisory of 70 ng/L for PFOS and PFOA combined in drinking water [10].

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Nomenclature

AFFFs	aqueous film-forming foams
6:2 FTS	6:2 fluorotelomer thioether amino sulfonate
8:2 FTS	8:2 fluorotelomer thioether amino sulfonate
PFAS	per- and polyfluorinated compounds
PFCA	per- and polyfluorinated carboxylic acids
PFSA	per- and perfluorinated sulfonates
PFHxA	perfluorohexanoic acid
PFHpA	perfluoroheptanoic acid
PFOA	perfluorooctanoic acid
PFNA	perfluorononanoic acid

PFDA	perfluorooctanoic acid
PFUnDA	perfluoroundecanoic acid
PFDoDA	perfluorodecanoic acid
PFBS	perfluorobutane sulfonic acid
PFPeS	perfluoropentane sulfonate
PFHxS	perfluorohexane sulfonate
PFHpS	perfluoroheptane sulfonate
PFOS	perfluorooctane sulfonate
PFNS	perfluorononane sulfonate
PFDS	perfluorodecane sulfonate
TOC	total organic carbon
TOF	total organic fluorine

Due to the high strength of C–F bonds, PFAS are not easily degraded by microbes under environmental conditions [7]. Only partially fluorinated chains are biodegradable [2]. Conventional techniques for treatment of groundwater such as reverse osmosis, nano-filtration, and activated carbon are not effective at removing PFASs, but sono-chemical degradation can be effective [8,11]. Sono-chemical effects are produced by cavitation caused by interactions of ultrasonic irradiation with aqueous solutions [12–14]. During cavitation, temperatures produced inside bubbles are from 4000 to 10,000 K, and at or near the interface of the bubble, temperatures can be 1000–1500 K, which can cause pyrolytic degradation of PFASs. Volatile compounds degrade inside the bubbles, while many compounds present in the bulk solution can be oxidized by hydroxyl radicals [15–17]. Rates of sono-chemical degradation depend on properties of PFASs, including hydrophobicity, surface tension, surface excess properties, and volatility. Other factors that contribute to degradation are frequency of operation, intensity of irradiation and geometry of the sono-chemical reactor [18–20]. Results of several investigations have demonstrated that sono-chemical degradation of PFASs is effective for reducing lengths of fluorocarbon chains and decreasing concentrations of PFASs from initial concentrations of mM to nM. However, few studies have considered the sono-chemical degradation of AFFFs [6]. These studies have been performed using small-scale reactors (up to a few liters). Due to issues of scalability, studies conducted using large-scale sono-chemical reactors have been very limited.

There are several factors related to the design of large-scale sono-chemical reactors. Designs vary in numbers and locations of transducers, frequency of operation, geometries of reactors, power dissipation per unit volume and cavitation yield. The efficiency of sono-chemical reactors depends on optimization of these parameters [21]. Most of the work reported on mapping of cavitation activity has been conducted using measurements by hydrophones or liberation of iodine at various locations in reactors [22]. During a pilot-scale study, in which a sono-chemical reactor was used to degrade dichloromethane, trichloromethane and the dye methyl orange, rates of degradation were four-fold faster than those during laboratory-scale studies. Analyses of power budgets of reactors indicated that nearly one-third of applied power was converted into sono-chemical activity [30]. In this study, sono-chemical degradation of AFFFs using a multi-transducer, dual-frequency based large-scale reactor of 91-L capacity is reported. Effects of pH, dilution ratio, and acoustic frequency on degradation of two commercially available AFFFs were examined. Concentrations of fluoride (F^-) and sulfate (SO_4^{2-}) released, removal of total organic carbon (TOC), and chain lengths of PFASs were monitored.

2. Experimental section

2.1. Materials

Samples of AFFFs were provided by the Davis-Monthan Air Force Base in Tucson (Arizona, USA). AFFFs were manufactured by 3M (St.

Paul, Minnesota, USA) or ANSUL (Marinette, Wisconsin, USA). Concentrations of total organic fluorine (TOF) in undiluted samples were 92.8 mg/L for 3M-AFFF and 47.9 mg/L for ANSUL-AFFF [16]. Samples were diluted using ultrapure water obtained using a MilliQPlus IV system (18 M Ω -cm). Hydrochloric acid, sodium hydroxide, total ionic strength adjustment buffer (TISAB – II), sodium fluoride, sodium sulfate, and potassium hydrogen phthalate were purchased from Fisher Scientific Inc. (Hampton, NH, USA). Nitrogen (N) (ultrapure) and compressed dry air was provided by Micro/Nano Fabrication Center (The University of Arizona, Tucson, USA). Compressed argon was supplied by Cryogenics and Gas Facility (The University of Arizona). Authentic standards of PFAS, mass labeled PFAS and chemicals required for high performance liquid chromatography–mass spectrometry (HPLC/MS) and combustion ion chromatography (CIC) analysis were provided by the Toxicology Center, University of Saskatchewan, Saskatoon, SK, Canada.

2.2. Sono-chemical reactor

The multi-transducer sono-chemical reactor, made of stainless steel (SS 316), was fabricated by PCT System Inc. (Fremont, CA, USA). Total power supplied to transducers was 12,000 W (~ 8 W/cm 2). The reactor was provided with a cooling system for extracting heat generated during acoustic sonication of aqueous solutions and for maintaining desired temperatures in the reactor. A Re-circulating chiller (process fluid temperature range: 5–35 °C, reservoir volume: 2 L, temperature stability: ± 0.1 °C) provided by ThermoFisher Scientific (Hampton, NH, USA) was used for cooling solutions in the reactor. Transducers and electronic circuits were cooled by use of a continuous supply of nitrogen (5–10 psi). A schematic of the reactor including locations of transducers is shown in Fig. 1a and b. Dimensions of the reactor are 20.9 \times 26.0 \times 175.3 cm, and working reaction volume is 91 L. The calorimetric efficiency (power dissipated in a reaction volume to actual power supplied to the reactor) of the reactor was 24.5%. Three sampling ports were present to check the concentrations of solutions at various locations. The reactor was provided with three pumps P_D , P_R , and P_F , used for draining, and filling the reactor and recirculation of liquid in the reactor, respectively. Pumps were operated using clean, dry air (60–80 psi) supplied to the reactor. Pump P_R was in the ‘on’ mode when the reactor was in the operational mode to maintain a uniform concentration of species in the reactor. There was a safety interlock mechanism in the reactor in case of failure.

2.3. Experimental methodology

Diluted aqueous solutions of AFFF were prepared using ultrapure deionized water. The pH of the solutions was adjusted by use of 1 M HCl or 1 M NaOH, as needed. The reactor was first filled with a diluted AFFF aqueous solution, which was saturated with argon gas by bubbling the solution with the gas for 30 min before the experiment and maintaining a blanket of this gas during the experiment. Degradation of per-

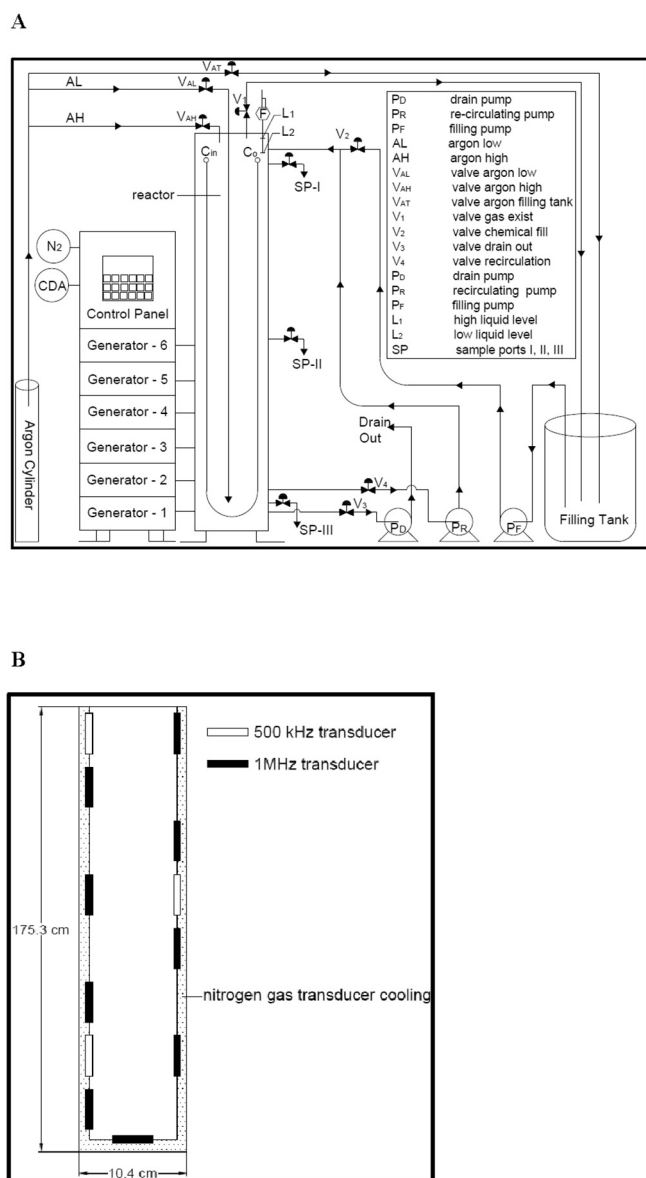


Fig. 1. (A) Sonochemical reactor of 91-L capacity utilized for treatment of AFFFs. (B) Location of transducers in sonochemical reactor.

fluorochemicals is directly proportional to maximum temperature attained during collapse of bubble formed during cavitation [31]. Maximum temperature in collapsing bubbles was calculated (Eq. (1)).

$$T_{\max} = T_{\text{in}} [P_a (\gamma - 1) / P_{\text{in}}], \quad (1)$$

where: T_{in} and P_{in} are initial temperature and pressure in bubbles at the end of expansion, respectively. P_a is the acoustic pressure and γ is the specific heat ratio of gas inside bubbles. Argon has a higher specific heat ratio as compared to other gases such as oxygen, nitrogen, and air [32], which results in higher temperatures inside cavitating bubbles containing Ar. Samples from port – II (SP-II) (see Fig. 1a) were collected to monitor the progress of degradation.

2.4. Analysis

Total organic fluorine (TOF) and concentrations of PFASs in samples was measured by use of CIC and HPLC/MS, respectively. Methods used for measurement of TOF and PFAS have been reported previously [23]. Procedures for measurements of concentrations of F^- and SO_4^{2-} ion released, and TOC have also been reported previously [15,16].

3. Results and discussion

AFFFs used consisted of PFASs, hydrocarbons, and water. 3M-AFFF formulation consisted of amphoteric fluoroalkyl amide derivatives (1–5%), perfluoroalkyl sulfonate salts (0.5–1.5%), alkyl sulfate salts (1–5%), triethanolamine (0.5–1.5%), tolyltriazole (0.05%), diethylene glycol butyl ether (20%), water (69–71%), and unknown quantities of residual organic fluorochemicals [24]. The ANSUL-AFFF consisted of hydrocarbon surfactants, fluorosurfactants, inorganic salts, and water. Major hydrocarbons present in AFFF ANSUL are diethylene glycol monobutyl ether, hexylene glycol, and 1-propanol [25]. Treatment of PFASs depends on saturation concentrations of target pollutants in vicinities of bubbles and physicochemical properties of AFFFs [4–6]. Efficiency of sono-chemical degradation of AFFFs depends on acoustic frequency, intensity, and physicochemical properties of organic pollutants. Properties of organic compounds that are related to their degradation potential are the octanol-water partition coefficient (K_{ow}), Henry's law constant, diffusivity, and solution parameters such as ionic strength and pH [22,26]. Efficiency of the sono-chemical reactor is enhanced by optimization of parameters, such as pH, initial concentration of AFFFs, and acoustic frequency.

3.1. Effect of pH

The pH of solutions affects temperatures reached during collapse of bubbles formed during cavitation, radical yield, reactivity, and consequently kinetics of degradation of AFFFs [3–5]. Treatment of PFASs depends on saturation concentrations of target chemicals in vicinities of bubbles and physicochemical properties of AFFFs [4–6,27]. One advantage of acidic pH is that it facilitates production of hydroxyl radicals (generated via thermal decomposition) that have stronger oxidation potentials ($E^\circ = 27.8 \text{ V}$) at acidic pH than at neutral/basic pH ($E^\circ \leq 1.80 \text{ V}$) which is useful for enhancing sono-chemical degradation [26]. So, degradation of ANSUL-AFFF was investigated at pH values of 6.5, 4.0 and 3.0.

3.1.1. ANSUL-AFFF

Results for concentrations of released F^- and SO_4^{2-} (corrected for background concentrations of sulfate) and TOC during sono-chemical degradation of ANSUL-AFFF (500× dilution) at a dual frequency of 1 MHz and 500 kHz are shown in Fig. 2. When pH was decreased from 6.5 to 4.0, concentrations of F^- increased from 38.9 ± 0.4 to $55.6 \pm 0.3 \mu\text{M}$. When pH was further decreased to 3.0, concentrations of F^- were marginally increased after 13 h. Release of F^- increased linearly with time. Concentrations of released SO_4^{2-} increased from 15.6 ± 0.5 to $28.9 \pm 0.3 \mu\text{M}$, when the pH was decreased from 6.5 to 4.0, and a further decrease in pH to 3.0 resulted in a decrease of amounts of SO_4^{2-} released to $21.5 \pm 0.6 \mu\text{M}$. Maximum concentration of SO_4^{2-} was observed after 2 h sonication and further increase with time was marginal. Concentrations of SO_4^{2-} released from ANSUL-AFFF at pH 4 were 20.7 ± 0.2 and $28.9 \pm 0.3 \mu\text{M}$ after 2 and 13 h, respectively. Proportions of TOC removed were 42.3 ± 1.3 , 39.3 ± 1.1 and $39.6 \pm 1.6 \mu\text{M}$ for pH 6.5, 4.0, and 3.0, respectively. Most of the removal of TOC, which was marginal, was observed in the first 2 hrs. Based on removal of F^- , SO_4^{2-} and TOC, reducing pH to 3.0 did not result in a significant increase in release/removal of ions or TOC. Thus, pH 4.0 was determined to represent the optimum pH for further investigations.

Rates of sono-chemical degradation of PFOS and PFOA at 358 kHz were inversely proportional to pH between 11 and 4 and did not change further when pH was decreased from 4.0 to 3.0 [20]. The authors reported first-order rate for sonolysis of groundwater at pH 4.0 for PFOS with rate constant values of 0.0094/min and 0.021/min for PFOS [20].

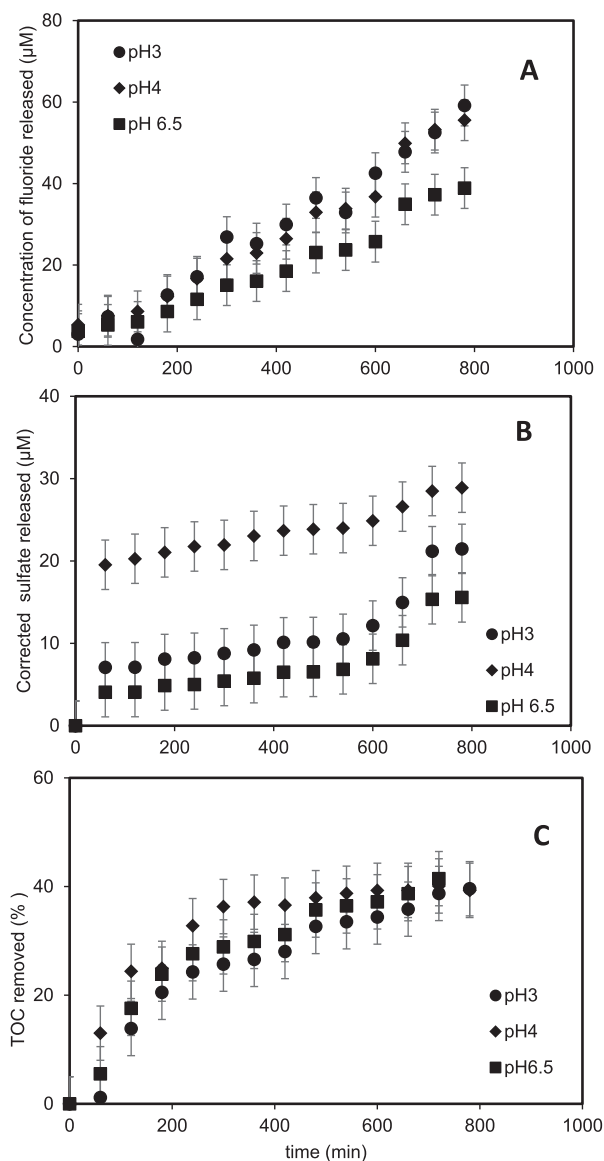


Fig. 2. Effect of solution pH on the sonochemical degradation of AFFF ANSUL (dilution: 500 \times , dual frequency operation of 1 MHz + 500 kHz). (A) Concentration of fluoride released, μM . (B) Corrected concentration of sulfate released, μM . (C) % removal of TOC.

3.2. Effect of dilution

Defluorination of AFFFs depends on the physicochemical properties of chemicals present in AFFFs [28,29]. Efficiency of removal of F^- for the process depends on the concentration of fluorinated compounds in the vicinity of bubbles [28,29]. Therefore, investigation of dilution of PFAS is crucial for enhancing defluorination of AFFF.

3.2.1. AFFF ANSUL

Effects of 900 \times , 500 \times , 100 \times and 25 \times dilution on sono-chemical degradation of PFAS (ANSUL-AFFF) was examined in experiments conducted at an initial pH of 4.0 with sonication by dual frequency 500 kHz + 1 MHz. Concentrations of F^- and SO_4^{2-} released and removal of TOC as a function of time indicate that removals of F^- were inversely proportional to dilution from 900 \times to 500 \times (Fig. 3). Marginal increases of release of F^- were observed with less dilution from 500 \times to 25 \times . Concentrations of F^- released at the end of 780 min were 27.6 ± 0.5 , 55.6 ± 0.3 , 60.9 ± 0.2 , and $58.6 \pm 0.6 \mu\text{M}$ for

dilutions of 900 \times , 500 \times , 100 \times and 25 \times , respectively. Similar trends were observed for releases of SO_4^{2-} . Concentration of SO_4^{2-} released were inversely proportional to dilution from 900 \times to 100 \times . A further decrease in dilution resulted in a decrease in SO_4^{2-} concentration. Maximum concentrations of SO_4^{2-} released after 13 h were 16.6 ± 0.1 , 28.9 ± 0.3 , 170.2 ± 2.5 , and $127.4 \pm 2.6 \mu\text{M}$ for dilutions of 900 \times , 500 \times , 100 \times and 25 \times , respectively. Rates of release of SO_4^{2-} were greater in the time scale of 0–2 h, after which further sonication resulted in only marginal additional release of SO_4^{2-} . Percentage of TOC removed decreased initially with a reduction in dilution from 900 \times to 500 \times and decreased proportionally with dilution from 500 \times to 25 \times . Percentages of TOC removed after 780 min was 45.6 ± 1.2 , 39.3 ± 1.1 , 39.8 ± 1.8 and 39.8 ± 1.7 for dilutions of 900 \times , 500 \times , 100 \times and 25 \times , respectively. However, the mass of TOC was inversely proportional to dilution from 900 \times to 25 \times .

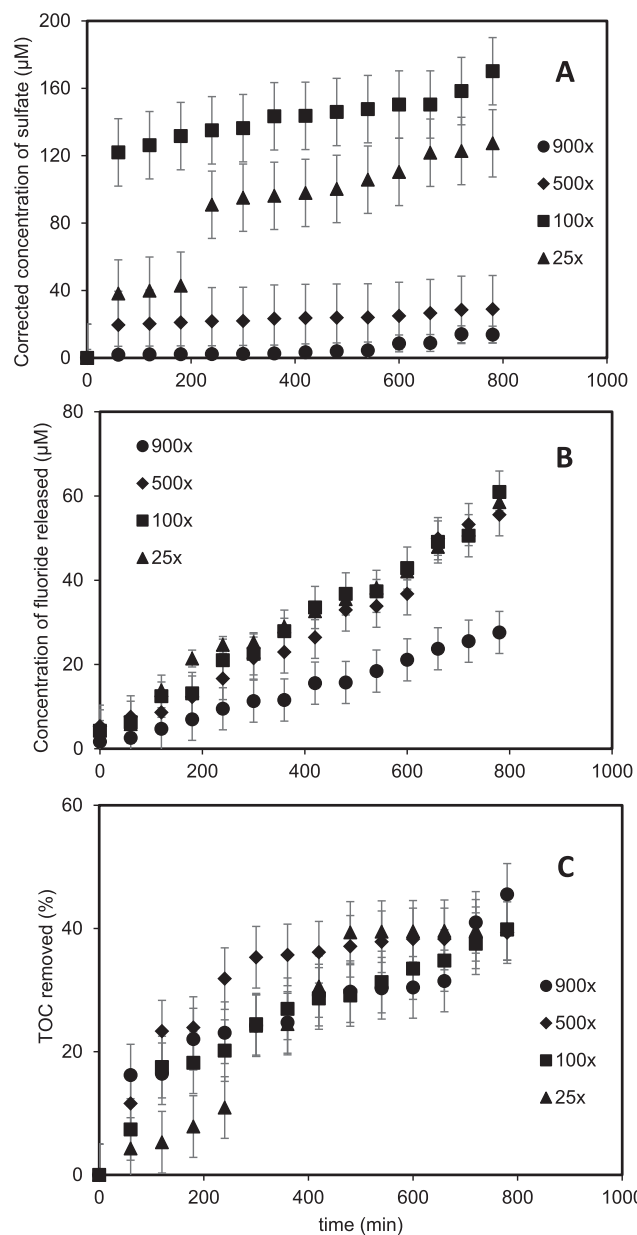


Fig. 3. Effect of dilution on the sonochemical degradation of AFFF ANSUL (pH 4, dual frequency operation of 1 MHz + 500 kHz). (A) Concentration of fluoride released, μM . (B) Corrected concentration of sulfate released, μM . (C) Percentage removal of TOC.

Concentration of TOC removed were 770 ± 9 , 1430 ± 16 , 16971 ± 306 and $41502 \pm 706 \mu\text{M}$ for dilutions of $900\times$, $500\times$, $100\times$ and $25\times$, respectively.

3.2.2. 3M AFFF

At an initial pH of 4, effects of dilution of $500\times$, $100\times$, $25\times$ and $10\times$ on the sono-chemical degradation of 3M-AFFF under dual frequency operation using 500 kHz and 1 MHz were examined. Concentrations of F^- and SO_4^{2-} released and removal of TOC, as a function of time indicate that release of F^- was inversely proportional to dilution from $500\times$ to $10\times$ (Fig. 4). Concentrations of F^- released after 13 h were 19.9 ± 0.7 , 94.2 ± 1.6 , 217.1 ± 2.4 , and $534.2 \pm 4.5 \mu\text{M}$ for dilutions of $500\times$, $100\times$, $25\times$ and $10\times$, respectively. Maximum amounts of SO_4^{2-} released at the end of 780 min were 19.3 ± 0.8 , 140.9 ± 5.5 , 130.9 ± 3.4 and $115.3 \pm 2.9 \mu\text{M}$ for dilutions of $500\times$, $100\times$, $25\times$ and $10\times$, respectively. Percentage removals of TOC were inversely proportional to dilution from $500\times$ to $10\times$. Maximum removal of TOC after 13 h were 33.5 ± 1.7 , 24.9 ± 0.9 , 18.1 ± 0.6 and 10.1 ± 0.4 for dilutions of $500\times$, $100\times$, $25\times$ and $10\times$, respectively. During sono-chemical degradation of AFFFs, C–S bonds are cleaved, which results in loss of the ionic head group (Reactions (1) and (2)). Released SO_3 or SO_3F^- hydrolyze immediately to yield SO_4^{2-} . Degradation of intermediate fluorochemicals occurs via bond cleavage to yield two fluoro-alkyl radicals ($\text{R}_\text{F}^1\cdot$, $\text{R}_\text{F}^2\cdot$) [6]. The resulting electrophilic fluoro-chemicals then react with a hydrocarbon species (R–H) to produce smaller non-radical fluoro-chemicals products (Reactions (3) and (4)) [6]. Hydrocarbons present in AFFFs degrade via hydroxyl radicals.



Concentrations of F^- and SO_4^{2-} released were greater for 3M-AFFF compared to ANSUL-AFFF. This result might be due to the greater concentrations of long-chain PFAS and alkyl SO_4^{2-} present in 3M-AFFF [24,25]. Defluorination of ANSUL- and 3M-AFFF can be explained based on properties of PFASs and non-fluorinated compounds (hydrocarbon) present in the AFFFs [21,29,30]. Hydrophobic compounds with lesser pKa values are attracted towards the bubble cavity, and compounds with greater Henry's constant (volatility) occupy the bubble cavity. Compounds that remain in bulk solution (hydrocarbons) might be susceptible to degradation via hydroxyl radicals formed by the collapse of cavities and degradation rate is greater for the compounds in close proximity of bubbles [28,29]. During sonolysis, most of the PFAS and alkyl- SO_4^{2-} present in the AFFFs degrade via pyrolysis due to their greater hydrophobicity and lesser pKa values. Properties of hydrocarbons present in ANSUL- and 3M-AFFF (Table S1, Supplementary Data section) indicate that hydrocarbons present in ANSUL-AFFF have positive *Kow* coefficients (except triethanolamine) or tend to occupy near regions in vicinities of bubbles formed during cavitation, experience lesser forces of attraction between negatively charged bubbles and dissociated ions of these compounds. Henry's constant represents volatility of compounds in aqueous solution. Compounds with greater Henry's constants tend to be present inside bubbles and are pyrolyzed under higher temperature and pressure [20,28]. Compared to other compounds present in ANSUL-AFFF, triethanolamine has a high Henry's constant. Compounds such as diethylene glycol butyl ether and tolyl-triazole with lesser hydrophobicity and pKa values remain in bulk solution or near the bubbles and might be degraded by reaction with hydroxyl radicals [29]. Triethanolamine can be degraded partially by hydroxyl radical attack and partially due to the high temperature and pressure conditions produced inside bubbles. Hydrocarbon compounds present in 3M-AFFF remain in the hydrophilic form and stay in bulk of

solution due to their lesser *Kow* coefficients and greater pKa values [19,29].

Results reported here, are consistent with previously reported results (1 MHz frequency and power 250 W) where kinetic rate constants for defluorination increased from 1.5 ± 0.1 to $2.1 \pm 0.2 \mu\text{M}/\text{min}$, and rates of degradation of TOC in 3M-AFFF remained constant at $21.8 \pm 8.0 \mu\text{M}/\text{min}$ with increasing concentrations of PFAS from 0.8 to 3.7 mM. In the same study, rates of defluorination determined for ANSUL-AFFF increased from 2.2 ± 0.2 to $5.6 \pm 0.4 \mu\text{M}$ and rate of degradation of TOC increased from 7.9 ± 0.2 to $14.8 \pm 0.9 \mu\text{M}$ when dilution went from $900\times$ to $200\times$ [16]. A study investigating sono-chemical degradation of PFOS, an important component in some AFFFs,

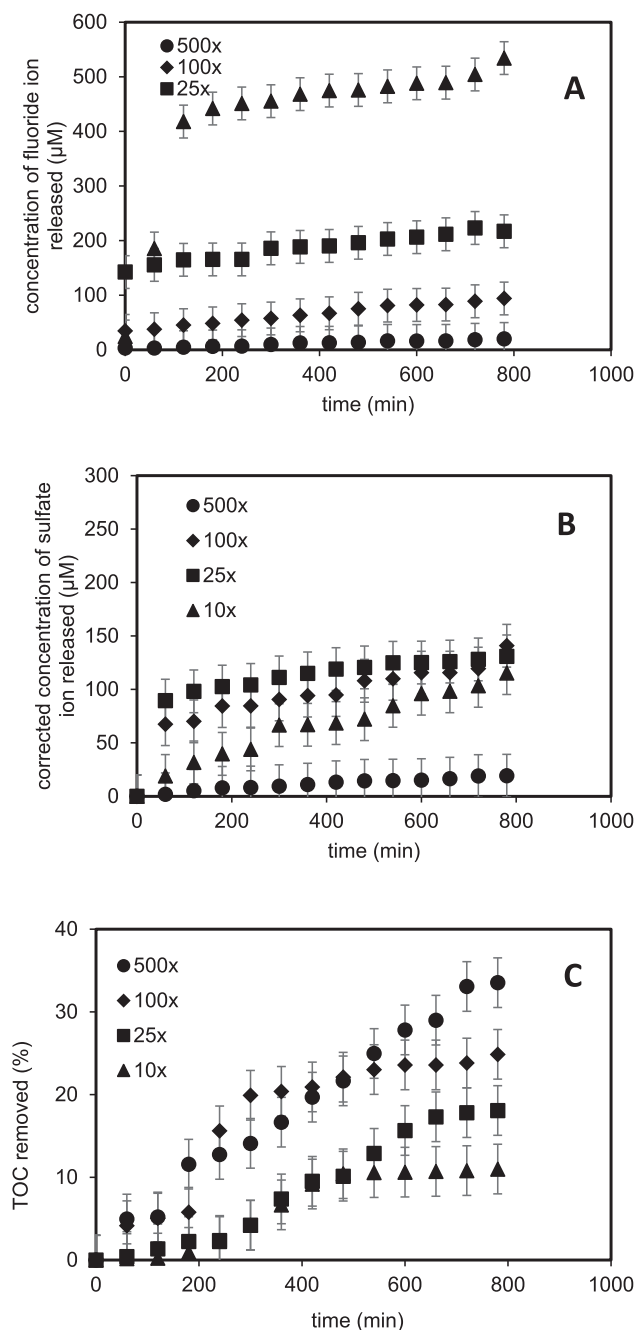


Fig. 4. Effect of dilution on the sonochemical degradation of AFFF 3M (pH 4, dual frequency operation of 1 MHz + 500 kHz). (A) Concentration of fluoride ion released, μM . (B) Corrected concentration of sulfate ion released, μM . (C) Percentage removal of TOC.

observed that defluorination rate constants for dilutions of $50,000 \times (1460 \times 10^{-3} \mu\text{M})$, $5000 \times (1.46 \mu\text{M})$, $500 \times (14.6 \mu\text{M})$ and $250 \times (29.2 \mu\text{M})$ were 0.34 ppb/min, 13.75/min, $-1.0/\text{min}$ and 0.010/min, respectively. It was proposed that different kinetic rate equations should be used for various dilution ratios [6]. Langmuir-type mechanism, which occurs predominantly at bubble-water interfaces, was shown to exist under the experimental conditions used [32].

3.3. Effect of frequency

There are several advantages of using a combination of acoustic frequencies for degradation of pollutants, including enhanced distribution of cavitation activity and higher degradation rates [12]. However, selection of a combination of frequencies depends on temperature and pressure generated during collapse of cavities, which is required for degradation of pollutants [13,14]. Investigation of a combination of frequencies is essential for enhancing defluorination rate.

Effect of a single (1 MHz) versus dual frequency (1 MHz and 500 kHz) on degradation of 3M- and ANSUL-AFFF (dilution factor: $25 \times$, pH: 4.0) was studied (Figs. 5 and 6). Total power requirement for single operation was 9900 W, but 11,100 W for dual frequency (500 kHz and 1 MHz). Concentration of F^- released from degradation of ANSUL-AFFF was 58.6 ± 0.6 (single frequency) and $34.4 \pm 0.4 \mu\text{M}$ (dual frequencies), while for 3M-AFFF it was 142.6 ± 1.5 (single frequency) and $217.1 \pm 2.4 \mu\text{M}$ (dual frequencies) in 780 min. Corrected concentrations of SO_4^{-2} released during degradation of ANSUL-AFFF were $173.8 \pm 3.5 \mu\text{M}$ (single frequency) and $127.4 \pm 2.6 \mu\text{M}$ (dual frequency), while for 3M-AFFF it was 200.1 ± 3.1 (single frequency) and $130.9 \pm 3.4 \mu\text{M}$ (dual frequency) in 780 min (Figs. 5b and 6b). Removal of TOC from ANSUL-AFFF by use of a single frequency was $41.9 \pm 2.1\%$, while removal from 3M-AFFF was $14.9 \pm 0.2\%$. When a dual frequency was applied removal of TOC from ANSUL-AFFF was $39.8 \pm 1.7\%$, while the proportion of TOC removed from 3M-AFFF was $18.1 \pm 0.6\%$ during 780 min sonications (Figs. 5c and 6c). Concentration of TOC removed from ANSUL-AFFF and 3M-AFFF during single frequency operation was $47,509 \pm 998 \mu\text{M}$ and $4879 \pm 10 \mu\text{M}$ and for dual frequency, it was $41,502 \pm 747 \mu\text{M}$ and $6071 \pm 37 \mu\text{M}$, respectively. These results indicate that concentrations of F^- released during dual frequency operation were greater during sonications with a single frequency. In contrast, single frequency operation was more efficient for the release of SO_4^{-2} .

Concentration of F^- ion released are due to interfacial phenomena at the gas-liquid interface and depends on resultant time varying pressure (P_t) and given (Eq. (2)) [14].

$$P_t = P_0 - P_a \sin(2\pi f_a t) - P_b \sin(2\pi f_b t + \phi) \quad (2)$$

where P_0 is the ambient pressure, P_a and P_b are pressure amplitudes of waves with frequencies f_a and f_b respectively, ϕ is the phase difference between waves and t is time for pressure varying field. Pressure amplitude (P_a and P_b) is related to intensity of ultrasonic field (I), density of medium (ρ) and speed of sound in the cavitating medium (c) and given (Eq. (3)). [13]:

$$P_a = (2I\rho c)^{\frac{1}{2}} \quad (3)$$

Formation of radicals depends on collapsing conditions of bubbles and heat and mass transfer effects. It occurs at bubble-liquid interfaces and inside bubbles during their collapse [12]. When bubbles expand, water vapors transfer into bubbles and during the collapse phase, vapors partially undergoes condensation and those remaining produce radicals. Formation of radicals is expected to increase with size/radius of bubbles and is calculated from the Rayleigh-Plesset relationship equation [13,14]

$$r \frac{d^2 r}{dt^2} + \frac{3}{2} \left(\frac{dr}{dt} \right)^2 + \frac{4\mu}{\rho r} \left(\frac{dr}{dt} \right) = \frac{1}{\rho} \left(P_i - P_o - P_v - \frac{2\sigma}{r} \right) \quad (4)$$

where r is the radius of cavitation bubble at any time, μ is viscosity of the liquid medium, σ is the surface tension, and P_i is the pressure inside the bubble. Radii of bubbles are inversely proportional to total resultant pressure (P_t). P_t is inversely proportional to intensity of ultrasonic/acoustic fields and frequencies of operation (Eq. (4)). Acoustic field produced from dual frequencies is such that it expands bubbles to greater volumes and compresses bubbles to smaller volumes [31,32]. Expansion of bubbles is mainly driven by the acoustic wave pattern

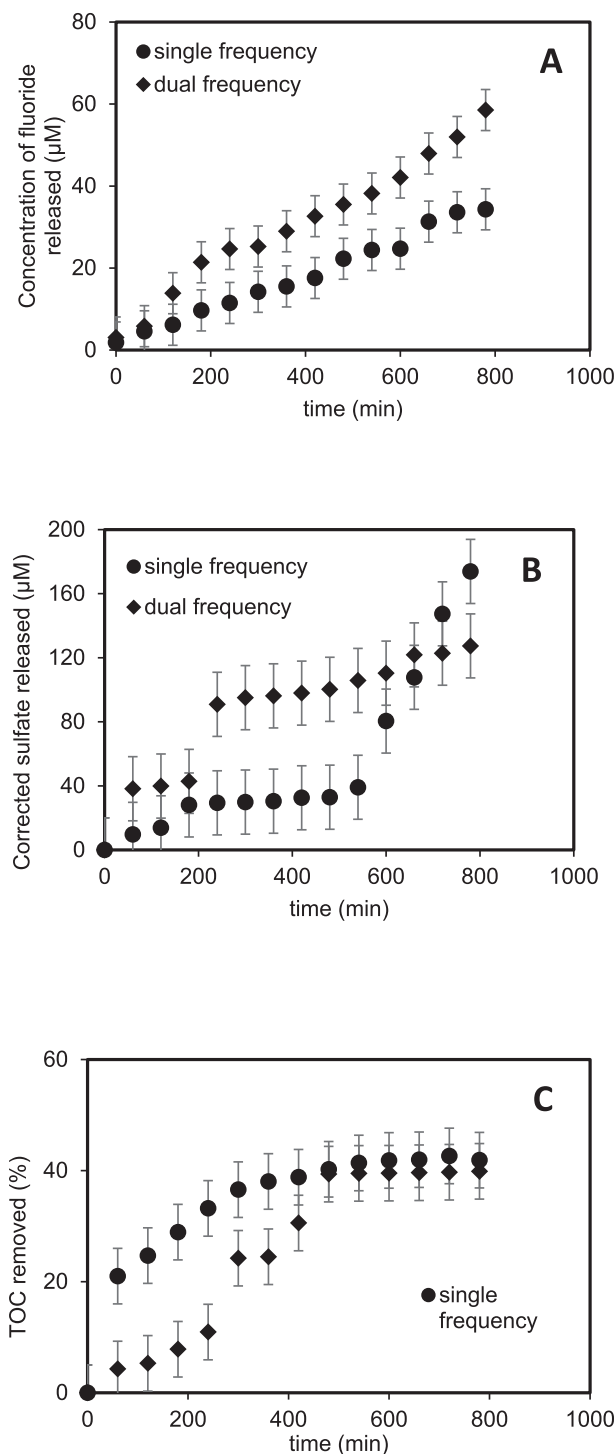


Fig. 5. Effect of frequency on the sonochemical degradation of AFFF ANSUL (dilution: $25 \times$, pH 4, dual frequency operation of 1 MHz + 500 kHz). (A) Concentrations of fluoride ion released, μM . (B) Corrected concentrations of sulfate released, μM . (C) Percentage removal of TOC.

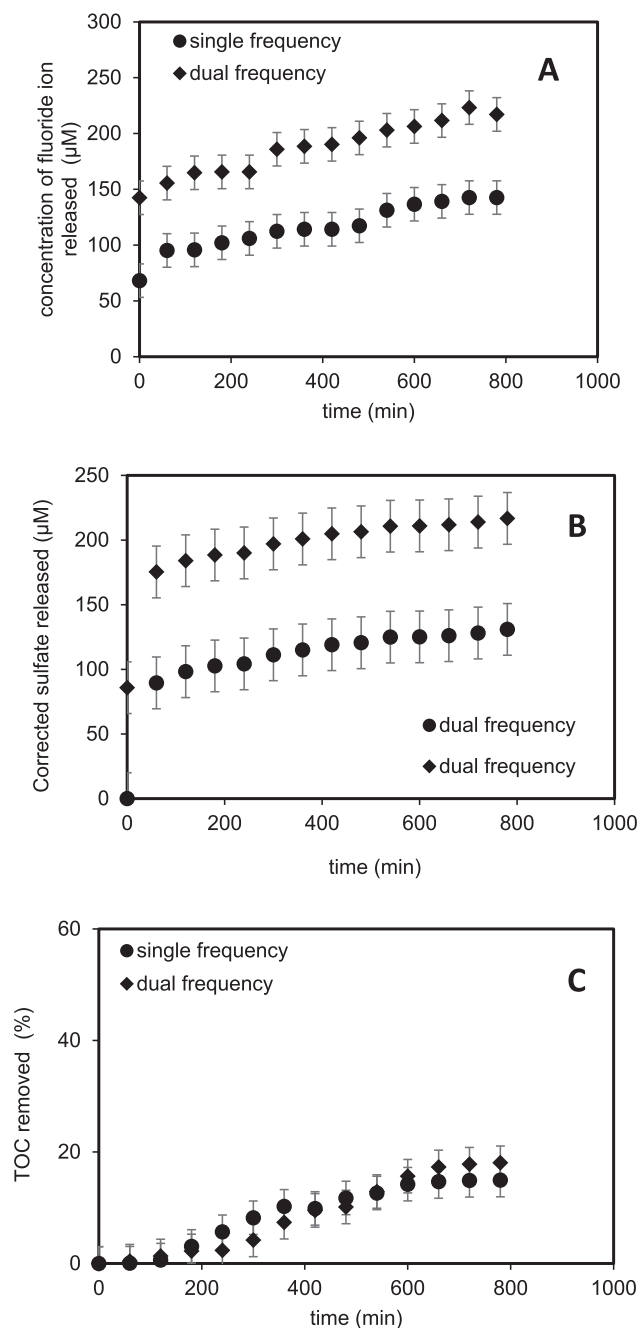


Fig. 6. Effect of frequency on the sonochemical degradation of AFFF 3M (dilution: 25 \times , pH 4). (A) Concentration of fluoride ion released, μM . (B) Corrected concentration of sulfate released, μM . (C) Percentage removal of TOC.

produced from synergic effects of combined frequencies. Synergic effects of dual frequencies enhances cavity size and life span of cavity [14]. Enhancement of cavitation size and span of cavity increases diffusion rates of PFAS and residence time of ions on bubble cavity, which will increase rate of release of fluoride ions [12]. Numbers of cavitation events might also increase when dual frequencies are applied, due to splitting of bubbles and interactions between acoustic waves of different frequencies which reduce bubble coalescence and stable cavitation activity [32]. This might be useful for enhancing pyrolysis and hydroxyl radical activities [13].

Amounts of power utilized for removal of ions and synergic effects was calculated for single and dual frequencies. Cavitation yields,

expressed as ions released/TOC removed per kJ of energy utilized (Table 1) confirm that the synergic effect of the combination of frequencies is useful for defluorination and TOC removal. The results confirmed that the synergistic effect of dual frequencies is highly useful for enhancement of cavitation activity in the reactor.

3.4. Degradation products formed during sono-chemical treatment

Bioaccumulation and environmental persistence of PFAS depend on the several factors, including length of the per- or poly-fluorinated carbon chain [2,7]. Compounds with the same length of fluorocarbon chain, but different terminal functional groups, behave differently. According to regulatory criteria of bioaccumulation (1000–5000 L/kg), PFCA with seven or fewer fluorinated carbons and PFAS with six or fewer are not considered to be bioaccumulative [1,2]. PFOS, PFOA, and longer-chain PFAS are persistent compounds, compared to some other shorter chain and fluorotelomers compounds [17,29]. Monitoring the effectiveness of sono-chemical treatment of longer-chain PFAS to shorter-chain compounds is crucial to decrease the recalcitrance of PFAS compounds present in the AFFFs.

Concentration of 16 PFASs (PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFBS, PFPeS, PFHxS, PFHpS, PFOS, PFNS, PFDS, 6:2 FTS and 8:2 FTS) in ANSUL- and 3M AFFF (500 \times dilution, initial pH = 4) were monitored after 120 and 780 min of sono-chemical treatment (Figs. 7 and 8). Concentrations of PFAS determined were grouped into five categories:

- Perfluoroalkyl carboxylates (PFCA) ≤ 6 : PFCA with fluorocarbon chain length 6 and below (PFHxA, PFHpA) with carboxylic tail;
- PFCA > 6 : PFCA with fluorocarbon chain length above 6 (PFOA, PFNA, PFDA, PFUnDA, PFDoDA) with carboxylic tail;
- Perfluoroalkyl sulfonates (PFSA) ≤ 6 : PFSA with fluorocarbon chain length 6 and below (PFBS, PFPeS, PFHxS, PFHpS) with sulfonate tail;
- PFSA > 6 : PFSA with fluorocarbon chain length above 6 (PFOS, PFNS, PFDS) with sulfonate tail, and
- FTS: 6:2 fluorotelomer thioether amino sulfonate and 8:2 fluorotelomer thioether amino sulfonate.

Concentrations of TOF decreased with time for both AFFFs samples, with maximum removal of TOF observed at 120 min. Percentage of removal of TOF were the same for both AFFF samples, but the TOF concentration removed was greater for 3M-AFFF due to the greater concentration of TOF and long-chain PFSA in this AFFF formulation. The concentration after 780 min was 105.3 μM (48.4% removal) for 3M-AFFF, and 280.5 μM (46.6% removal) for ANSUL-AFFF.

3.4.1. AFFF ANSUL

Initial concentration of FTS was greater in ANSUL-AFFF. Concentrations of PFCA > 6 present in ANSUL-AFF initially increased from 0.52 ± 0.002 to 0.67 ± 0.004 μM then decreased to 0.62 ± 0.003 μM , while the change in concentrations of PFSA > 6 exhibited a similar trend as PFCA > 6 (Fig. 8a). However, the initial increase in concentration for PFSA > 6 was greater compared to PFCA > 6 . The concentration of PFSA > 6 present in AFFF ANSUL was 0.56 ± 0.05 , 20.64 ± 1.4 and 0.74 ± 0.08 μM to 0, 120 and 780 min, respectively. There was little effect of cavitation observed on PFCA ≤ 6 and increase in concentration was observed from 0.35 ± 0.04 to 0.34 ± 0.06 μM (Fig. 7a). Concentration of PFSA ≤ 6 , increased from 0.01 ± 0.0001 to 2.75 ± 0.04 μM but then decreased to 0.02 ± 0.001 μM (Fig. 7b). Concentration of FTS present in ANSUL-AFFF decreased from 154.83 ± 7.56 to 95.35 ± 4.75 μM (37.7%) in 780 min (Fig. 7a). Concentrations of PFSA indicate that initial sono-chemical degradation of FTS was greatest in the first 120 min, compared to degradation at the end of 780 min. Most of the FTS was converted into PFSA > 6 , but some into PFCA > 5 . As degradation progressed, most PFSA > 6 were

Table 1

Summary of results of degradation of AFFF using a 91-L sonochemical reactor (solution pH = 4.0; treatment time = 13 h).

Foam	Frequency	Dilution	Released ion concentration (μM)		TOC removal (%)	Cavitation yield $\times 10^{-5}$ ($\mu\text{M}/\text{KJ}$)		
			Fluoride	Corrected sulfate		Fluoride	Sulfate	TOC
ANSUL	Dual	900 \times	27.6 \pm 0.5	16.6 \pm 0.1	45.6 \pm 1.2	4.7 \pm 0.2	3.0 \pm 0.2	137.3 \pm 4.6
ANSUL	Dual	500 \times	55.6 \pm 0.3	28.9 \pm 0.3	39.3 \pm 1.1	9.2 \pm 0.1	3.5 \pm 0.3	254.5 \pm 8.9
ANSUL	Dual	100 \times	60.9 \pm 0.2	170.2 \pm 2.5	39.8 \pm 1.8	9.9 \pm 0.6	30.3 \pm 0.9	3,017.5 \pm 12.1
ANSUL	Dual	25 \times	58.6 \pm 0.6	127.4 \pm 2.6	39.8 \pm 1.7	9.6 \pm 0.7	22.7 \pm 0.8	18534.3 \pm 22.5
ANSUL	Single	25 \times	34.4 \pm 0.4	173.8 \pm 3.5	41.9 \pm 2.1	7.4 \pm 0.6	37.5 \pm 1.4	10253.9 \pm 18.1
3M	Dual	500 \times	19.9 \pm 0.7	19.3 \pm 0.8	33.5 \pm 1.7	4.2 \pm 0.4	3.4 \pm 0.3	89.1 \pm 5.8
3M	Dual	100 \times	94.2 \pm 1.6	140.9 \pm 5.5	24.9 \pm 0.9	16.8 \pm 1.2	25.1 \pm 1.5	130.0 \pm 7.8
3M	Dual	25 \times	217.1 \pm 2.4	130.9 \pm 3.4	18.1 \pm 0.6	39.9 \pm 1.6	23.3 \pm 1.7	1080.9 \pm 12.4
3M	Dual	10 \times	534.2 \pm 4.5	115.3 \pm 2.9	10.1 \pm 0.4	92.1 \pm 2.8	20.5 \pm 1.8	1816.5 \pm 18.6
3M	Single	25 \times	142.6 \pm 1.5	200.1 \pm 3.1	14.9 \pm 0.2	31.9 \pm 0.3	43.2 \pm 2.4	1053.0 \pm 8.2

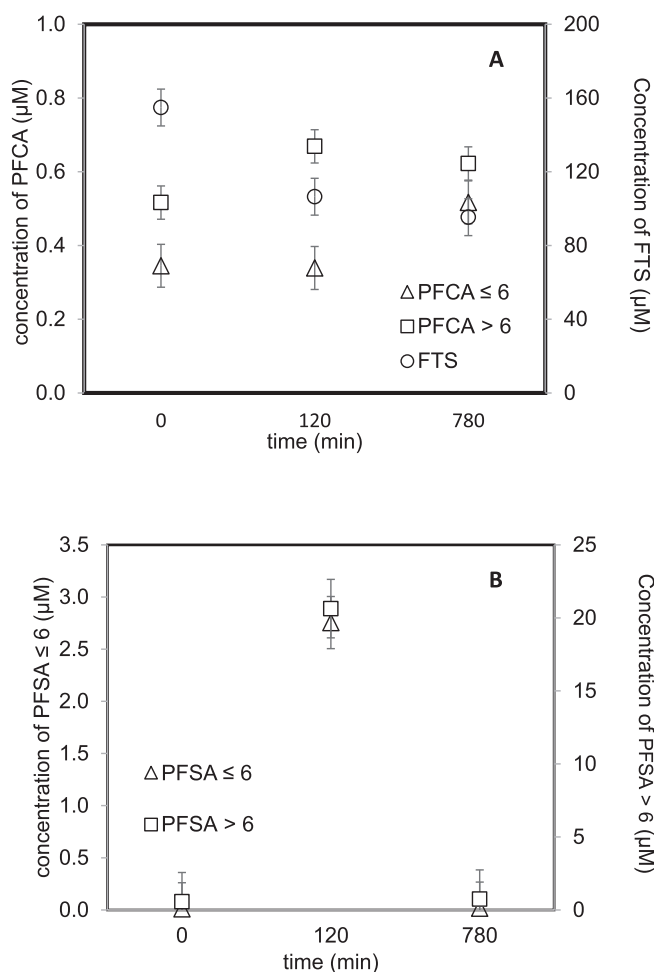


Fig. 7. Concentrations of PFAS as a function of treatment time (dilution: 500 \times , pH 4, dual frequency operation of 1 MHz + 500 kHz) during the degradation of AFFF ANSUL. (A) (Δ) PFCA ≤ 6 ; (\square) PFCA > 6 ; (\circ) FTS. (B) (Δ) PFSA ≤ 6 ; (\blacktriangle) PFSA > 6 .

converted into the smaller chain compounds (PFSA ≤ 6) or might be completely mineralized to CO_2 . Similar mineralization was observed for PFCA > 6 , but the rate of mineralization was greater as compared to PFSA > 6 .

3.4.2. 3M-AFFF

3M-AFFF has greater concentrations of PFSA > 6 . Sono-chemical degradation of 3M-AFFF in 780 min shows that concentrations of PFSA > 6 decreased by 90.6% from 924.4 \pm 46.2 to 87.4 \pm 4.3 μM (Fig. 8b). While concentrations of PFCA > 6 decreased by 26.7%, from

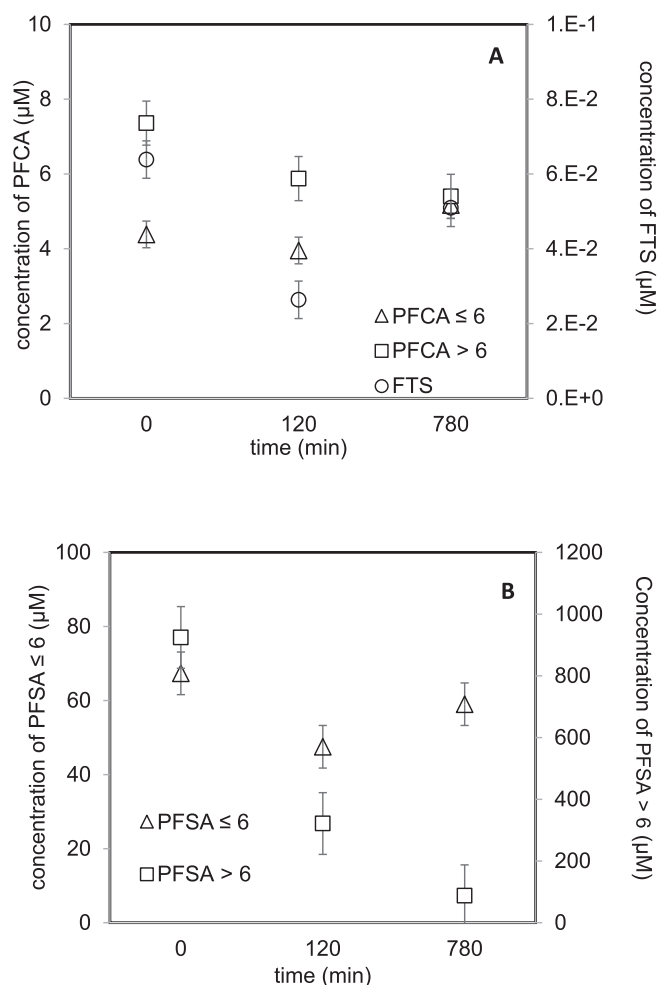


Fig. 8. Concentration of PFAS as a function of treatment time during the degradation of AFFF 3M (dilution: 500 \times , pH 4, dual frequency operation of 1 MHz + 500 kHz). (A) (Δ) PFCA ≤ 6 ; (\square) PFCA > 6 ; (\circ) FTS. (B) (Δ) PFSA ≤ 6 ; (\blacktriangle) PFSA > 6 .

7.6 \pm 0.4 (0 min) to 5.9 \pm 0.3 (120 min) and 5.4 \pm 0.3 μM (780 min), (Fig. 8a). Concentrations of shorter-chain PFCA ≤ 6 initially decreased from 4.4 \pm 0.2 to 3.9 \pm 0.2 μM and then increased to 5.2 \pm 0.3 μM while concentrations of PFSA ≤ 6 initially decreased from 67.4 \pm 4.4 to 47.5 \pm 2.4 μM and then increased to 59.0 \pm 3.0 μM (Fig. 8a). There was a small concentration of FTS present in 3M-AFFF, and concentrations of FTS decreased from 0.06 \pm 0.003 to 0.03 \pm 0.001 μM and then increased to 0.05 \pm 0.002 μM (Fig. 8a). Degradation of PFSA > 6

Table 2

Energy and cost required for 99% defluorination of ANSUL and 3M AFFF (500× dilution).

Foam	Initial PFAS concentration (mg/L)	Energy, (kJ/L)	Cost of energy ^a (\$/L)	Cost of energy (\$/bbl)
ANSUL	29.6 ± 0.05	7.3 ± 0.02	0.015 ± 0.0001	2.5 ± 0.02
3M	27.4 ± 0.04	6.9 ± 0.03	0.019 ± 0.0002	3.0 ± 0.03

^a Average cost of electricity in the US: \$ USD 0.1075/kWh.

(3.2×10^{-2} mg/L-h) was greater than PFCA > 6 (6.9×10^{-5} mg/L-h). PFSA > 6 and PFCA > 6 can be converted into shorter chain FPAS or mineralized to CO₂ or shorter-chain fluorocarbons. Based on concentrations of PFSA removed, conversion of longer-chain PFSA and PFCA to shorter-chain compounds was less (e.g. mg of PFSA > 6, PFSA ≤ 6 and PFCA > 6 removed 25.6 ± 0.4 , 0.25 ± 0.0003 and 0.05 ± 10^{-4} , respectively and mg PFCA ≤ 6 added was 0.03 ± 10^{-4}). The study on sono-chemical treatment of various longer-chain (frequency: 358 kHz, power density: 250 W/L) reported that rate of defluorination increased with carbon-fluorine chain length [29]. Sono-chemical degradation of 3M-AFFF (dilution: 5000×, frequency: 505 kHz and power density: 188 W/L) resulted in concentrations of PFOS, PFHS, and PFBS (after 120 min of sonication) of 2.5 ± 0.9 μM, 0.53 ± 0.04 μg/L and 0.27 ± 0.01 μM [6], which were consistent with trends reported previously [17].

3.5. AFFF defluorination kinetics

Rate of degradation of fluorinated compounds present in AFFF is given (Eq. (5)) [16]

$$\frac{d[F^-]}{dt} = r_{\max} \cdot \theta \quad (5)$$

where: θ is a function of the initial TOF concentration and sono-chemical partitioning coefficient, K_s , and calculated by use of Eq. (6).

$$\theta = \frac{K_s \cdot [TOF]}{1 + K_s \cdot [TOF]} \quad (6)$$

Substituting Eq. (6) into Eq. (5) results in Eq. (7).

$$\frac{d[F^-]}{dt} = r_{\max} \cdot \frac{K_s \cdot [TOF]}{1 + K_s \cdot [TOF]} \quad (7)$$

Defluorination of AFFF depends c-order kinetic parameters (k_{3M}) of defluorination for 3M-AFFF were 27.7×10^{-3} μM/min ($R^2 = 0.977$, 500×), 76.9×10^{-3} μM/min¹ ($R^2 = 0.99$, 100×), 96.7×10^{-3} μM/min ($R^2 = 0.977$, 25×), whereas those for ANSUL-AFFF (k_{ANSUL}) were 65.1×10^{-3} μM/min ($R^2 = 0.975$, 500×), 67.9×10^{-3} μM/min ($R^2 = 0.968$, 100×), 60.6×10^{-3} μM/min ($R^2 = 0.975$, 25×). Kinetic parameters were calculated by inverting Eq. (7). Defluorination rate for 3M-AFFF was less than that for ANSUL-AFFF for 500× dilution and increased for 100× and 25× dilution. Rate of defluorination rate for 3M-AFFF was 0.4, 1.1 and 1.6 times the defluorination rate of ANSUL-AFFF for 500×, 100×, and 25× dilutions, respectively. The maximum rate of defluorination for 3M-AFFF (r_{\max} : 1.31×10^{-1} μM F⁻/min) was 1.8 times (r_{\max} : 7.41×10^{-2} μM F⁻/min) that of ANSUL-AFFF, whereas the TOF concentration for 3M-AFFF was twice that for ANSUL-AFFF. The K_s values for 3M- and ANSUL-AFFF were 6837 and 548/μM, respectively. Sono-chemical (1 MHz, power density: 8 W/cm² and volume: 200 mL) defluorination of 3M- and ANSUL-AFFF observed r_{\max} for 3M and ANSUL-AFFF as 2.3 and 12.3 μM F⁻/min, respectively and K_s as 2397 and 273/M for ANSUL- and 3M-AFFF, respectively [16].

3.6. Energy consumption

Energy required for 500× dilution (initial concentration of PFAS for

ANSUL-AFFF: 29.6 ± 0.05 mg/L; 3M: 27.4 ± 0.04 mg/L; pH of solution 4) for 99% of removal of the initial concentration of PFAS is 7.3 ± 0.02 kJ/L or 6.9 ± 0.03 kJ/L for ANSUL-AFFF and 3M-AFFF, respectively (Table 2). Costs of energy required per L of ANSUL-AFFF and 3M-AFFF are $\$0.015 \pm 0.0001$ and $\$0.019 \pm 0.0002$, respectively.

4. Conclusions

Detailed studies focusing on degradation of PFAS present in commercial AFFFs produced by ANSUL or 3M using a sono-chemical reactor confirmed the applicability of treatment for destruction of PFAS at industrial scale of operations. Concentrations of F⁻ released were inversely proportional to pH and dilution ratio of PFAS. Concentration of F⁻ released were greater for 3M-AFFF. The total amount of TOC of both AFFFs removed increased with the initial concentration of AFFFs, and it was greater for ANSUL-AFFF as compared to 3M-AFFF. The sono-chemical treatment was very effective at reducing the length of fluorocarbon chains. Estimated costs of energy for treating solutions at 500× dilution were $\$0.015$ and $\$0.019$ per liter for ANSUL- and 3M-AFFFs, respectively. Our results confirm that the sono-chemical reactor design developed in the present work is useful for degradation of AFFFs.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.ultsonch.2018.02.014>.

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