



## Chain-length dependent ultrasonic degradation of perfluoroalkyl substances

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### ABSTRACT

Per- and polyfluoroalkyl substances (PFAS) have been found all over the world and are particularly persistent, potentially carcinogenic, and bioaccumulative in the environment. Degradation of short-chain perfluorinated carboxylic acids of varying carbon chain lengths (from 4 to 8 carbons), higher-chain perfluoro carboxylic acids of varying carbon chain lengths (from 9 to 14 carbons), and perfluorosulfonic acids of varying carbon chain lengths (6 and 8 carbons) were tested in a flow through ultrasonic cavitation reactor to determine the efficacy of the high frequency ultrasound process. Temperature, frequency, power density, pH, sodium chloride, and sodium bicarbonate concentrations are examined as process parameters. The frequency and length of the PFAS chain were found to be vital components in the sonolytic degradation process. Degradation of all PFAS was shown to be particularly rapid at room temperature, basic pH, and a power density of 252 W/L. At a power density of 144 W/L, all of the PFAS were degraded by more than 97% in 8 h, with the exception of perfluorobutonic acid (83%) and perfluorohexanoic acid (94%). The bond dissociation energy of C-F bonds was found to be much higher than experimental sonolytic activation energies, supporting cavitation bubble as a catalyst for thermolytic destruction of PFAS compounds. Optimizing the reactor geometry has the potential to make this approach even more appealing for treating small volumes of concentrated wastes.

### 1. Introduction

Perfluoroalkyl substances (PFAS) are of great and increasing concern due to their pervasive prevalence, environmental persistence, and toxicity to humans and wildlife. [1–4]. Groundwater and drinking water supplies have been contaminated with PFAS due to the production, disposal, and use of formulations and products containing PFAS or PFAS-precursors (for example, aqueous film-forming foams) [5,6]. The U.S. Environmental Protection Agency on June 2022 has issued more stringent health advisories of 0.004 ng/L, 0.02 ng/L, 2000 ng/L for perfluorooctanoic acid (PFOA), perfluorooctanesulfonate (PFOS), perfluorobutane sulfonic acid (PFBS), respectively, due to their high prevalence, toxicity, and resistance to transformation [7].

The elimination of perfluoroalkyl acids from water by traditional water treatment procedures is ineffective [8,9]. Due to the durability of the carbon-fluorine bond, previous studies have shown that standard advanced oxidation processes (AOPs) such as ultraviolet radiation (UV), ozone (O<sub>3</sub>), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) are ineffective for PFAS transformation [8,10]. Activated persulfate [11], plasma [12,13],

incineration [14], and electrooxidation [15] have been used to decompose PFAS, although they require considerable chemical and/or energy inputs. Researchers and practitioners have concentrated on activated carbon [16–18] and membrane based method [19] to remediate PFAS-contaminated water. Shorter-chain PFAS breakthrough activated carbon rather quickly, and both processes (filtration and AOPs) produce a residual waste that needs removal or further treatment [8,16–18,20]. Recently plasma [13,12], electrochemical oxidation [15,21,22], incineration [14], alkaline hydrothermal reactions [23], UV-Chlorine [24] have shown defluorination of PFAS compounds, however, these techniques form smaller chain PFAS as byproducts and are biased for longer chain PFAS.

In this work, water treatment using ultrasonic cavitation was studied to determine its efficacy in breaking down PFAS of varying chain lengths into its inorganic form. Ultrasonic cavitation is a sophisticated oxidation technique that generates radicals on-site (in and around collapsing cavity) and does not require large amounts of chemicals. Chemicals are only employed to enhance degradation. Moreover, ultrasonic cavitation can generate a wide variety of reactive species, including powerful

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oxidants and reductants [25,26]. Environmental matrices contains complex mixture of PFAS with varying chain lengths and functional groups [5,27,28]. Very little research has been reported on various PFAS because most studies on PFAS degradation using high-frequency ultrasound have focused on single PFAS like PFOA and/or PFOS [25,26,29–34], except [30,35].

Prior research of PFAS degradation was conducted using batch reactor and for shorter periods [10,26,29,30,32,36–39]. The primary goal of the present study is to evaluate the efficacy of a flow through reactor configuration for long-term degradation of perfluorocarboxylic acids (PFCAs) with carbon chain lengths between 4 and 14 and perfluorosulfonic acids (PFSAs) with carbon chain lengths between 6 and 8 across a range of ultrasonic frequency, power density, pH, aqueous sample temperature, sodium chloride concentration, and sodium bicarbonate concentration.

## 2. Materials and methods

### 2.1. Materials

Perfluorobutanoic acid (PFBA, C4, molecular weight (MW): 214.04, >98%); Perfluoropentanoic acid (PFPeA, C5, MW: 264.05, >98%); Perfluorohexanoic acid (PFHxA, C6, MW: 314.05, >98%); Perfluoroheptanoic acid (PFHpA, C7, MW: 364.06, >98%); Perfluorooctanoic acid (PFOA, C8, MW: 414.07, >98%); Perfluorononanoic acid (PFNA, C9, MW: 464.08, >98%); Perfluorodecanoic acid (PFDA, C10, MW: 514.08, >98%); Perfluoroundecanoic acid (PFUnDA, C11, MW: 564.08, >95%); Perfluorododecanoic acid (PFDDA, C12, MW: 614.10, >95%); Perfluorotridecanoic acid (PFTTrDA, C13, MW: 664.11 >97%); Perfluorotetradecanoic acid (PFTeDA, C14, MW: 714.11, >96%); Perfluorohexanesulfonic acid potassium salt (PFHxS, CS6, MW: 438.20, >98%); Perfluorooctanesulfonic acid potassium salt (PFOS, CS8, MW: 538.22, >98%); HPLC grade methanol (>99.9%); Sodium chloride (NaCl, > 99%); Acetonitrile (>99.9%); Sodium bicarbonate (NaHCO<sub>3</sub>, > 99.7%) and HPLC water were purchased from Sigma Aldrich, USA. We received perfluorooctanoic acid (<sup>13</sup>C<sub>8</sub> PFOA, 99%) and perfluorooctanesulfonate acid (<sup>13</sup>C<sub>8</sub> PFOS, 99%) stable-isotope surrogates from Cambridge Isotope Laboratories, Inc. Water Corp (Milford, MA, USA) supplied Oasis weak anion exchange (WAX; 3cc cartridge 60 mg 30 μm) cartridges for solid-phase extraction (SPE) of PFAS. All of the

compounds were of the analytical grade and were utilised directly. Deionized water was used to prepare all spiked solutions. Ion chromatography reference standards of the highest purity (1000 ppm - fluoride, sulfate, nitrate, nitrite) were procured from Fluka Analytical, Sigma-Aldrich.

### 2.2. Experimental methods

A batch reactor was used for the majority of earlier ultrasonic degradation research [25,31,36]. Continuous operation of the high frequency transducer generates heat, which is then transferred to the aqueous sample and increases its temperature. There is a coolant in the jacketed reactor surrounding the aqueous sample, even then the batch reactor transducer cooling is difficult because aqueous sample is in direct contact with the hot transducer. The temperature of the aqueous sample adversely affects the ultrasonic degradation of organic compounds and can also reduce the efficiency of the transducer. To overcome this drawback, we ran our experiments in a flow-through mode, recirculating the aqueous sample through the heat exchanger at a constant rate, which helped maintain the aqueous sample's optimal temperature and reduced transducer heating. Fig. 1 shows flow through type reactor setup and heat exchanger.

Sonication of perfluorocarboxylic acids (PFCAs) having chain length from C4 to C14 and perfluorosulfonic acids (PFSAs) having chain length C6 and C8 using Meinhardt multi-frequency generator (575 kHz, 853 kHz, 1132 kHz) and flat plate type transducer having total output power of 200 W. To maintain the desired temperature of the sample in the sonication reactor, sample was circulated at rate of 50 mL/min through steel coiled heat exchanger which was submerged in the coolant bath tub (VWR scientific refrigerated bath, Model 1160) maintained at 2 °C. The retention time of sonicated sample was 6 min. After the beginning of the sonication process in our experiment, it took 15 min for the temperature of the solution to stabilize, and it remained constant for the remainder of the experiment. All experiments were carried out in triplicate (unless specified).

The current study included seven distinct sets of experiments. In the first set of experiments, we used ultrasonic frequencies of 575 kHz, 853 kHz, and 1132 kHz to sonicate individual PFAS at power density of 144 W/L at about 50 ppb each. Then, the experiment with individual compounds were compared to the sonication of a mixture of these 13 PFAS to

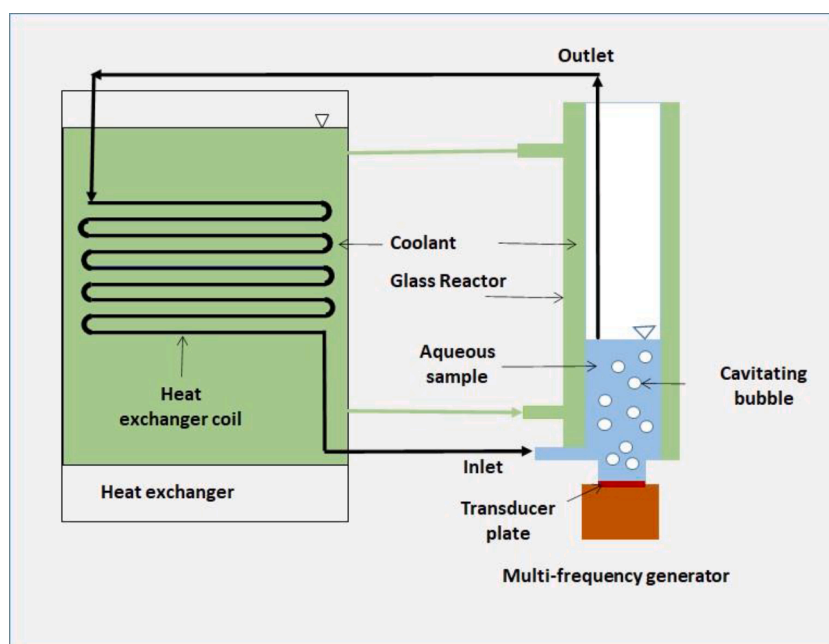


Fig. 1. High frequency ultrasonic system reactor setup for degradation of perfluoroalkyl substances (not to scale).

understand how the mixture affected the breakdown of PFAS at ultrasonic frequencies of 575 kHz, 853 kHz, and 1132 kHz. The mixture of 13 PFAS was sonicated at varied power densities (50 - 336 W/L) in the second set of experiments by altering the volume (150 - 1000 mL) of the aqueous solution at 575 kHz. In the third and fourth sets of experiments, at 575 kHz, the influence of initial pH (2.72 - 12.26) and initial aqueous temperature (11 - 30.5 °C) on degradation of a mixture of 13 PFAS was studied. The fifth and sixth sets of experiments involved sonication at 575 kHz of a mixture of 13 PFAS with sodium chloride (0 - 10 g/L) and sodium bicarbonate (0 - 5 g/L), respectively. In seventh set of experiment, 350 mL of PFAS mixture was sonicated for 8 h at 575 kHz and the formation fluoride, sulfate, and nitrate were monitored.

Many compounds (i.e. hydrogen peroxide, nitrate, nitrite etc.) are formed when an aqueous solution is sonicated over an extended period of time [36]. Solid-phase extraction of PFAS was carried out using Waters Oasis WAX cartridge to minimize the matrix effects owing to formation of other chemicals during assessment [37,38]. To reduce potential matrix effects on quantitation, labelled-isotope surrogate standards ( $^{13}\text{C}_8$  PFOA,  $^{13}\text{C}_8$  PFOS) were spiked to standards as well as samples. To determine PFAS concentrations, ultra-performance liquid chromatography (UPLC) was utilized. The UPLC system consisted of a Waters Acquity UPLC connected to a Waters Xevo TQ-s mass spectrometer using a BEH C18 ( $2.1 \times 50$  mm,  $1.7 \mu\text{m}$ ) column. All the samples were analyzed for the 13 selected analytes mentioned above (unless specified). The section S1 of the supporting information provides method adopted to perform PFAS analysis, LC-MS-MS conditioning, and solid-phase extraction [36-38]. Recovery efficiencies of 13 PFAS ranged from 80% - 138% (Table S3). Fluoride, nitrate, and sulfate were analyzed using a Metrohm 930 Compact flex ion chromatography (IC) fitted with a Metrosep-A supp 150/4.0 mm column. Flow rate of the mobile phase was 0.7 mL/min and the column temperature was 30 °C. Mobile phase concentrations were 0.32 M  $\text{Na}_2\text{CO}_3$  and 0.1 M  $\text{NaHCO}_3$ . Fluoride, nitrate, and sulfate anions could all be detected down to 0.1 mg/L using the IC.

### 3. Results and discussion

#### 3.1. Ultrasonic frequency

The percentage degradation of a PFAS mixture in 120 min along with experimental parameters over a range of frequency, power density, pH, temperature, NaCl concentration and sodium bicarbonate concentration is shown in Figure S2 of supporting information. Based on the data, we observed that the degradation rate of PFCAs increases with chain length up to carbon 9, and then begins to decrease beyond that. However, the degradation rate dropped noticeably at chain length 7 (PFHpA). At 575 kHz, PFAS degrade at an especially rapid pace. These results agree with results reported by others [25,29,31,32,37,40]. Degradation of PFAS was faster in mixtures than for individual PFAS, regardless of frequency (Fig. 2). Ultrasonic frequency of 575 kHz showed that pseudo-first-order-rate constant ( $k$ ) of PFBA was  $0.003 \text{ min}^{-1}$ , whereas rate kinetic of PFNA was  $0.022 \text{ min}^{-1}$  (Fig. 2). At ultrasonic frequencies of 575 kHz, 853 kHz, and 1132 kHz, degradation of specific PFAS ranged for 32-94%, 18-75%, and 16-79%, respectively. Mixtures of PFAS degraded faster than their constituent chemicals. Ultrasonic frequencies of 575 kHz, 853 kHz, and 1132 kHz resulted in 55-92%, 3475%, and 35-83% degradation after 120 min (Figure S2a). The outcomes of our study exhibit quantitative agreement with the findings of [35] concerning the degradation of PFAS across a spectrum of chain-lengths.

Contrary to the results of [32,33], we did not observe formation of shorter chain PFCAs (PFBA, PFPeA, PFHxA etc.) analyzed in this study during ultrasonic degradation of individual PFAS. Vecitis *et al.* [10,25] reported formation of fluorochemical intermediates gasses such as polyfluorinated alkanes ( $\text{CHF}_3$ ,  $\text{CH}_2\text{F}_2$ ,  $\text{CH}_3\text{F}$ ,  $\text{C}_2\text{F}_5\text{H}$ ,  $\text{C}_3\text{F}_7\text{H}$ ), polyfluorinated alkenes ( $\text{C}_2\text{F}_2\text{H}_2$ ,  $\text{C}_2\text{F}_4$ ,  $\text{C}_3\text{F}_6$ ,  $\text{C}_4\text{F}_8$ ), and C4-C8 polyfluorinated alkenes during sonolytic degradation of PFOA and PFOS [10,25]. However, in this study, we did not perform a non-target analysis of the samples. Vecitis *et al.* [25] and Shende *et al.* [36] hypothesised that PFOA and PFOS undergo ultrasonic degradation in a series of sequential pyrolytic processes at the cavity-water interface. Also, the adsorption of PFAS at the cavity-water interface during cavity collapse is a key factor in the subsequent sonolytic breakdown of PFAS into PFAS-sono-intermediate [25,31,36]. Therefore, it is hypothesised that the rate-limiting step in the sonolytic reaction is the adsorption of

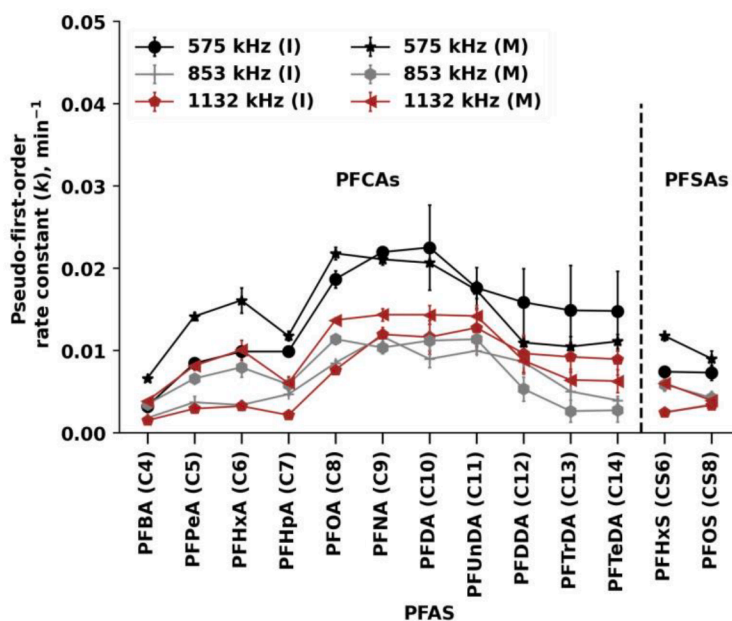


Fig. 2. Pseudo-first-order rate constant ( $k$ ) of perfluoroalkyl carboxylic acid (C4-C14) and perfluoroalkyl sulphonic acid (CS6, CS8) degradation over a range of ultrasonic frequency (575 kHz, 853 kHz, 1132 kHz), where I represents degradation of a single PFAS compound and M represents degradation of PFAS compounds in a mixture of 13 PFAS compounds.

PFAS on the cavity-water interface via diffusion. The air-water interface partitioning coefficient of PFAS increases [29,41,42] while the vapor pressure decreases [14] with increasing chain length, at least up to a carbon chain length of ten. With increasing chain length from 4 to 8, the aqueous diffusivity of PFCAs and PFSA's decreases [43,44].

Short-chain PFAS have higher volatility and aqueous solubility than long chain PFAS [14]. They will most likely remain in the bulk solution, or would diffuse through the interface and partition into the cavity. Hence, they are unlikely to have a significant presence or adsorption on the interface. On the other hand, longer-chain PFAS have lower solubility, would diffuse to the cavity and their hydrophobic end adsorb at the interface. Short-chain PFAS were observed, in this study and by others [29,30,31,35,36], to degrade more slowly than medium-chain PFAS. This implies that the adsorption of PFAS is the rate-limiting factor for the pyrolytic decomposition of PFAS at the cavity-water interface during cavity collapse.

While the PFAS concentration in a single compound trial was around 34–50 ppb, the total PFAS concentration in a mixture of 13 compounds was around 560 ppb. As the total amount of PFAS molecules increases, the probability of adsorption of PFAS at the cavity-water interface also increases, as was previously shown [25,36]. The rate of breakdown of PFAS mixtures is thus greater than that of individual PFAS molecules.

### 3.2. Power density

Fig. 3 shows that, for all PFAS, the degradation rate increases with increasing power density. Previously reported results [25,26,29,32,35,36,38,45] are consistent with the magnitude of the degradation rate seen in the present work for PFBA, PFHxA, PFOA, PFOS, PFHxS,. However, PFAS degradation rates vary greatly with chain length. PFAS degraded from 69% to 97% in 120 min at a power density of 336 W/L. At a power density of 202 W/L, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, and PFUnDA degraded by more than 90% in 120 min. When compared to the aforesaid compound, the degradation rate of PFAS with chain lengths more than 12 was lower across the board. PFTTrDA and PFTTeDA showed a negligible degradation rate below 100 W/L. Xiao *et al.*'s thermogravimetric analysis of PFAS compounds has demonstrated that the temperature required to breakdown PFAS during thermolytic degradation rises with the length of the carbon chain [46]. This may be reason for lower rate at which longer-chain PFAS degrade.

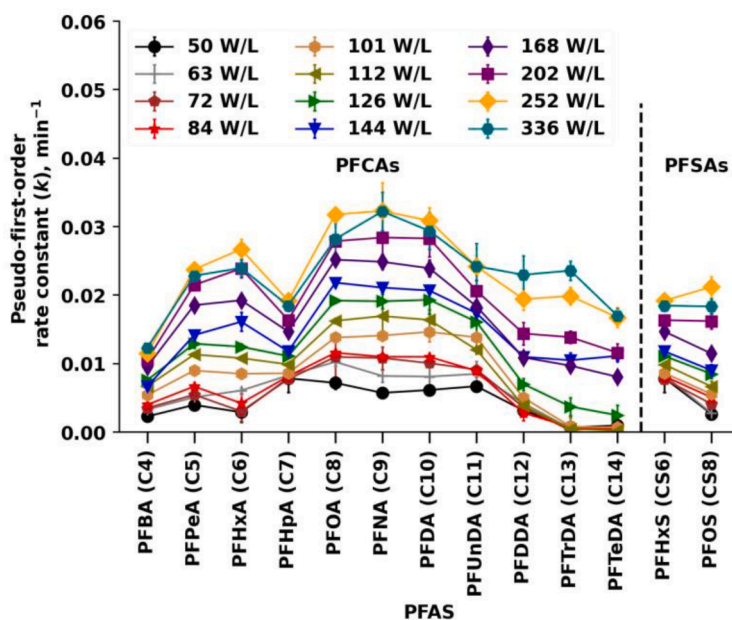


Fig. 3. Pseudo-first-order rate constant ( $k$ ) of perfluoroalkyl carboxylic acid (C4-C14) and perfluoroalkyl sulphonic acid (CS6, CS8) degradation over a range of power density (50 – 336 W/L) at 575 kHz frequency.

### 3.3. pH

Fig. 4 displays a trend showing that as pH increases, the degradation rate of most PFAS also increases. The rate of PFBA degradation is the lowest at all pH. According to Fig. 4, a solution pH of up to 10.01 is optimal for the degradation of PFAS in DI water. However, as pH was raised from 2.72 to 12.26, a decrease in the degradation rate of PFOS, PFTTrDA, and PFTTeDA was also observed. The degradation rate of PFBA was 17% in 120 min at pH 2.72, while the degradation rate of PFTTeDA was 81.81%. Degradation percentages varied from 50 to 90 percent in 120 min at a pH of 4.01, but only from 23 to 92 percent at a pH of 5.65. More than 85% of PFPeA, PFHxA, PFOA, PFNA, PFDA, PFUnDA, and PFDDA were degraded in 120 min at pH 10.01. The results imply that a basic pH (6–10) is advantageous for the degradation of the majority of PFAS. Degradation rates of PFAS were slowed by both very high pH (>11) and low pH (< 3).

For PFCAs, the  $pK_a$  is less than 4 even at chain lengths of 10 [47,48]. Therefore, most PFAS would be in the anionic form at the pH levels used in the experiments. The interface between the bubble and the water is hydrophobic and negatively charged [49]. In an aqueous solution of PFAS, the concentration of protonated  $H^+$  ions is higher at acidic pH than at basic pH. Due to this, the adsorption of  $H^+$  ions and PFAS ions become competitive at the cavity-water interface. The cavity-water interface is relatively negatively charged, hence positively charged  $H^+$  ions have a greater chance of adsorbing there than negatively charged PFAS ions. This shows that at acidic pH, PFAS ions are less likely to interact with the water-cavity interface than at basic pH. A more basic pH has a higher concentration of  $OH^-$  and a lower concentration of  $H^+$  ions. With less  $H^+$  to compete with, PFAS ions are able to adsorb onto the cavity-water interface in greater numbers or faster rate at basic pH. This may explain why higher pH levels lead to faster degradation of PFAS.

### 3.4. Temperature

With an increase in sample temperature from 10 to 30 °Celsius, the degradation of PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFBS, PFHxS, and PFOS increases (Fig. 5). PFTTrDA and PFTTeDA, on the other hand, had a slower degradation rate as temperature was raised. The rate of PFBA and PFDDA degradation was not noticeably affected by solution temperature. Over a wide temperature and PFAS compound range, the



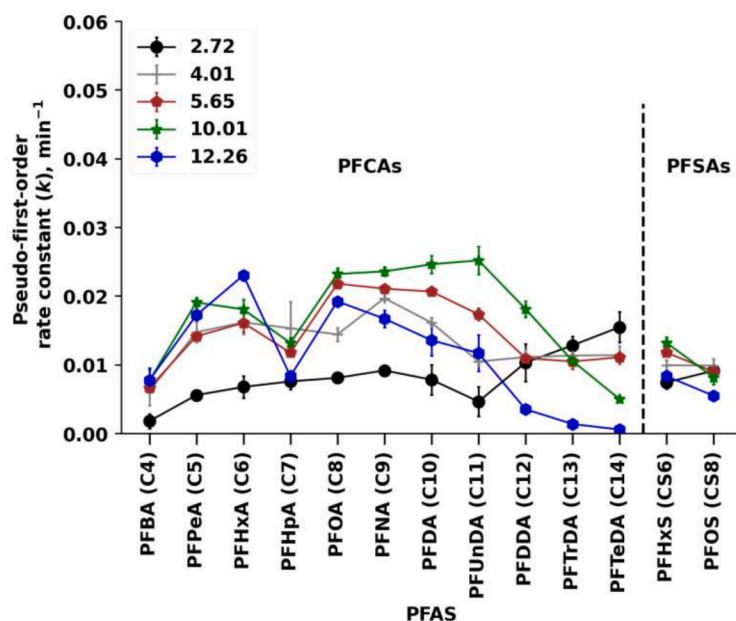


Fig. 4. Pseudo-first-order rate constant ( $k$ ) of perfluoroalkyl carboxylic acid (C4-C14) and perfluoroalkyl sulphonics acid (CS6, CS8) degradation over a range of pH (2.72 – 12.26) at 575 kHz frequency.

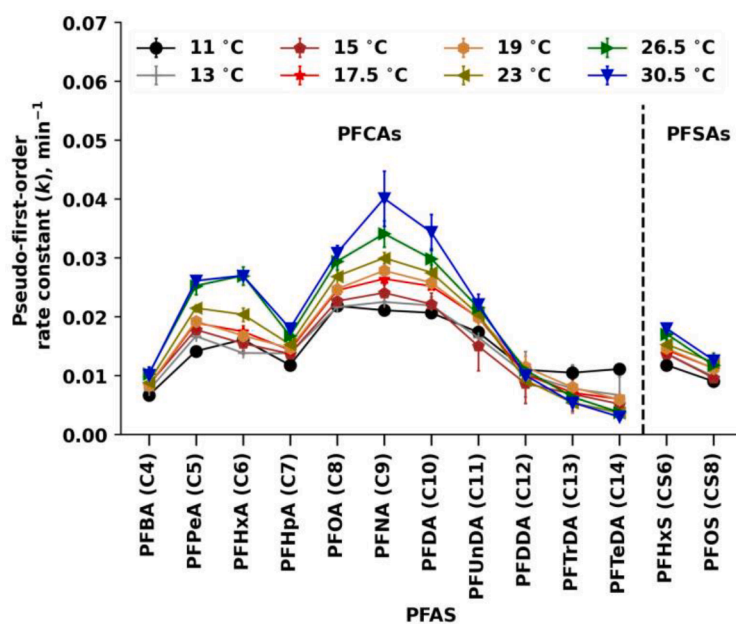


Fig. 5. Pseudo-first-order rate constant ( $k$ ) of perfluoroalkyl carboxylic acid (C4-C14) and perfluoroalkyl sulphonics acid (CS6, CS8) degradation over a range of Temperature (11 – 30.5 °C) at 575 kHz frequency.

degradation rate of PFAS varied from 23% to 98.9%. The degradation rate of PFTTrDA at 23 °C was 30%, while that of PFNA was 98% within 120 min (see Figure S1). PFOA, PFNA, PFDA has more than 90% degradation in 120 min over a range of temperature. More than 80% of PFPeA, PFHxA, PFHpA, PFUnDA, and PFHxS, were degraded in 120 min across the whole temperature range. Degradation of PFOS ranged from 62% to 77% in 120 min.

The sonolytic activation energy ( $E_a$ ) of PFAS degradation is estimated using the Arrhenius equation  $k = Ae^{-\frac{E_a}{RT}}$ , here,  $k$  is a reaction rate constant,  $A$  is a frequency factor,  $R$  [ $J K^{-1} mol^{-1}$ ] is a gas constant and  $T$  [K] is the temperature. Sonication-assisted PFAS degradation required 10–41 kilojoules of energy per mole for activation (Table 1). The actual bond dissociation energy is greater than 400 kJ/mole, hence this

activation energy is far smaller. Consequently, it follows that cavitation acts as a catalyst, decreasing the required activation energy of the reaction. The findings indicate that the chain length of PFAS plays a crucial role on sonolytic degradation and that the temperature of the sample influences the degradation of PFAS. Coalescences of cavities are less likely when the bulk water temperature is higher because the cavities are smaller and the viscosity is lower at higher temperatures. When the bulk water temperature rises, the kinetic energy of the PFAS in water increases, leading to more frequent collisions with the active cavity. Furthermore, the quantity of cavities produced at a higher frequency is significantly greater than that which is generated at a lower frequency [37]. This explains why PFAS degrade more quickly when the bulk water temperature rises.

**Table 1**

The activation energy associated with the degradation of per- and poly-fluoroalkyl substances (PFAS) at a frequency of 575 kHz.

PFAS	Sonolytic activation energy ( $E_a$ ) (kJ/mole)
PFBA	14
PFPeA	21
PFHxA	25
PFHpA	13
PFOA	14
PFNA	23
PFDA	18
PFUnDA	12
PFDDA	10
PFTTrDA	19
PFTeDA	41
PFBS	30
PFHxS	14
PFOS	12

### 3.5. NaCl and NaHCO<sub>3</sub>

Fig. 6a indicates that a modest quantity of NaCl (0.15 g/L) added to the solution increases the degradation rate of both small chain PFAS (PFBA, PFPeA, PFHxA, and PFHpA,) and higher chain PFAS (PFUnDA, PFDDA, PFTTrDA, PFTeDA). However, there was no apparent shift in the degradation rates of PFOA, PFNA, PFDA, or PFOS at 0.15 g/L. In comparison to other PFAS, the rate at which PFBA degraded was the slowest. The degradation rates of PFAS in 120 min ranged from 61% to 95% for most PFAS except PFBA, as shown in Figure S1. Previous studies have shown that the degradation rate of organic compounds and the intensity of sonoluminescence across a spectrum of frequencies (20 kHz–1 MHz) both increase when salt is added to an aqueous solution [50–52]. An increase in salt concentration has been hypothesised to reduce bubble coalescence, salting out effect on dissolved gas, and lower the oxygen content, all of which contribute to a more intense sonoluminescence [52]. In contrast to these findings, we found that as salt concentration increased, the degradation rate of most PFAS decreased. A decrease in the rate kinetic of numerous PFAS was reported by [35] in groundwater

with low total dissolved solid (TDS) comprising of chloride, sulfate, calcium, etc., when compared to DI water, which is consistent with the present findings. The surface tension of a PFAS aqueous solution decreases as its ionic strength increases [53]. In turn, this modifies PFAS surface activity at the airwater interface in the cavity during its expansion phase. It's possible that the lower surface tension at the cavity-water interface is responsible for the slight improvement in PFAS degradation at NaCl concentration of 0.15 g/L. Solubility of PFAS in water decreases with increasing salt concentration [54]. As a result, PFAS have a lower possibility of being absorbed by water in a collapsible cavity. Since this is the case, it stands to reason that a greater concentration of NaCl would slow the degradation rate of most PFAS.

We observed (Fig. 6b) that the degradation rate of small chain PFAS (PFBA, PFPeA, PFHxA, PFHpA,) was enhanced by the addition of NaHCO<sub>3</sub> to the solution and then began to decrease at concentrations over 0.5 g/L. However, with increasing NaHCO<sub>3</sub> concentration, the degradation rate of higher chain PFAS (PFDA, PFUnDA, PFDDA, PFTTrDA, PFTeDA) and PFHxS, and PFOS began to decrease. The degradation rate of PFBA is the slowest in the figure, whereas the rates of PFOA and PFNA are the fastest. Degradation of PFOS and PFHxS was slower than that of PFHxA and PFOA, respectively. In 120 min, most PFAS degraded by between 27% and 94%, as shown in Figure S1. Degradation of all PFAS is likewise shown to be reduced with increasing NaHCO<sub>3</sub> concentrations (Fig. 6b). Reduced rate of PFAS degradation upon addition of and NaHCO<sub>3</sub> may be because high concentrations of Na<sup>+</sup> ions compete with PFAS ions for adsorption at the cavity-water interface. Previous experimental work shows that in an aqueous environment, bicarbonate acts as scavengers of produced radical (sulfate, hydroxyl, hydrated electron) during sonolysis, photolysis and photocatalysis [10]. Bicarbonate also prevented PFAS from being adsorbed to the catalyst [55]. According to Wood *et al.*, [32] the degradation of PFOS occurs due to pyrolysis and hydrated electron generated during cavity collapse at the cavity-water interface. Since the degradation rate of PFAS slows down when bicarbonate is present, this suggests that bicarbonate reacts with chemical species/radicals including hydrated electrons formed during sonolysis. The sonolysis of aqueous solutions forms a

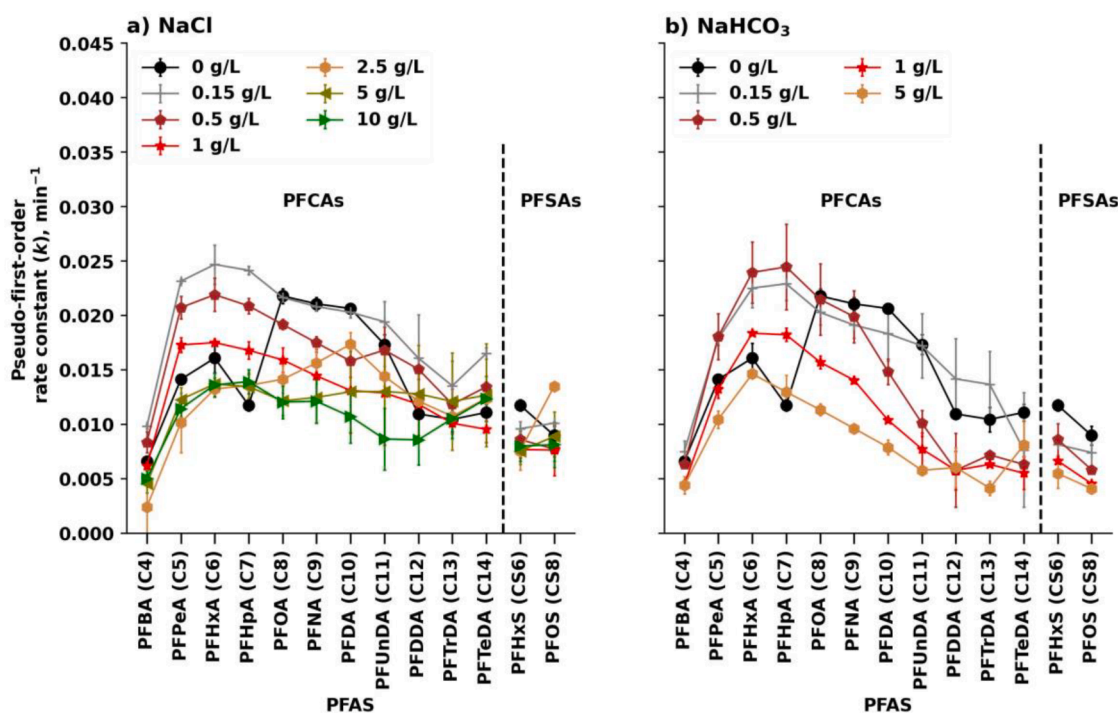


Fig. 6. Pseudo-first-order rate constant ( $k$ ) of perfluoroalkyl carboxylic acid (C4-C14) and perfluoroalkyl sulphonic acid (CS6, CS8) degradation over a range of a) sodium chloride (0 – 10 g/L) and b) sodium bicarbonate (0 – 5 g/L) at 575 kHz frequency.

complex matrix of different chemical species, which may have altered the interfacial pyrolysis condition necessary for PFAS degradation.

### 3.6. PFAS degradation for extended time and fluoride formation

Fig. 7a displays that at 575 kHz, PFAS were degraded from 83% to 99.3% in 8 h. PFBA and PFHxA had the lowest amount of degradation after 8 h, at 83% and 94%, respectively. The degradation rate of every other PFAS could reach greater than 97%. The fluoride formation curve shown in Fig. 7b exhibits a rapid increase in the first four hours, followed by a modest increase in fluoride formation over the next four hours. The ultrasonic destruction of PFAS mixture produced 0.23 ppm of fluoride after 8 h, which is equivalent to 63% of the theoretical fluoride of initial concentration of PFAS mixture. The findings indicate that there is a likelihood of accumulation of PFAS-sono-intermediates in the aqueous sample [10,36] as only 63% of defluorination was observed. Additionally, after 8 h, the nitrate concentration was measured at 128 ppm. Prior work showed that high-frequency ultrasonic cavitation of water causes a sequential conversion of atmospheric nitrogen (dissolved in water) into nitrite and nitrate [36]. This indicates that a substantial amount of nitrate was produced as a byproduct of prolonged sonication of water, which may require additional processing and might have hindered defluorination.

### 3.7. Energy efficiency

Energy efficiency of ultrasonic degradation of PFAS was evaluated using the following formula,

$$G - \text{value} = \frac{\Delta CN_0V}{tP}, \quad (1)$$

where, G-value is the number of molecules degraded per unit of energy input into the system [molecules/kJ] [26,30,32,56,57],  $\Delta C$  is the change in the PFAS concentration over a given time interval  $t$  [s],  $V$  is volume of aqueous sample,  $P$  [W] is input power to the reactor and  $N_0$  is avogadro's number ( $6.023 \times 10^{23} \text{ mol}^{-1}$ ). The G-value for degradation of 13 PFAS mixture is  $14.23 \times 10^{13}$  molecules/kJ. The estimated G-value for degradation of PFOA using electrochemical method [15] and

plasma [12] is  $7.07 \times 10^{13}$  molecules/kJ and  $1312 \times 10^{13}$  molecules/kJ respectively. This suggests that ultrasonic degradation of a mixture of PFAS is a viable alternative, albeit one that is less energy efficient than plasma methods.

## 4. Conclusions

The efficacy of collapsible cavitating bubbles in the degradation of perfluoroalkyl substances is dependent on the adsorption of individual PFAS on the interface between cavity and water. PFAS with a carbon chain length less than seven exhibit solubility, while those with a carbon chain length greater than eleven possess a higher molecular weight and lower water solubility. The lower rate of degradation of lower chain (C4-C7) and higher chain ( $>C11$ ) PFAS implies that they persist within the bulk solution. This suggests that the likelihood of PFAS adsorption at the interface between cavities and water restricts the thermolytic decomposition of both short and long-chain PFAS. The results indicate that a mixture of 13 PFAS undergoes 63% defluorination, suggesting the accumulation of PFAS-sono-intermediate compounds in the aqueous solutions despite extended sonication of PFAS. The current work demonstrated that circulating the sonicated sample through a heat-exchanger not only helps maintain the desired temperature of the aqueous sample for prolonged periods of time (up to 8 h), but also helps avoid heating the transducer, preserving the efficiency with which PFAS of varying chain-lengths are degraded. The results of this research also suggest that a flow-through ultrasonic reactor may be devised, in future, to degrade potentially harmful pollutants. Since ultrasonic cavitation mineralizes PFAS compounds into their inorganic form, high frequency sonolysis offers a promising method for remediation of PFAS [26,56] of a range of chain length and need further investigation.

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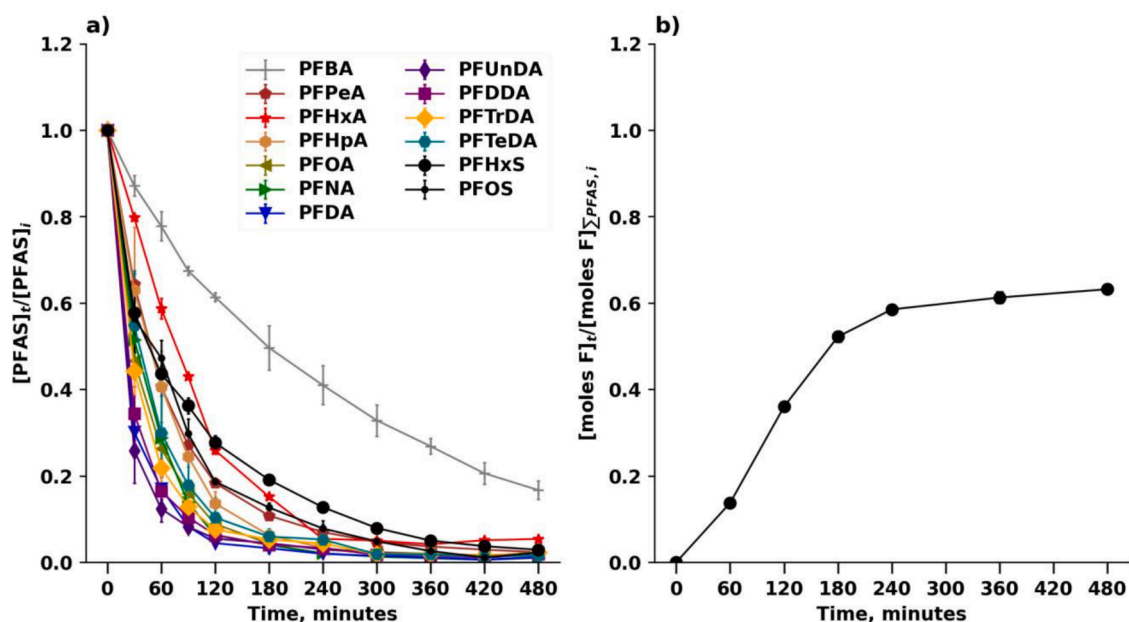


Fig. 7. a) Degradation profile of a mixture of PFCAs (C3 - C14) & PFSA (CS6-CS8), and b) formation of fluoride anion in 8 h [Volume = 350 mL, pH = 5.65, power density = 144 W/L, Temperature = 11 °C, power intensity = 2.82 W/cm<sup>2</sup>, PFBA (C4) = 50 ± 1 ppb, PFPeA (C5) = 50 ± 2 ppb, PFHxA (C6) = 40 ± 6 ppb, PFHpA, (C7) = 41 ± 2 ppb, PFOA (C8) = 51 ± 0.1 ppb, PFNA (C9) = 53 ± 4 ppb, PFDA (C10) = 52 ± 0.1 ppb, PFUnDA (C11) = 25 ± 4 ppb, PFDDA (C12) = 18 ± 5 ppb, PFTrDA (C13) = 19 ± 3 ppb, PFTeA (C14) = 31 ± 8 ppb, PFHxS, (CS6) = 30 ± 2 ppb, PFOS (CS8) = 51 ± 4 ppb.].

## Supporting information (SI)

S1: Material and Methods; S1.2 Instrumental analysis; S1.3 Solid-phase extraction; S1.4 Experiments; S2 Results and discussion;

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

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## Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.cej.2023.100509](https://doi.org/10.1016/j.cej.2023.100509).

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