

# Power density modulated ultrasonic degradation of perfluoroalkyl substances with and without sparging Argon

Takshak Shende, Gangadhar Andaluri, Rominder Suri\*

NSF – Water and Environmental Technology (WET) Center, Civil and Environmental Engineering Department, Temple University, Philadelphia, United States

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## ABSTRACT

The power density modulates the dynamics of the chemical reactions during the ultrasonic breakdown of organic compounds. We evaluated the ultrasonic degradation of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) at various power densities (30 W/L–262 W/L) with and without sparging Argon. We observed pseudo-first-order degradation kinetics at an initial PFASs concentration of 100 nM over a range of power density. The rate kinetics of degradation shows a non-linear increase with an increase in power density. We proposed a four-parameter logistic regression (4PLR) equation that empirically fits the degradation rate kinetics with the power density. The 4PLR equation predicts that the maximum achievable half-life of PFOA and PFOS sonochemical degradation are 1 and 10 min under a given set of experimental conditions. The high bulk-water temperature (i.e., 30 °C) of the aqueous sample helps increase the degradation rate of PFOA and PFOS. The addition of oxidants such as iodate and chlorate help enhance PFOA degradation in an argon environment at an ultrasonic frequency of 575 kHz.

## 1. Introduction

Perfluoroalkyl substances (PFASs) are highly stable aliphatic fluorinated compounds [1]. Some of the PFASs, such as perfluorooctanoic acid (PFOA) and perfluorooctane sulphonic acid (PFOS), are emerging contaminants of concern due to their widespread use in commercial and industrial products in the past [2] and potential toxicity [3]. PFOA and PFOS are listed in the United Nations' persistent organic pollutants (POPs) list to eliminate and restrict production. Further, the United States Environmental Protection Agency (US-EPA) has announced implementing PFASs action plan to protect public health [4]. The pervasive presence of PFASs in the ecosystem, its recalcitrant properties and potential toxicity are major concerns for the general public, researchers, and policymakers [5–11]. Sorption and advanced oxidation processes (i.e. electrochemical [12–14], photocatalytic [15–17], persulfate [18–20], plasma techniques [21,22], and ultrasound [23–28]) have been tested for removal and defluorination of PFASs from water.

The high-frequency ultrasound has shown great potential to defluorinate PFASs into its inorganic compounds such as fluoride and sulphur [23,24,29–32]. The high-frequency ultrasound generates microbubble in an aqueous solution owing to compression (due to the positive pressure) and rarefaction (due to the negative pressure) phase of

ultrasound [33–35]. These microbubble cavities violently and adiabatically collapse due to an imbalance between hydrodynamic forces and acoustic pressures. These collapsible cavities act as microreactors for sonochemical reactions due to high pressure and high temperature in the core of the cavity (4000–10000 K) and cavity-water interface (1000–1500 K) [36–38]. The degradation of PFASs depends on the adsorption of the PFASs on the cavity-water interface of the active collapsible cavity [23,25,26]. The high temperature at the cavity-water interface [23] and hydrated electron generated during plasma formation inside a collapsible cavity [39] could be the reason for the PFAS's defluorination at a high-frequency ultrasound. The ultrasound's operation parameter significantly affects the PFASs degradation process, and the slight change in these parameters' changes reaction pathways of PFASs degradation [25]. The power density, frequency, bulk water temperature, inert gases and additives chemicals are major governing operational parameters [40–47].

Power density applied to the aqueous solution modulates the PFASs degradation, as it controls the dynamics of cavity collapse (i.e., growth of cavity, cavity-water interface velocity during the collapse, temperature and pressure in the core of cavity). Thus, Campbell *et al.* (2015) evaluated the effect of power density on the degradation of PFASs, i.e., perfluorobutyric acid (PFBA), perfluorohexanoic acid (PFHxA),

\* Corresponding author.

E-mail address: [rsuri@temple.edu](mailto:rsuri@temple.edu) (R. Suri).

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perfluorohexanesulfonic acid (PFHxSA), perfluorooctanoic acid (PFOA), perfluorobutanesulfonic acid (PFBS), and perfluorooctanesulfonic acid (PFOS). Campbell *et al.* (2015) reported a linear increase in degradation rates with an increased power density [48]. However, some studies [44,48,49] showed an S-shaped relationship during power density-dependent degradation of organic compounds.

Degradation of contaminants during sonication depends on the formation, growth, and collapse of the cavity. Cavitation in a liquid depends on acoustic pressure, *i.e.*, applied acoustic power. The acoustic pressure is a primary factor in a sonochemical system that modulates the generation, growth, and collapse of cavities [50]. The acoustic pressure generated by the ultrasonic transducer is directly proportional to the acoustic power delivered to the solution [51,52]. Thus, acoustic power stimulates the generation of active collapsible cavities that participate in ultrasonic chemical conversion reactions. The degradation of contaminant is directly related to acoustic power density. The compression ratio, cavity-water interface radial velocity during a collapse, and temperature of the core of the cavity vary depending on acoustic power modulated hydrodynamic interactions. An increase in acoustic pressure leads to the asymmetric collapse of the cavities and jet formations [51,53–56]. Under such conditions, cavities cannot generate sufficient temperature for thermolytic degradation of non-volatile contaminants such as PFASs. Consequently, the degradation rate of contaminants cannot linearly increase with an increase in power density, and the degradation rate must reach an asymptotic degradation rate. A similar asymptotic degradation rate must also be observed at a much lower power density. Thus, we postulate that degradation rate as a function of power density should have a non-linear S-type shape. The four-parameter logistic equation [57–59] can represent the S-shaped relationship between degradation rate and power density. Four parameters logistic regression equation represent S-shaped type relationship between two parameters. It is commonly used in toxicity studies and population growth studies. In toxicity studies, the dose of a toxic compound and the magnitude of response by organism/receptor after a specific exposure may show an S-shaped behaviour. This S-shaped type dose–response curve is generally modelled using a four-parameter logistic equation. Analogous to the dose–response in toxicity study, the sonolytic degradation rate could be considered a response, and applied power density as dose. The population of active collapsible cavity present in the solution is a controlling factor for the degradation of compounds. This population of active cavities mostly depends on applied acoustic pressure and, thus, on applied power density. Most of the previous work showed a linear increase in the rate of degradation of contaminants with an increase in acoustic power; however, in this work, we observed a non-linear increase, which can be modelled using a four-parameter-logistic regression equation.

Additives in the sonochemical process generate highly reactive radicals that enhance the degradation rate/kinetics. Hao *et al.* [60] and Lee *et al.* [31] reported enhanced PFOA removal with persulfate and periodate at low-frequency ultrasound, respectively. However, those studies were carried out at a high initial concentration, which is not environmentally relevant. Further, there is a lack of information on the effect of highly reactive oxidants on PFOS degradation. Literature reports that the presence of rare gas such as Argon during sonication increases the chemical reaction rate; however, we observed a decrease in the degradation rate of PFOA and PFOS with gases such as Argon, Helium, Oxygen, Ozone, and Nitrogen [25] at a power density of 77 W/L. As power density drastically affects the degradation kinetics, further evaluation is required on the effect of inert gases such as Argon on PFASs degradation over a range of power density. This study reports the effect of power density on the degradation of PFOA and PFOS with and without sparging of argon gas. A four-parameter logistic regression equation was used to represent the observed non-linear relationship. The 4PLR equation helped to estimate the maximum and minimum achievable degradation rates under specific experimental conditions.

## 2. Material and method

### 2.1. Chemicals

Analytical grade heptadecafluorooctanesulfonic acid potassium salt (PFOS, 98%), perfluorooctanoic acid (PFOA, 96%), HPLC grade methanol (>99.8%), potassium persulfate (>99%), sodium periodate (>99.8%), sodium iodate (>99%), sodium perchlorate (>98%), sodium chlorate (>99.0%), acetonitrile (>99.9%) and HPLC water were purchased from Sigma Aldrich, USA. Stable-isotope surrogate of sodium perfluorooctanesulfonate ( $^{13}\text{C}_8$  PFOS, 99%) and perfluorooctanoic acid ( $^{13}\text{C}_8$  PFOA, 99%) were procured from Cambridge isotope laboratories, Inc. Oasis weak anion exchange (WAX; 3 cc cartridge 60 mg 30  $\mu\text{m}$ ) cartridges were purchased from Water Corp (Milford, MA, USA) for solid-phase extraction (SPE) of PFOS and PFOA. Argon was purchased from Airgas., Philadelphia, USA. The aqueous solutions were prepared with Milli-Q water (>18.2  $\text{M}\Omega\text{ cm}^{-1}$  resistivity). All materials were used as received.

### 2.2. Sonication experiment and PFAS analysis

The mixture of PFOS and PFOA was sonicated at various power densities by varying volume (50–500 mL) of the aqueous solution with and without sparging Argon. The ultrasonic waves of 575 kHz were delivered to the aqueous solution from the bottom of the reactor using a Meinhardt multi-frequency transducer (model E/805/T/M, the diameter of active area 5.3 cm). The reaction temperature was maintained using a VWR scientific refrigerated bath (Model 1160) by circulating the coolant around the glass reactor. The temperature of the bulk water solution increases due to heat loss during ultrasonic wave propagation and transducer heating. Our experimental setup took 15 min upon initiation of sonication for the solution temperature to become constant for the remaining 105 min. The working solution of a mixture of PFOA and PFOS was prepared by spiking a specific volume of the PFOA and PFOS. The sonication experiments were conducted at constant ultrasonic power of 120 W in duplicate. Argon gas bubbled into the aqueous solution for 20 min before sonication and was continuously bubbling during the experiment. Detailed information of the experimental procedure, setup and by-products formations during sonolytic degradation of PFOA and PFOS were reported elsewhere [25,26]. It should be noted that fluoride formation (*i.e.* defluorination) was not measured in this study as the initial concentration of PFOA and PFOS in the aqueous solution was low. However, short-chain PFASs (C3–C7) were monitored.

Sonication of the aqueous solution for a prolonged time forms many chemicals (*i.e.* hydrogen peroxide, nitrate, nitrite *etc.*) [26]. Thus, solid-phase extraction of PFOA and PFOS using Oasis WAX cartridge was carried out to reduce the matrix effect while analyzing PFOA and PFOS. Labelled-isotope surrogate standard ( $^{13}\text{C}_8$  PFOA,  $^{13}\text{C}_8$  PFOS) was added in all samples and standard solutions to evaluate potential matrix effects. Ultra-performance liquid chromatography (UPLC) was used for the quantitative analysis of PFAS. The UPLC was equipped with Waters Acquity UPLC BEH C18 (2.1  $\times$  50 mm, 1.7  $\mu\text{m}$ ) column coupled to a Waters Xevo TQ-S mass spectrometer. Details of PFOA/PFOS analysis, solid-phase extraction, and LC/MS/MS conditions are reported elsewhere [25,26].

Three different sets of experiments were conducted in the present study. In the first set, sonication of the mixture of PFOA and PFOS were carried out at low initial PFASs concentration and bulk water temperature without sparging gas as given in Table 1. The second set of experiments were conducted at high initial concentration and bulk water temperature with sparging Argon to evaluate the effect of an increase in concentration and temperature over a range of power density as given in Table 2. To check the effectiveness of oxidants' addition on PFASs degradation, the third set of experiments was carried by sonicating a mixture of PFOA and PFOS with 1 g/L of oxidant at a power density of 30 W/L. The oxidants used were potassium persulfate, sodium

**Table 1**  
Experimental conditions during PFASs sonication without sparging gas.

Power Density (W/L)	Initial concentration (nM)		Solution temperature (°C)
	PFOA	PFOS	
262	85 ± 10	102 ± 2	30 ± 1
147	97 ± 1	109 ± 2	25 ± 2
77	104 ± 1	120 ± 2	13 ± 2
52	101 ± 1	118 ± 1	13 ± 1
30	97 ± 1	114 ± 5	13 ± 3

**Table 2**  
Experimental conditions during PFASs sonication with Argon gas.

Power Density (W/L)	Initial concentration (nM)		Solution temperature (°C)
	PFOA	PFOS	
262	140 ± 2	119 ± 4	30 ± 2
147	139 ± 5	128 ± 8	25 ± 1
77	120 ± 4	119 ± 7	21 ± 1
52	153 ± 1	157 ± 1	21 ± 2
30	138 ± 2	152 ± 2	20 ± 1

periodate, sodium iodate, sodium chlorate, and sodium perchlorate.

### 3. Four parameters logistic regression (4PLR) equation

Calorimetric power ( $P_c$ ) delivered to the aqueous solution [61] and calorimetric power density ( $PD$ ) were measured using,

$$P_c = C_p M \frac{dT}{dt}, \quad (1)$$

$$PD = \frac{P_c}{V}, \quad (2)$$

where  $M$  is the mass [kg] of an aqueous solution,  $C_p$  is the heat capacity [J/(kg K)],  $T$  is the temperature [K], and  $t$  is the time [s] and  $V$  the volume of the aqueous sample [L]. Ultrasonic degradation of contaminants depends on the power density, amongst other parameters. The degradation kinetics and power density, in the present work, follow a non-linear relationship [44], similar to the S-shaped dose-response curve. Therefore, an empirical four-parameter logistic regression (4PLR) equation (Eq. (3)) was proposed to represent the non-linear relationship between an ultrasonic power density ( $PD$ ) and the degradation rate kinetics ( $k$ ). The following assumptions were made: (a) ultrasonic degradation of contaminants initiates only after the collapse of active cavities; (b) the number of active cavity collapse events modulate chemical conversion rate; (c) the power density, which is the function of acoustic pressure, controls the amount of active collapsible cavities presents in the solution; (d) the power density represents applied dose to the solution, and (e) the chemical conversion rate in terms of rate kinetics constant represents the response.

$$k = k_{max} + \frac{(k_{min} - k_{max})}{1 + \left(\frac{PD}{P_I}\right)^b} \quad (3)$$

where,  $k_{min}$  is the minimum rate kinetics constant;  $k_{max}$  is the maximum rate kinetics constant;  $P_I$  is a point of inflexion, *i.e.*, a power density at which  $\left(\frac{k_{min} + k_{max}}{2}\right)$ ; and  $b$  is the curve's hill slope. Depending on the chemical conversion process, the rate kinetics constant of the reaction could be zero order, first order, second order, or pseudo-first-order. Thus, the unit of rate kinetics constant depends on the ultrasonic chemical reactions. Note that the four-parameter logistic regression equation is commonly used in toxicity studies.

Degradation rate kinetic values obtained at different power densities

were used to estimate the constant parameters of the 4PLR equation using Excel-Solver methods that use the GRG non-linear algorithm [62]. The four-parameter logistic regression (4PLR) equation could be used as an engineering tool to modulate the contaminant's power density-dependent degradation in an ultrasonic reactor. It helps estimate the maximum and minimum achievable degradation rate for a given reaction under specific experimental conditions. The 4PLR equation helps specify an optimized power density value for the maximum degradation of contaminants, which helps reduce the ultrasonic reactor's operational electricity cost.

## 4. Results

### 4.1. Calorimetric power

Although the constant ultrasonic power of 120 W was supplied to the solution during all experiments, an increase in the volume of the solution resulted in a higher calorimetrically measured power and an exponential decrease in the calorimetric power density (Fig. 1). An increase in the dissipation of acoustic power to the aqueous solution was observed with an increase in the volume from 50 to 1000 mL. Asakura *et al.* (2008) reported a similar increase in calorimetric power with an increased height of the aqueous sample in the reactor over a frequency range (45–490 kHz) [63].

### 4.2. Effect of power density

The time-dependent degradation profiles of PFOA and PFOS (at 575 kHz) was evaluated at power densities of 30, 53, 77, 147, and 262 W/L without sparging any gas (Fig. 2) and with sparging Argon gas (Fig. 3). PFASs degradation followed pseudo-first-order kinetics with  $R^2$  of 0.97–0.999 over a range (30–262 W/L) of power density (Fig. 4). We did not observe changes in PFOA and PFOS concentrations in a control experiment over a range of bulk water temperature (0–40 °C) without ultrasound. The degradation of PFOA non-linearly increased from 43% to 98% with an increase in power density. Similarly, the degradation of PFOS non-linearly increased from 34% to 97% with an increase in the power density during 120 min of sonication. The magnitude of the rate of degradation observed in the present work is consistent with the results reported previously in the literature [23,25,26,48]. Similar to our previous work [25,26] and Vecitis *et al.* (2008) [23], we did not observe the formation of short-chain perfluoroalkyl substances (C3–C7) during PFOA and PFOS sonolytic degradation. Thus, PFASs followed the degradation mechanism proposed by Vecitis *et al.* (2008) [23]. Thermolytic degradation of PFASs occurs at the cavity-water interface. Moreover, sono-intermediate compounds are formed before PFOA and PFOS undergo complete mineralization into their inorganic compounds (*i.e.* sulphate and fluoride). The bond of dissociation energy of the C–S bond and C–C bond is 714.1 kJ/mol and 610 kJ/mol, respectively [64]. Thus, the C–S bond cleavage requires higher thermolytic energy compared to the C–C bond cleavage. Thus, the C–S bond present in PFOS requires high thermolytic energy compared to the C–C bond present in PFOA. The temperature of a cavity-water interface is much lower than the core of the cavity [38,49,59,60] but being a non-volatile surfactant PFASs adsorb to the cavity-water interface [23]. Consequently, PFOA has a higher rate of ultrasonic degradation compared to PFOS [25,26,29,30].

The four parameters logistic regression equation was evaluated using pseudo-first-order kinetics data of PFASs degradation. Fig. 4a,b, and the lower sum of squared difference (SSD) values (Table 3) confirm that the 4PLR parameter fits experimental data. The 4PLR parameters give valuable information on the power density-dependent degradation of PFASs. It aids to find out the minimum and maximum degradation rate that the system can achieve for a specific compound under specific conditions.

In an air environment (*i.e.* without sparging argon), 4PLR equation

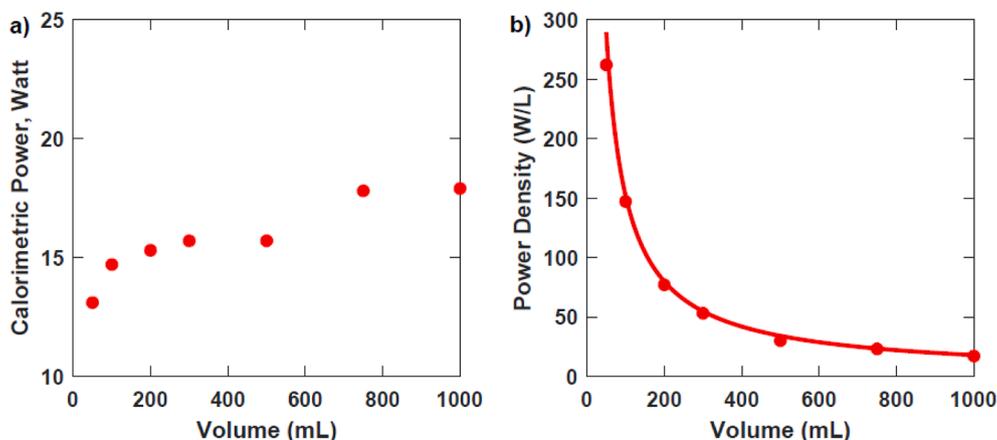


Fig. 1. Calorimetrically determined ultrasonic power as a function of a volume of a solution b) The calorimetric power density plotted as a function of volume.

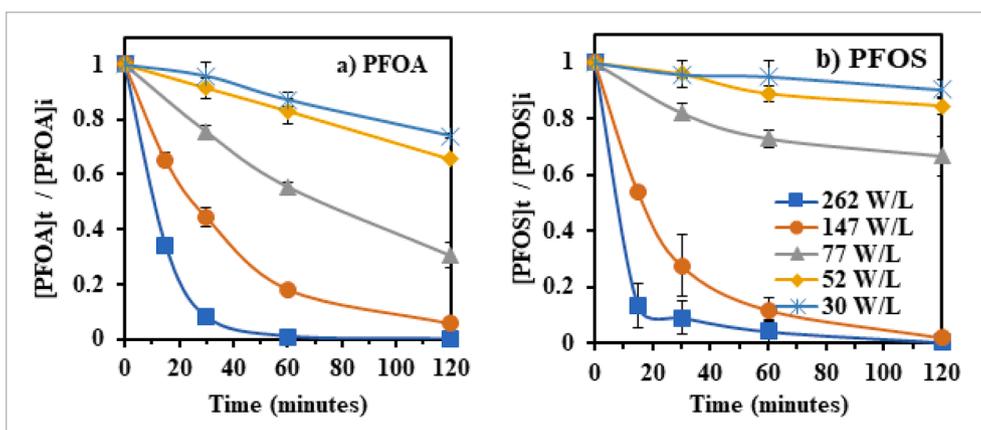


Fig. 2. Normalized time-dependent plot of sonolytic degradation of a mixture of PFOA & PFOS over a range of power density without sparging any gases. a)  $[PFOA]_t/[PFOA]_i$  vs time in minutes b)  $[PFOS]_t/[PFOS]_i$  vs time in minutes.

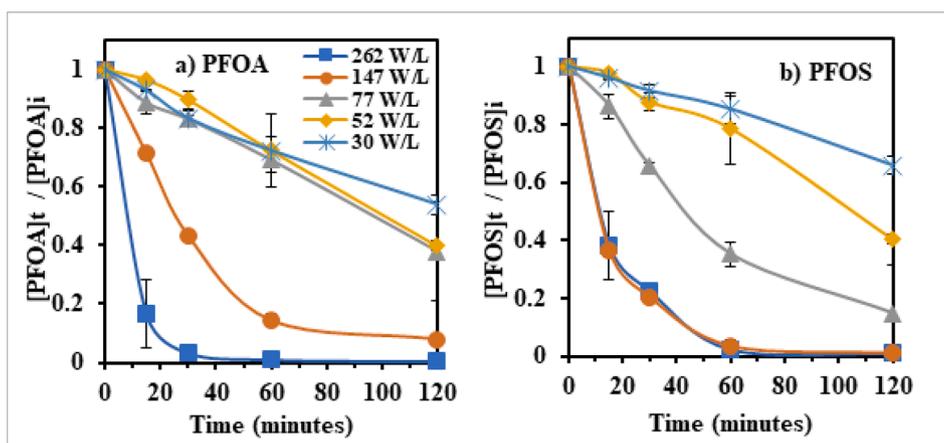


Fig. 3. Normalized time-dependent plot of sonolytic degradation of a mixture of PFOA & PFOS over a range of power density in an Argon environment. a)  $[PFOA]_t/[PFOA]_i$  vs time in minutes b)  $[PFOS]_t/[PFOS]_i$  vs time in minutes.

suggests that maximum achievable degradation rate of PFOA ( $k = 6.9 \times 10^{-1} \text{ min}^{-1}$ , half-life = 1 min,  $PD = 4000 \text{ W/L}$ ) is 9 times higher compared to PFOS ( $k = 7.1 \times 10^{-2} \text{ min}^{-1}$ , half-life = 9 min,  $PD = 600 \text{ W/L}$ ) at a frequency of 575 kHz. The estimated degradation rates at point of inflexion were  $3.5 \times 10^{-2} \text{ min}^{-1}$  ( $PD = 580 \text{ W/L}$ , half-life = 2 min) and  $3.6 \times 10^{-2} \text{ min}^{-1}$  ( $PD = 145.5 \text{ W/L}$ , half-life = 19 min) for PFOA and PFOS, respectively. Further, the model suggests that a

minimum degradation rate of PFOA and PFOS was  $2.7 \times 10^{-3} \text{ min}^{-1}$  (half-life = 240 min) and  $7.5 \times 10^{-4} \text{ min}^{-1}$  (half-life = 919 min). Similarly, in an Argon environment (i.e. with sparging argon), 4PLR equation suggests that maximum achievable degradation rate of PFOA ( $k = 6 \times 10^{-1} \text{ min}^{-1}$ , half-life = 1.2 min,  $PD = 8000 \text{ W/L}$ ) was 6 times higher compared to PFOS ( $k = 9.99 \times 10^{-2} \text{ min}^{-1}$ , half-life = 7 min,  $PD = 2000 \text{ W/L}$ ) at ultrasonic frequency of 575 kHz. The estimated

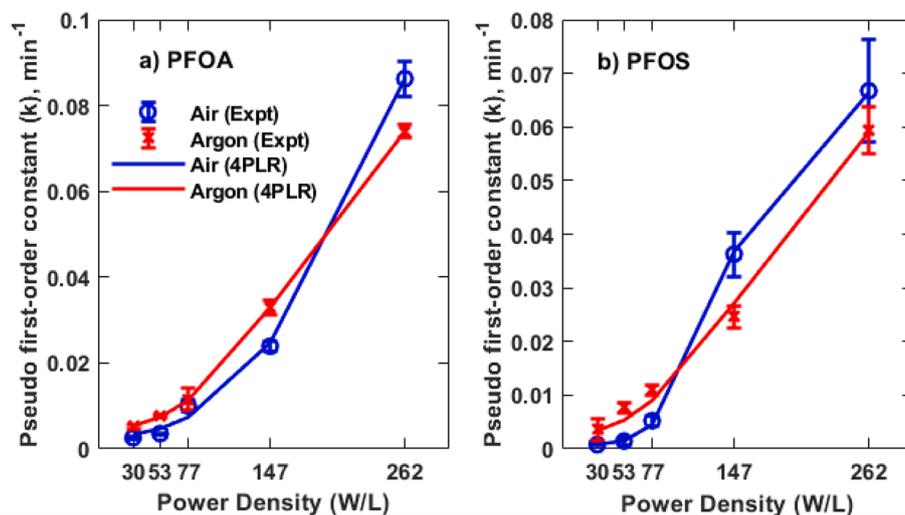


Fig. 4. Pseudo-first-order rate constant dependence on power densities a) PFOA and b) PFOS, with and without sparging Argon. Experimental values (Expt) and curve fitted using a four-parameter logistics regression (4PLR) equation.

Table 3  
4PLR equation parameters.

Attribute	Unit	Without Argon		Argon	
		PFOA	PFOS	PFOA	PFOS
$k_{min}$	Per min	$2.91 \times 10^{-3}$	$7.54 \times 10^{-4}$	$2.08 \times 10^{-3}$	$2.71 \times 10^{-3}$
$b$	–	2.49	4.50	1.66	2.44
$P_i$	(W/L)	580	145	868	230
$k_{max}$	Per min	$6.9 \times 10^{-1}$	$7.0 \times 10^{-2}$	$6 \times 10^{-1}$	$9.99 \times 10^{-2}$
SSD		$9.9 \times 10^{-6}$	$8.9 \times 10^{-6}$	$4.2 \times 10^{-6}$	$1.6 \times 10^{-6}$

degradation rates at point of inflexion were  $3 \times 10^{-2} \text{ min}^{-1}$  ( $PD = 868 \text{ W/L}$ , half-life = 2.3 min) and  $5.1 \times 10^{-2} \text{ min}^{-1}$  ( $PD = 230 \text{ W/L}$ , half-life = 13.6 min) for PFOA and PFOS, respectively. Further, the model suggests that a minimum degradation rate of PFOA and PFOS was  $2.08 \times 10^{-3} \text{ min}^{-1}$  (half-life = 332 min) and  $2.7 \times 10^{-3} \text{ min}^{-1}$  (half-life = 255 min). These results indicate that the 4PLR equation could be a helpful engineering tool to optimize the power density required to achieve the desired degradation of a specific compound under specified conditions.

#### 4.3. Effect of oxidants

The degradation profile of the PFOA and PFOS with different oxidants with sparging Argon gas are shown in Fig. 5a,b. We observed the zero-order rate constant with oxidants at a power density of 30 W/L in an Argon environment. Fig. 5c shows that iodate's addition in an aqueous solution enhanced the degradation rate of PFOA and PFOS by 82% and 53%, respectively. However, the addition of periodate did not affect the degradation rate of PFOA but reduced the degradation rate of PFOS by 40%. The addition of chlorate, persulfate and perchlorate enhanced the degradation rate of PFOA by 88%, 35%, 23%, respectively, but there was no significant improvement in PFOS degradation rate (<12%). These results imply that the addition of oxidants iodate and chlorate could significantly improve PFOA degradation; however, these oxidants could not aid to improve PFOS degradation in an Argon environment.

## 5. Discussion

### 5.1. Effect of power density

The calorimetrically measured ultrasonic power provides valuable information on the performance of the sonochemical degradation of the

contaminants. The attenuation of sound in a liquid depends on the viscosity of the solution and ultrasonic frequency. The standing wave and travelling wave formation in the aqueous sample depend on the distance of the water surface from the transducer and the frequency of ultrasonic waves. An increase in calorimetric power with an increase in volume (Fig. 1) suggest that reactor configuration [45] and height of aqueous sample in the reactor [63] affects the dissipation of ultrasonic power to the solution in the reactor. Asakura *et al.* (2008) visualised the sonochemical reaction field using sonochemical luminescence over a range of liquid height (50 mm to 500 mm) at an ultrasonic frequency of 490 kHz [63]. They reported higher sonochemical luminescence intensity near the solution's surface for an aqueous solution having a height of >100 mm at 490 kHz. On the contrary, Wood *et al.* (2019) [39] visualised sonoluminescence intensity during PFOS degradation and reported that the configuration of standing waves and travelling waves during sonication influences the spatial distribution of the sonochemical reaction field. They reported two active zones with higher sonoluminescence intensity separated by inactive zones at an ultrasonic frequency of 400 kHz and 500 kHz [39]. These results indicate that the changing volume or height of the solution affects the degradation of the contaminants due to changes in the spatial distribution of the active cavitation zone. Thus, reactor configuration and the spatial distribution of active cavitation zones are critical factors that should be considered while evaluating the sonolytic degradation mechanism and process optimization.

Fig. 4a,b shows that at lower power density, PFOA and PFOS degradation kinetics had a stable increase, followed by a steep increase with an increase in power density. It can be inferred from Fig. 4b (an experiment without sparging Argon) that power density-dependent PFOS kinetics follows a sigmoidal S-shape curve similar to like dose-response curves. These results contrast with (Campbell & Hoffmann, 2015), where a linear increase in degradation kinetics of PFOA and PFOS was reported with an increase in a power density an ultrasonic frequency of 358 kHz and 610 kHz. However, data reported by Campbell and Hoffman (2015) on power density-dependent degradation kinetics of perfluorobutanoic acid (PFBA), perfluorobutane sulfonic acid (PFBS) and perfluorohexonic acid (PFHxA) at an ultrasonic frequency of 202 kHz and 610 kHz shows the pattern of stabilized kinetics rate at higher power density values [48]. These results are similar to those reported by Andaluri *et al.* (2012), where a non-linear relationship between power density and rate kinetics has been reported for sonochemical degradation of estrogen hormones [44].

Based on the Gilmore equation's cavity collapse analysis, we have reported that the compression ratio, cavity-water interface radial velocity, and maximum temperature of 2  $\mu\text{m}$  cavitating bubble increases

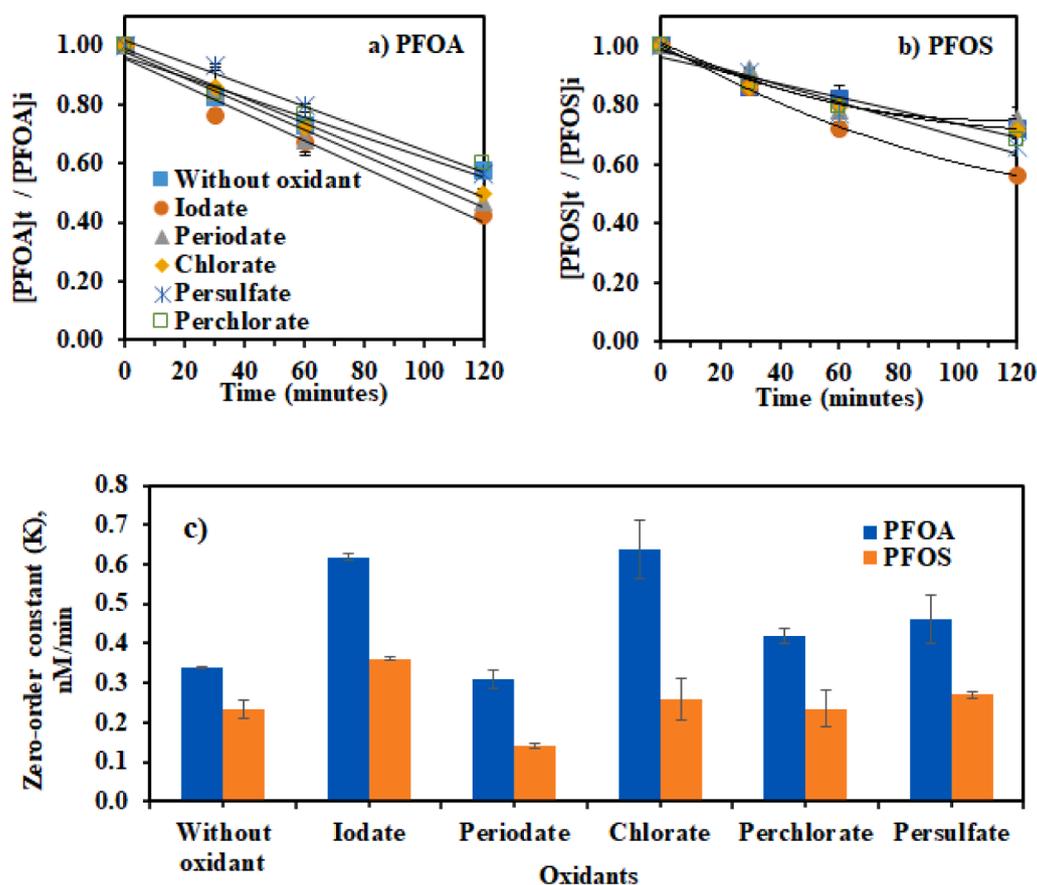


Fig. 5. Effect of oxidants on the sonochemical degradation of a mixture of PFOA & PFOS with Argon. Normalized time-dependent degradation plot of a) PFOA b) PFOS. c) zero-order kinetics over a range of oxidants. Power density. 30 W/L,  $PFOA_0 = 95 \pm 8$  nM,  $PFOS_0 = 102 \pm 10$  nM,  $Temp_f = 18$  °C.

with increasing acoustic power [25]. This could be a reason for the increase in the degradation rate with an increase in the applied power/power density. The collapse of the cavity must be symmetric and towards the core of the cavity for generating conditions required for sonochemical degradation. The bubble's size increases more than ten times its original size at higher acoustic pressure, and bubble wall velocity is above supersonic [25]. Under such conditions, the probability of having symmetric collapse toward the centre of the cavity reduces. A slight imbalance in the hydrostatic and acoustic pressure might lead to the asymmetric collapse of a cavity and jet formation [51,53]. Thus, the constant degradation rate at higher applied power/power density could be due to asymmetric collapse of the cavity when the compression ratio is higher, and bubble-radial velocity is supersonic.

The sound wave at high frequency cannot travel for long-distance. Stokes's law of sound attenuation states that as sound moves away from the source, the amplitude of sound decreases exponentially. The attenuation of sound depends on the frequency and viscosity of the fluid and acoustic scattering. Thus, acoustic pressure near-source will always be higher, and it will decrease as the acoustic wave moves away from the source in water. However, the reflection of sound from the surface of water and glass wall boundaries generates a standing and travelling wave pattern in the liquid. This leads to the containment of active collapsible cavities in specific nodes and antinodes of standing waves. Thus, the spatial distribution of the active cavitation zone depends on the distance of the liquid boundary from the transducer. Cavitation activities can be visualised using sonoluminescence or sonochemical luminescence. The sonoluminescence is due to the collapse of an active cavity. In contrast, sonochemical luminescence could be due to the reaction of luminating chemical (e.g., luminol + sodium carbonate) inside the cavity or interaction of high energy radicals (e.g., hydroxyl radical, superoxide radical anion [65] etc.) formed during cavitation with

luminol outside the active cavity. Hydroxyl radical cannot degrade PFASs; thus, PFASs must interact with the active collapsible cavity to mineralise it into its inorganic form [23,26].

Sonoluminescence images reported by Wood *et al.* (2019) during PFOS degradation in 200 mL solution at an ultrasonic frequency of 400 kHz and 500 kHz suggest that the active cavitation zone lies away from the source. The sonoluminescence images of Wood *et al.* (2019) shows that the active cavitation zones are separated by inactive cavitation zone at an ultrasonic frequency of 400 and 500 kHz. Note that Wood *et al.* (2019) observed >99% mineralisation of PFOS into fluoride at ultrasonic frequency 400 kHz, 500 kHz and 1000 kHz; however, the intensity of sonoluminescence at 1000 kHz was insignificant compared to the 400 kHz and 500 kHz [39]. This suggests that the correlation of cavitation zone observed using sonoluminescence cannot always represent actual cavitation zones. The compression ratio of the cavities in the standing waves near the ultrasonic source will be relatively higher than the compression ratio of cavities away from the source (e.g., near-surface) due to sound attenuation. Further, the standing wave formation and active cavitation zone during sonication are often moved toward the aqueous solution surface with an increase in the volume of aqueous solution at high frequency [39,63,66]. The density of active collapsible cavities decreases with an increase in the volume of solution. This could be the reason for a higher degradation rate at higher power density, i.e., at a lower volume and lower degradation rate at a lower power density.

We performed a two-sample T-test at  $p < 0.05$  to check the statistical difference in the first-order rate constant of PFOA and PFOS with and without Argon at each power density. The statistical T-test had a  $p$ -value ranging from 0.15 to 0.7 over a range of power density, suggesting a statistically insignificant difference in the rate constant of PFOA and PFOS with and without sparging argon. These results suggest that the presence of Argon during an experiment did not significantly improve

the degradation of PFOA and PFOS over a range of power density.

The mass transfer of oxygen and nitrogen from the surrounding in the aqueous sample could increase due to sparging of Argon gas compared to the without sparging of gas. This mass transfer occurs due to the unstable/turbulent solution's top surface due to ultrasonic vibration and the violently floating Argon bubbles. We hypothesise that the hydroxyl radical-based reaction scheme could dominate in an Argon environment due to available excess oxygen with sparging Argon [25], leading to a decrease in the rate of degradation of PFASs. Note that hydroxyl radicals alone cannot degrade PFOA and PFOS. In an air environment, oxygen mass transfer into the aqueous sample could be minimum due to the lack of floating turbulent/violent gas bubbles. Thus, the hydroxyl radical based reaction scheme is not dominant. This helps PFASs actively adsorb on the cavitating bubble's surface for its degradation at high temperature.

## 5.2. Effect of oxidants

Periodate has a reduction potential of +1.6 V, which aids to generate free and highly reactive radicals ( $\text{IO}_3\cdot$ ). The addition of periodate did not influence the degradation rate of PFOA in an Argon environment at an ultrasonic frequency of 575 kHz. These results contrast with Lee *et al.* (2016), wherein they reported enhancement in PFOA degradation rate during sonication of PFOA with periodate at an ultrasonic frequency of 40 kHz [31]. The initial PFOA concentration was 170  $\mu\text{M}$  in Lee *et al.* study [31], whereas in the present study, the initial PFOA concentration was 100 nM. Thus, the difference in results could be due to a difference in initial PFOA concentration and ultrasonic frequency. Low-frequency ultrasound generates bigger size cavities than high-frequency ultrasound; thus, reactive radicals formed during sonication of periodate at low frequency would be different from those at high frequency.

Iodate ( $\text{IO}_3^-$ ) and periodate ( $\text{IO}_4^-$ ) are oxyanions of iodine with an oxidation state of +5 and +7, respectively. Ultrasonic irradiation and collapse of cavities might help to activate the number of reactive free radicals of iodine, such as periodyl radical ( $\text{IO}_3\cdot$ ), iodyl radical ( $\text{IO}_4\cdot$ ), similar to photoactivation [67]. Thus, to check the influence of iodine's highly reactive radicals formed during sonication on PFOA/S degradation, we evaluated the effect of Iodate on PFOA/S degradation in addition to periodate. Fig. 5 shows significant improvement in PFOA and PFOS degradation with iodate compared to periodate at an ultrasonic frequency of 575 kHz. The periodate radicals are highly reactive compared to the iodate radicals [67,68]. The amount of strongly oxidizing periodate radicals might have formed in large quantity from iodate compared to periodate during cavitation. This could be a reason for enhancement in the degradation of PFOA and PFOS with Iodate compared to periodate.

Chlorate and perchlorate have an oxidation potential of 1.47 V and 1.42 V, respectively, under acidic conditions [69]. Thus, we evaluated the effect of chlorate and perchlorate on PFOA and PFOS degradation in an Argon environment. Fig. 5c shows that the addition of chlorate significantly improved the degradation of PFOA as compared to perchlorate. This may be due to the higher oxidation potential of the chlorate compared to perchlorate. Little variation in PFOS degradation rate with chlorate and perchlorate suggests that PFOS degradation was not affected by these oxidants' addition during sonication. The energy required to dissociate the C-S bond and C-C bond is 714.1 kJ/mol and 610 kJ/mol. Thus, PFOS requires higher energy to break the C-S bond compared to the C-S bond. These may be the reason for the insignificant effect of Chlorate addition on PFOS degradation during sonication.

Sulfate radicals ( $\text{SO}_4\cdot^-$ ) have shown the potential to defluorinate PFOA due to their high redox potential ( $E_0 = 2.5\text{--}3.1$  V) compared to hydroxyl radical ( $\text{OH}\cdot$ ). Sulfate radicals directly break the C-F bond of the PFOA. However, they cannot degrade PFOS. We observed that the addition of persulfate increases (35%) the degradation rate in the Argon environment. This improvement could be due to the production of sulfate radicals in the aqueous solution during cavitation. These results

contrast with Hau *et al.*, wherein the authors reported 99% degradation of PFOA with the ultrasound-persulfate system [60]. Hau *et al.* conducted all experiments at a very high initial PFASs concentration (10–46  $\mu\text{M/L}$ ) and ultrasonic frequency of 20 kHz [60], whereas, initial concentration of PFOA in this study was two orders of magnitude lower (0.01 – 0.012  $\mu\text{M/L}$ ). Further, a high dose of persulfate in the aqueous solution generates many sulfate radicals, which may act as self-scavengers, limiting the degradation rate of contaminants [60]. Thus, lower initial concentration and scavenging of sulfate radicals by themselves could be the reason for low enhancement in the degradation of PFOA with persulfate in this study.

This study confirms that the sonochemical degradation of PFOS depends on the adsorption at the cavity-water interface followed by thermolytic breakdown into its inorganic form. On the contrary, highly reactive radicals such as sulfate radicals and chlorate enhance PFOA degradation during sonication and the thermolytic breakdown at the cavity-water interface.

## 6. Conclusion

The effect of power density was explored on the degradation of a mixture of perfluoroalkyl substances – PFOA and PFOS with and without sparging Argon. A non-linear power density-dependent degradation kinetics of PFASs, modelled using the 4PLR equation, suggests that the minimum achievable degradation rate for PFOA and PFOS is 0.0029  $\text{min}^{-1}$  and 0.0007  $\text{min}^{-1}$  at lower power density, respectively, and the maximum achievable degradation rate is 0.69  $\text{min}^{-1}$  and 0.07  $\text{min}^{-1}$  at higher power density, respectively, under-tested experimental condition. 4PLR could be utilized as a helpful engineering tool to optimize power density requirement for ultrasonic degradation under a specific condition.

The cavity collapse at high acoustic pressure is asymmetric, and literature reports the formation of the jet during cavity collapse. Consequently, most of the cavities do not collapse toward the core of cavities, which affects the temperature at the core of the cavity and the cavity-water interface. This hampers the continuous increase of degradation kinetics with an increase in power density, as observed in the present study. Enhancing PFASs degradation is possible by optimising the acoustic and hydrodynamic parameters of ultrasonic cavitation. The bulk water temperature, gas composition, initial PFASs concentrations, power density, and additives oxidants modulate the PFASs degradation kinetics. The chlorate and iodate could significantly enhance the degradation of PFOA at an ultrasonic frequency of 575 kHz. Perchlorate and persulfate could moderately enhance PFOA degradation. The addition of additive oxidants could not improve PFOS degradation. This indicates that highly reactive radicals of chlorate, perchlorate, iodate, periodate and persulfate formed during cavitation cannot break the strong C-S bond of the PFOS.

## CRedit authorship contribution statement

**Takshak Shende:** Conceptualization, Formal analysis, Investigation, Methodology, Writing - original draft, Writing - review & editing. **Gangadhar Andaluri:** Formal analysis, Investigation, Writing - review & editing. **Rominder Suri:** Conceptualization, Investigation, Writing - review & editing, Supervision, Funding acquisition.

## 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.

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