



Effect of sound frequency and initial concentration on the sonochemical degradation of perfluorooctane sulfonate (PFOS)



Lucia Rodriguez-Freire^{a,b}, Rajesh Balachandran^a, Reyes Sierra-Alvarez^b,
Manish Keswani^{a,*}

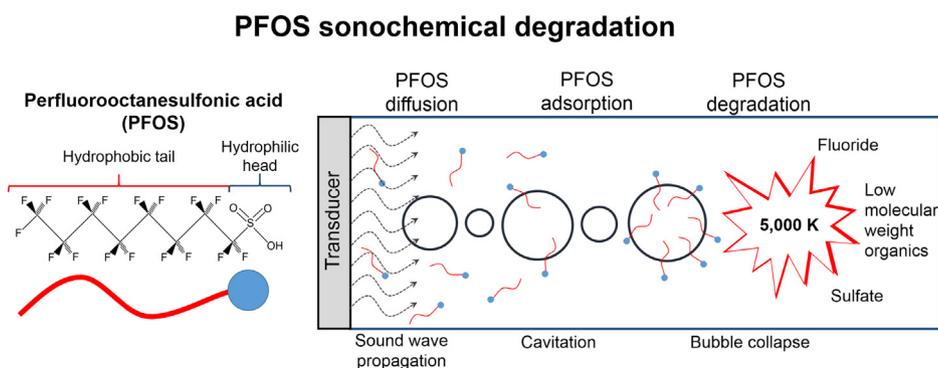
^a Department of Materials Science and Engineering, The University of Arizona, P.O. Box 210012, Tucson, AZ, USA

^b Department of Chemical and Environmental Engineering, The University of Arizona, P.O. Box 210011, Tucson, AZ, USA

HIGHLIGHTS

- Ultra- and mega-sonic frequencies effectively degrade high PFOS concentrations.
- Sonochemical PFOS degradation is controlled by saturation kinetics.
- PFOS degradation rate increases with higher initial concentrations until saturation.
- Higher frequencies enhance PFOS degradation.

GRAPHICAL ABSTRACT



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ABSTRACT

Perfluorooctanesulfonic acid (PFOS) is a perfluorinated compound (PFC) highly resistant to conventional advance oxidation processes, which was widely used in industrial activities due to its surfactant nature, oleophobic–hydrophobic properties, and chemical inertness. Sonochemical treatment has been suggested as an effective approach to treat aqueous solutions containing minimal levels of PFCs. This study investigates PFOS sonochemical degradation and its dependency on the initial concentration (10–460 μM), and the applied sound frequency (25 and 500 kHz, and 1 MHz). PFOS was degraded by sonochemical treatment at concentrations as high as 460 μM , as demonstrated by fluoride release and total organic content data. PFOS degradation rate was higher at megasonic frequencies (1 MHz) compared to ultrasonic frequencies (25–500 kHz). PFOS degradation was controlled by saturation kinetics as indicated by an increase in PFOS degradation rate with increasing PFOS concentration until a maximum, after which the degradation rate was independent of the concentration. The saturation conditions were dependent on the sound frequency, and they were reached at a lower concentration under 1 MHz (100 μM) compared to the 500 kHz frequency (>460 μM). Overall, the results of this study demonstrate that high PFOS concentration can be effectively sonochemically treated using megasonic frequencies.

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1. Introduction

Perfluorinated compounds (PFCs) include a large number of chemicals which are characterized by a fully fluorinated hydrophobic linear carbon chain bound to a hydrophilic head (e.g., carboxyl

* Corresponding author. Fax: +1 520 621 8059.

E-mail addresses: luciar@email.arizona (L. Rodriguez-Freire), hsejar85@gmail.com (R. Balachandran), rsierra@email.arizona.edu (R. Sierra-Alvarez), manishk@email.arizona.edu (M. Keswani).

or sulfonic group). PFCs are emerging contaminants that have been used for the past 60 years in numerous consumer and industrial formulations due to their unique physico-chemical properties which include high chemical and thermal stability, very high Brønsted acidity of the acid group, oleophobic-hydrophobic properties, and low surface activity and surface tension [1]. These properties make PFCs versatile wetting agents, which are used in fabric treatments, paper coatings, anti-static agents, shampoos, cleaning agents, paints, floor waxes, corrosion inhibitors, and fire extinguishing agents known as aqueous film-forming foams (AFFFs) [2,3].

Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) are some of the dominant forms of PFCs reported to be present in sewage treatment plants and other water bodies in varying concentrations based on their geographical location [3–6]. The nature of these compounds is such that they are bioaccumulative, resilient to oxidation, and inert to other chemical and biological pathways to degradation [7]. The chemical inertness of these compounds is attributed to the high strength of the C–F bond ($\sim 413 \text{ kJ mol}^{-1}$ for C–F bond in $\text{F}_3\text{C}-\text{CF}_3$) [8]. The widespread human exposure to PFCs is a concern because an increasing body of literature indicates that certain PFCs exhibit toxic and bioaccumulative properties. PFC accumulation in mammals, birds and fishes was first reported by Giesy and Kannan [9]. PFCs have also been detected in human tissue, including whole blood, plasma and serum [10]. For instance, in communities with drinking water contaminated by PFOA, the median PFOA concentrations in blood serum from this community were approximately 100-fold higher than the median PFOA concentration in the general population [11]. Although PFCs were previously considered to be biologically inactive, these compounds are now suspected to cause developmental and reproductive toxicity, immunotoxicity, hepatotoxicity, and tumor development [10,12]. Therefore, the release of these compounds into the environment without proper treatment has the potential to significantly affect wildlife and human health because of their chronic toxicity.

In the past, various PFOS treatment methodologies, such as thermolysis, direct photolysis, photocatalysis, sonochemical degradation, chemical reduction, thermal oxidation, filtration, sorption, ion exchange, evaporation, liquid-liquid extraction and biodegradation have been studied [13–15]. Due to the recalcitrant nature of PFCs, conventional oxidative processes such as ozone (O_3), O_3 combined with ultraviolet (UV) radiation (O_3/UV), UV and hydrogen peroxide ($\text{UV}/\text{H}_2\text{O}_2$) and Fenton's reagent ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$) have shown little success in breaking down the PFCs molecules [16,17]. PFCs reductive defluorination was investigated by Park et al. [8] in the presence of potassium iodide (KI) and UV light (wavelength, λ , 254 nm). In the presence of UV light, the iodide ion underwent photolysis to form aquated electrons which were further shown to react with PFCs compounds and reduce them. The disadvantage of this method was that the degradation rate was very low. Other researchers have studied the effect of electrochemical oxidation of PFOA on boron-doped diamond film electrodes [18]. Although reasonable degradation of PFCs could be obtained by this method, the technology is limited by factors, such as cost of operation and scalability [19]. Recent studies have suggested the use of sonolysis as an effective means to degrade PFCs.

“Sonochemical” refers to the breakdown of a molecule by means of acoustic energy. When an acoustic wave propagates through a medium such as water, two resulting effects are generally observed: (1) acoustic streaming, and (2) acoustic cavitation. Cavitation has been shown to be the primary precursor behind breakdown of organics either by oxidation or pyrolysis [20]. Pyrolysis is facilitated by high temperatures (near 4000 K) and pressure resulting from the oscillation of bubbles for several cycles (stable bubble) and eventual collapse (transient bubbles) [21,22]. A

secondary degradation mechanism could involve oxidation of the molecules with hydroxyl radicals ($\cdot\text{OH}$), which are formed due to the breakdown of water molecules under the high temperatures produced during stable bubble oscillations or transient bubble collapse. The sonochemical degradation of organic molecules occurs through the diffusion followed by adsorption of the molecule at the bubble interface and the subsequent pyrolysis under high temperatures releasing fluoride and sulfate as products [22]. Moriwaki et al. [23] investigated the sonochemical degradation of PFCs ($20 \mu\text{M}$) under an acoustic frequency of 200 kHz. The degradation rate constants determined for PFOS and PFOA during 60 min of sonolysis were 0.016 and 0.032 min^{-1} , respectively.

Published studies focusing on the sonochemical degradation of PFOS have generally utilized very low concentrations, typically in the ng L^{-1} to $\mu\text{g L}^{-1}$ range, which are representative of those found in contaminated groundwater or surface water [1]. However, investigation of the acoustic degradation of PFOS at higher concentrations is also needed to assess the potential of this technique to treat concentrated streams, such as aqueous film-forming foams (AFFF). These firefighting foams contain PFCs at very high concentrations ranging from 1 to 5% ($10\text{--}50 \text{ g L}^{-1}$ PFC) [24]. The use of AFFF in military bases, during fire-training exercises, has reportedly caused contamination of groundwater sources with PFC concentrations ranging from 125 to $7090 \mu\text{g L}^{-1}$ [25]. As of 2004, 11 million liters of AFFF are in storage in military facilities awaiting for treatment [24]. Therefore, the motivation of the current work has been primarily to investigate the effect of acoustic cavitation on the degradation of high PFOS concentrations, ranging from 10 to $460 \mu\text{M}$ ($5.4\text{--}250 \text{ mg L}^{-1}$), under ultrasonic and megasonic frequencies (25 kHz to 1 MHz).

2. Materials and methods

2.1. Chemicals and sonochemical equipment

Deionized (DI) water ($18 \text{ M}\Omega\text{-cm}$) was used to prepare all experimental solutions. Potassium perfluorooctane sulfonate (PFOS-K, 95%+) and sodium fluoride (99%) were purchased from Alfa-Aesar (Ward Hill, MA, USA). Terephthalic acid and 2-hydroxyterephthalic acid were procured from Sigma-Aldrich (St. Louis, MO, USA). Total ionic strength adjusting buffer (TISAB II) was purchased from Fisher Scientific Inc. (Waltham, MA USA). Hydrogen peroxide (30%) was purchased from Honeywell Inc. (Tucson, AZ, USA).

Two different reactors were used for conducting the sonolysis studies. For frequencies lower than or equal to 500 kHz , a multi-frequency, cubical reactor (12 L), custom made by Weber Ultrasonics Inc. (Village of Clarkston, MI, USA) (Fig. 1A), was used. In this reactor the transducers were attached to the side walls, such that the 25 kHz and 250 kHz transducers faced each other, while the other two sides consisted of $40/80/120 \text{ kHz}$ and 500 kHz transducers. For experiments conducted at 1 MHz , a Mini-meg[®] reactor (Fig. 1B) of 4.5 L purchased from PCT Systems Inc. (Fremont, CA, USA) was used. The transducer was affixed to a plate at the bottom of the tank. The power density was fixed at ca. 8 W cm^{-2} for all the transducers.

2.2. Experiment set-up

A glass reaction vessel containing 200 mL of test solution was placed at about 1 cm from the transducer surface, and was submerged in DI water recirculating bath, to maintain the temperature of the experimental solution at 30°C . A rectangular glass vessel was used for the 25 and 500 kHz experiments, while a round beaker was used for 1 MHz experiments. Different PFOS concentrations

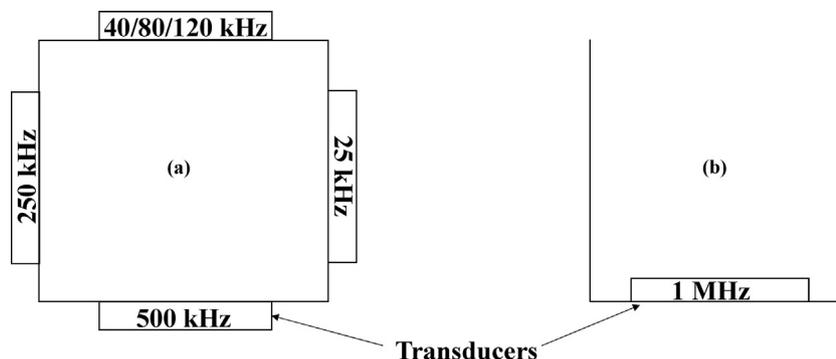


Fig. 1. Schematics of the sonochemical reactors utilized in this study: weber tank (A); and megasonic tank (B).

were used (10, 100 and 460 μM) for the degradation studies. All experiments were conducted using argon saturated solutions.

The effectiveness of the sonolysis treatment was determined by measuring the concentration of fluoride (F^-) and sulfate (SO_4^{2-}) released during the PFOS degradation. The change in the concentration of total organic carbon (TOC) was also monitored in some experiments.

2.3. Analytical techniques

The F^- concentration was determined using a fluoride selective electrode (ISE) purchased from Thermo Scientific Inc. (9609BNWP). The ISE was calibrated using standards prepared with varying concentrations of sodium fluoride (10^{-6} – 10^{-1} M). A total ion strength adjustment buffer (TISAB II) solution (5 mL) was added to the samples (5 mL) to ensure high ionic strength for potentiometric measurements. Sulfate concentration was measured using suppressed conductivity ion chromatography with a Dionex IC-3000 system (Sunnyvale, CA, USA) fitted with a Dionex IonPac AS18 analytical column (4×250 mm) and AG18 guard column (4×50 mm). The injection eluent (KOH) was 17 mM for 6 min. TOC analysis were performed using a Shimadzu total carbon analyzer V_{CSH} (Columbia, MD, USA). The samples were prepared using DI water and the pH adjusted to 2, using hydrochloric acid (HCl). The inorganic carbon was removed by sparging the samples with air. The remaining carbon was then combusted at 680 $^{\circ}\text{C}$ and analyzed. Additionally, the pH of the solutions was measured at the beginning and end of each experiment.

The $\bullet\text{OH}$, generated primarily due to decomposition of water during sonication, were measured in aqueous solutions containing 2 mM of terephthalic acid with pH adjusted to 8 using sodium hydroxide (NaOH). The alkaline pH of the solutions was necessary to achieve complete dissolution of terephthalic acid. Samples were collected in regular time intervals and analyzed for $\bullet\text{OH}$ using fluorescence spectroscopy. The technique is based on capture of $\bullet\text{OH}$ by terephthalic acid to form 2-hydroxyterephthalic acid [26,27]. When excited under a wavelength of 318 nm, 2-hydroxyterephthalic acid undergoes emission at 425 nm. The intensity of the peak at the emission wavelength was used to determine the concentration of $\bullet\text{OH}$ using a calibration curve prepared from fluorometric measurements of solutions containing known concentrations (0.39–125 μM) of 2-hydroxyterephthalic acid.

2.4. Calculation of PFOS concentration as a function of the sonication time

The change in PFOS as a function of the sonication time was estimated using the following equation:

$$[\text{PFOS}]_t = [\text{PFOS}]_0 - \frac{[\text{F}^-]_t}{17 \text{ mmol F}^- / \text{mmol PFOS}} \quad (1)$$

where

- $[\text{PFOS}]_t$ is the PFOS concentration (mM) at time t
- $[\text{PFOS}]_0$ is the initial PFOS concentration (mM)
- $[\text{F}^-]_t$ is the measured F^- concentration (mM) at time t

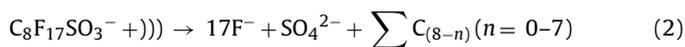
3. Results and discussion

The high toxicity and inherent persistence of PFOS and other FCs in the environment have motivated the search for an effective technology to degrade these emerging contaminants in solutions containing high PFOS concentrations. This study evaluates the sonochemical degradation of PFOS using different sound frequencies and its dependency on the PFOS concentration. The main findings are presented and discussed in the following sections.

3.1. Study of the complete sonochemical degradation of 100 μM PFOS under a 1 MHz sound frequency

The degradation of 100 μM PFOS was investigated under a 1 MHz frequency during 330 min of sonication time by measuring the increase of F^- and SO_4^{2-} concentrations in solution, as well as the removal of TOC. The evolution in the F^- , SO_4^{2-} , and TOC concentrations with sonication time are presented in Fig. 2. The F^- concentration increased with time at a rate of $7.4 \pm 1.2 \times 10^{-3} \text{ mM F}^- \text{ min}^{-1}$, and 2 mM F^- was released into solution in less than 300 min of sonication, which corresponded to 100% defluorination (Fig. 2A). Fig. 2B reveals that SO_4^{2-} was released as a product of PFOS degradation. The SO_4^{2-} concentration in the solution increased with time at a rate of $2.49 \pm 0.49 \times 10^{-4} \text{ mM SO}_4^{2-} \text{ min}^{-1}$, until reaching a steady state value of $0.069 \pm 0.009 \text{ mM}$, which corresponds to 68.6% of total theoretical sulfur content in the added PFOS. Finally, PFOS mineralization was quantified by measuring the amount of TOC as a function of the sonication time (Fig. 2C). The initial TOC concentration ($0.98 \pm 0.18 \text{ mM}$) decreased with increasing sonication time, leading to a TOC removal of 55.8% after 330 min of sonolysis.

Sonochemical degradation is known to occur at the solution–bubble interface, where the adsorbed molecules are degraded by the high temperatures produced by the bubble violent collapses (pyrolysis) or by OH^{\bullet} attack (chemical). PFOS degradation can be described with the reaction shown in Eq. (2):



where $\sum \text{C}_{(8-n)} (n = 0-7)$ represents the formation of lower molecular weight organic compounds.

If PFOS would be completely mineralized, the expected ratio between the change in F^- and SO_4^{2-} concentration

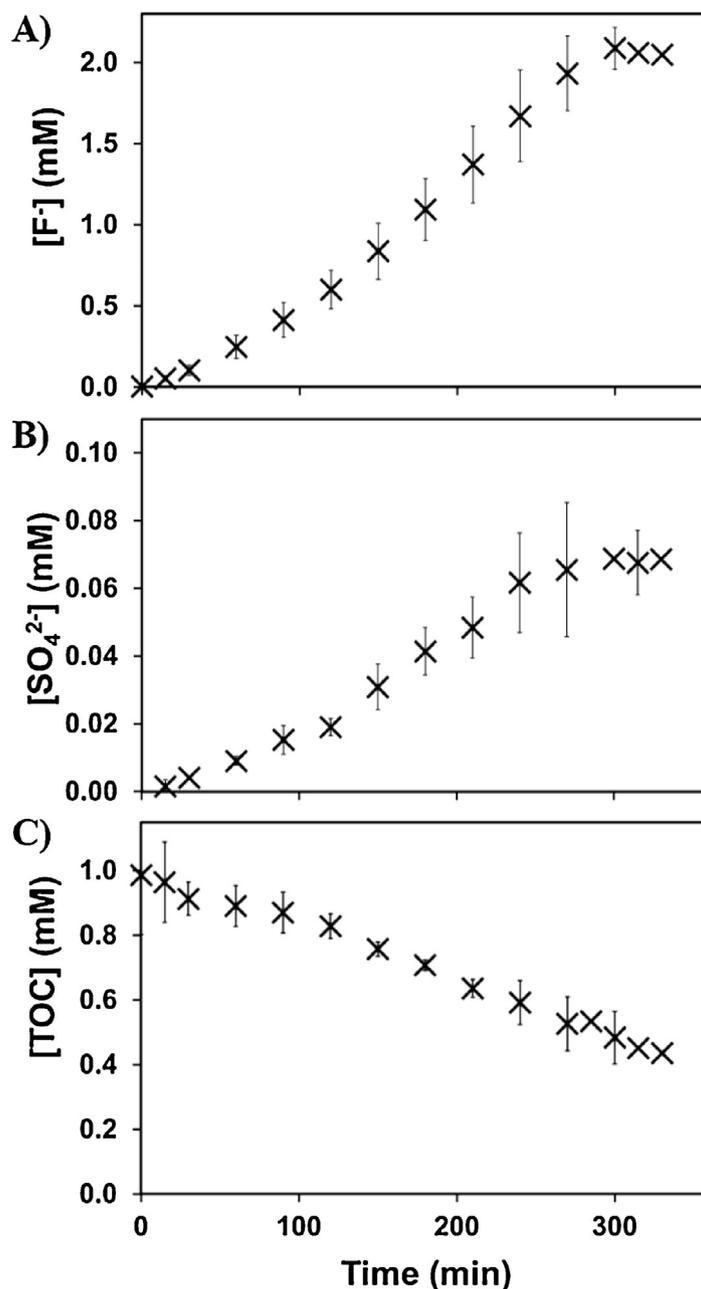


Fig. 2. Sonochemical degradation of PFOS (100 μM) under a 1 MHz sound frequency for an extended time (330 min) to achieve complete degradation. (A) F^- concentration released; (B) SO_4^{2-} concentration released; and, (C) TOC degradation.

$(\Delta[\text{F}^-]/\Delta[\text{SO}_4^{2-}])$ would be 17; however, the experimental $(\Delta[\text{F}^-]/\Delta[\text{SO}_4^{2-}])$ ratio was 31.0. The fact that the measured $(\Delta[\text{F}^-]/\Delta[\text{SO}_4^{2-}]) \gg 17$ suggests that the defluorination might have occurred at higher rates than the cleavage of the sulfonic head. This could be explained by the formation of shorter chain length fluorinated sulfonates. Moriwaki et al. [23] detected the formation of perfluoroheptane sulfonate and perfluorohexane sulfonate following the sonochemical degradation of PFOS under a 200 kHz sound frequency.

Similarly, the experimental $\Delta[\text{F}^-]/\Delta[\text{TOC}]$ ratio was 4.9, which is higher than the theoretical ratio expected for a unimolecular degradation of 2.1. Interestingly, the ratio between SO_4^{2-} and TOC was 7.7, which is very close to the theoretical ratio of 8. The low levels of SO_4^{2-} production and TOC removal can be also

attributed to the formation of low molecular weight compounds [23], which are not completely degraded under the conditions of this experiment. These results are in contrast with the mechanisms proposed by Vecitis et al. [22], who hypothesized that the first step for PFOS degradation is the quick cleavage of the sulfonic group without any release of F^- , followed by the pyrolytic degradation of the rest of the molecule. This mechanism was supported by results obtained during sonochemical degradation studies with PFOS using a frequency of 505 kHz [15]. While their experimental ratio $(\Delta[\text{TOC}]/\Delta[\text{SO}_4^{2-}])_{\text{Vecitis}}$ was 6.9, which is only 13% different from our reported value (7.7), the ratio $(\Delta[\text{F}^-]/\Delta[\text{SO}_4^{2-}])_{\text{Vecitis}}$ of 4.1 is much lower than the theoretical value. The different degradation mechanism could be explained by the two different experimental set-up, including sound frequencies and initial PFOS

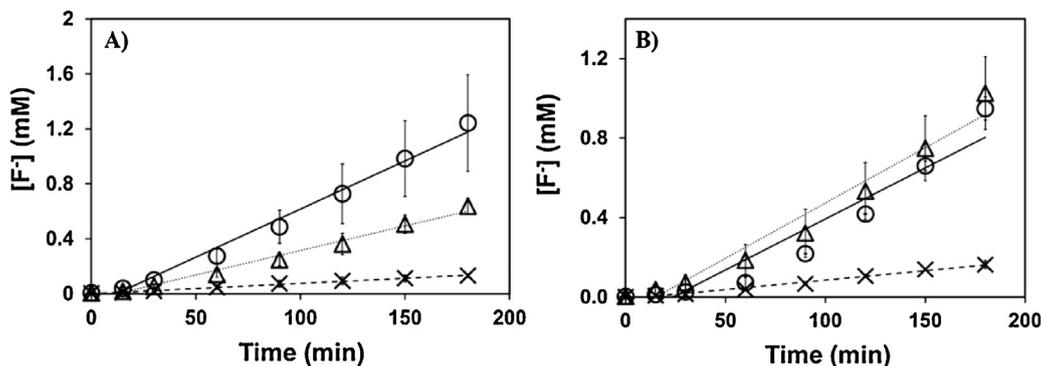


Fig. 3. Effect of the sound frequency and initial PFOS concentration on the sonochemical degradation of the perfluorinated compound. F⁻ concentration released as a function of sonication time under a sound frequency of 500 kHz (A); and 1 MHz (B) as a function of time: 10 μM (×), 100 μM (Δ) and 460 μM (○) Lines represent the linear fit of the data series as $[F^-]_t = [F^-]_0 + kt$ in the experiments conducted at 500 kHz (A): 10 μM (dashed line), $k = 7.39 \times 10^{-4} \text{ mM min}^{-1}$, $R^2 = 0.995$; 100 μM (dotted line), $k = 3.58 \times 10^{-3} \text{ mM min}^{-1}$, $R^2 = 0.983$; and, 460 μM (black line), $k = 7.01 \times 10^{-3} \text{ mM min}^{-1}$, $R^2 = 0.986$; and at 1 MHz (B): 10 μM (dashed line), $k = 9.47 \times 10^{-1} \text{ mM min}^{-1}$, $R^2 = 0.988$; 100 μM (dotted line), $k = 6.00 \times 10^{-3} \text{ mM min}^{-1}$, $R^2 = 0.968$; and, 460 μM (black line), $k = 5.13 \times 10^{-3} \text{ mM min}^{-1}$, $R^2 = 0.915$.

concentration. The effect of frequency and initial PFOS concentration on the sonochemical degradation will be addressed on the next sections.

3.2. Impact of sound frequency on the sonochemical degradation of PFOS

The sound frequency played an important role in the extent and rate of PFOS degradation. PFOS degradation rate increased with increasing frequency for the lowest initial concentrations. PFOS was degraded at a very slow rate when a low frequency (25 kHz) was applied. When PFOS (10 μM) was treated under a frequency of 25 kHz, the amount of F⁻ released after 180 min of sonication was only 6.8% of the total initial F⁻ ($0.011 \pm 0.009 \text{ mM}$, results not shown). Fig. 3 shows the F⁻ released as a function of the sonication time for the three different PFOS concentration under 500 kHz (Fig. 3A) and under 1 MHz (Fig. 3B) sound frequencies. For an initial PFOS concentration of 10 μM, the F⁻ concentrations at any given time were 11.4 times ($0.131 \pm 0.013 \text{ mM}$) and 14.2 times ($0.163 \pm 0.020 \text{ mM}$) greater at a frequency of 500 kHz and 1 MHz, respectively, compared to that at 25 kHz. Similarly, when the initial PFOS concentration was increased to 100 μM PFOS, the F⁻ released at the end of the experiment performed under a 500 kHz was $0.64 \pm 0.06 \text{ mM}$, which is 1.6-fold lower than if the frequency was 1 MHz ($1.03 \pm 0.18 \text{ mM F}^-$). However, when further higher initial PFOS concentration (460 μM) was tested, the degradation rates attained at 500 kHz and 1 MHz were relatively similar.

The effect of the sound frequency on the degradation kinetics of PFCs and other organic compounds has been reported in the literature. In general, for a given concentration, the rate of degradation increases with increasing frequency. However, several studies have observed an optimal frequency at which the degradation rate reaches a maximum. Colussi et al. [28] observed that the sonochemical degradation of volatile chlorinated alkanes and alkenes increased as the frequency increased until reaching a maximum rate at 618 kHz, after which it decreased when the sound frequency was increased to 1078 kHz (degradation rate trend: 205 kHz < 358 kHz < 618 kHz > 1078 kHz). Lim et al. [29] studied the degradation of chlorinated compounds (chlorobenzene, chloroform, and carbon tetrachloride) in the frequency range of 35 to 1000 kHz and observed a maximum degradation rate at 300 kHz. Campbell et al. [30] observed the same phenomenon when studying the degradation of PFCs at frequencies ranging from 202 to 1060 kHz and determined that the optimum frequency for the degradation of perfluorohexane sulfonic acid (0.23 μM) and perfluorobutane sulfonic acid (0.30 μM) were 358 kHz and 610 kHz,

respectively. However, the optimum frequency determined in this study for the degradation of PFOS at concentrations ranging from 10–100 μM PFOS was 1 MHz, the maximum frequency investigated. When the initial PFOS concentration increased to 460 μM, the degradation rates were very similar for both 500 kHz and 1 MHz. This may be explained by the higher number density of cavitating bubbles (but with lower oscillation frequency) produced in solutions irradiated with 500 kHz compared to 1 MHz. This causes the saturation limit to be reached faster at 1 MHz but below this limit the degradation rates are higher due to more frequent (two times higher) generation of high temperature conditions that cause degradation.

The PFOS degradation rate depends on the available interfacial sites for the adsorption of the molecules, frequency of oscillation of bubbles, and intensity of bubble collapse. The sound frequency will affect the number and size of the interfaces [31]. As the frequency increases, the speed of bubble oscillation increases, which will result in greater occurrences of “hot spots” and, therefore, higher degradation rates. The intensity of bubble collapse determines the temperature conditions inside the bubble and the extent and rate of degradation. For acoustic frequencies of 202 and 1060 kHz, the interfacial surface area has been estimated at $3.97 \times 10^{-3} \mu\text{m}^2$ (resonant radius of 17.8 μm) and $1.43 \times 10^{-2} \mu\text{m}^2$ (resonant radius of 3.4 μm), respectively [30,31].

The increase in cavitation events and intensity was quantified by measuring the concentration of hydroxyl radicals ($\bullet\text{OH}$) formed at the three different frequencies (25 kHz, 500 kHz, and 1 MHz). The formation of $\bullet\text{OH}$ is directly dependent on the number of cavitation events [26]. As expected from the PFOS degradation experiments, the $\bullet\text{OH}$ concentration increased with increasing sound frequency (Fig. 4). The $\bullet\text{OH}$ formation rate was 15.2-fold and 4.1-fold higher at a frequency of 1 MHz compared to frequencies 25 and 500 kHz, respectively. Therefore, the rate of $\bullet\text{OH}$ production was a function of the sound frequency, increasing exponentially with the frequency, as per the following equation:

$$\frac{d[\text{OH}^\bullet]}{dt} = 0.044 \times e^{(2.73 \times 10^{-3}) \times f} \quad (3)$$

where

- is the OH[•] formation rate in μM OH[•] min⁻¹
- *f* is the sound frequency in kHz

The mathematical relationship between the $\bullet\text{OH}$ formation rate and the sound frequency has not been previously reported. Mark et al. [32] reported an increase in $\bullet\text{OH}$ generation with frequency until reaching a maximum value, after which an increment in

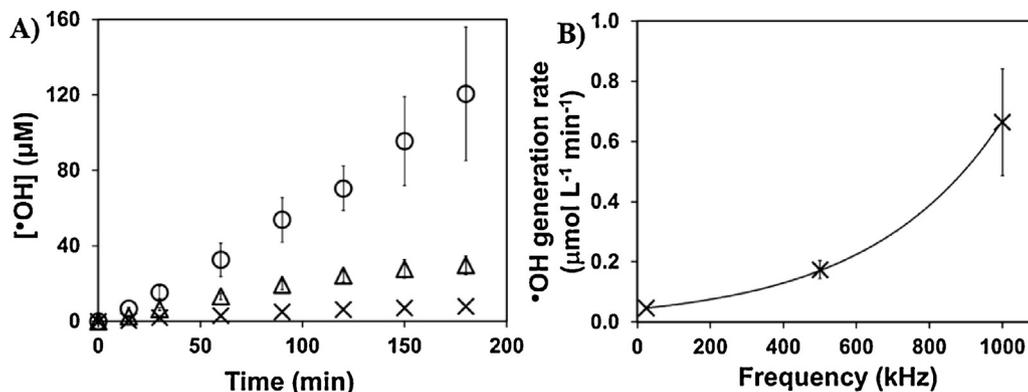


Fig. 4. Formation of hydroxyl radicals ($\cdot\text{OH}$) as a direct indicator of cavitation. (A) $\cdot\text{OH}$ concentration as a function of the sonication time for different frequencies: 25 kHz (\times), 500 kHz (Δ), and 1 MHz (\circ). (B) $\cdot\text{OH}$ generation rate determined at the three frequencies evaluated in this study. The dotted line is the exponential fit to the data series, as $d[\cdot\text{OH}]/dt = A \times e^{b \times f}$, $R^2 = 0.999$.

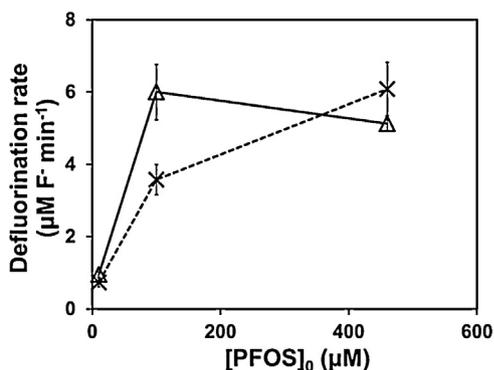


Fig. 5. Dependency of the PFOS defluorination rate on the initial PFOS concentration during sonochemical treatment at 500 kHz (\times) and 1 MHz (Δ).

frequency will decrease the $\cdot\text{OH}$ formation rate. Evidently, the maximum was not reached in the frequency range evaluated in this study. It may be noted that Eq. (3) is valid for the ultra and megasonic set ups used in the current study, and it may not necessarily apply when estimating hydroxyl radical generation rates for other sonication systems.

3.3. Effect of concentration on PFOS defluorination rate

The role of the PFOS concentration on the extent and rate of its sonochemical degradation was studied by measuring the concentration of F^- released by sonolysis of solutions containing 10–460 μM PFOS at two different sound frequencies, 500 kHz and 1 MHz. Fig. 5 shows the defluorination rate as a function of the initial PFOS concentration for the two studied frequencies. At 500 kHz, the rate of defluorination increased with increasing initial PFOS concentration. The defluorination rate averaged $7.4 \pm 1.2 \times 10^{-4} \text{ mM min}^{-1}$, $3.6 \pm 0.4 \times 10^{-3} \text{ mM min}^{-1}$, and $6.1 \pm 0.7 \times 10^{-3} \text{ mM min}^{-1}$ when the initial PFOS concentrations were 10, 100 and 460 μM , respectively. In contrast, when a sound frequency of 1 MHz was applied, the rate of defluorination increased with increasing initial PFOS concentration up to 100 μM and a further increment in PFOS concentration did not increase the extent of PFOS defluorination. The defluorination rate was $9.5 \pm 0.8 \times 10^{-4} \text{ mM min}^{-1}$ for the lowest initial PFOS concentration (10 μM), which is 6.3-fold less compared to the F^- released in experiments using initial PFOS concentrations of 100 and 460 μM ($6.0 \pm 0.7 \times 10^{-3} \text{ mM min}^{-1}$ and $5.1 \pm 0.2 \times 10^{-3} \text{ mM min}^{-1}$, respectively). These results suggest that over the range of concentrations studied, the reaction

followed a *pseudo-first* order kinetics when the applied frequency was 500 kHz. When the sound frequency was 1 MHz, the rate of PFOS defluorination also increased with concentration up to 100 μM , but at higher concentrations the reaction followed zero order kinetics with the rate becoming independent of the initial PFOS concentration.

In agreement with our results, Vecitis et al. [22] observed a change in the reaction order, from pseudo-first order ($[\text{PFOS}]_0 < 20 \mu\text{M}$) to zero-order reaction ($[\text{PFOS}]_0 > 40 \mu\text{M}$) as the initial PFOS concentration increased in experiments performed under a 358 kHz frequency, for PFOS concentrations ranging from 0.02 to 202 μM . The increasing defluorination rates observed at greater PFOS concentrations can be explained by higher availability of adsorbed PFOS molecules at the bubble-liquid interface and an increase in electrostatic repulsion between the bubbles due to the higher accumulation of PFOS molecules at the interface preventing the bubbles from coalescing, which will enhance the number density of cavitating bubbles [33]. However, the defluorination at high initial PFOS concentration is controlled by saturation kinetics following a Langmuir-type mechanism because degradation occurs at the bubble-liquid interface and depends on the availability of interfacial sites at any sonication time [22,23,28]. The rate of PFOS defluorination can be described as follows:

$$\frac{d[\text{F}^-]}{dt} = r_{\text{max}} \cdot \theta \quad (4)$$

where

– θ is the fraction of occupied interfacial sites (dimensionless). θ is a function of the initial PFOS concentration and the sonochemical surface activity, K_s , and it is calculated as shown in Eq. (5):

$$\theta = \frac{K_s \cdot [\text{PFOS}]}{1 + K_s \cdot [\text{PFOS}]} \quad (5)$$

Substituting Eq. (5) in (4) leads to the expression below, [Eq. (6)]. This model describes the change in reaction order as a function of the PFOS concentration, and independent of the sonication frequency.

$$\frac{d[\text{F}^-]}{dt} = r_{\text{max}} \cdot \frac{K_s \cdot [\text{PFOS}]}{1 + K_s \cdot [\text{PFOS}]} \quad (6)$$

At low PFOS concentrations the product $K_s \cdot [\text{PFOS}] \ll 1$, therefore,

$$\theta = K_s \cdot [\text{PFOS}] \quad (7)$$

Table 1
Summary of the kinetics parameters calculated in this study and by Vecitis et al. [35] for the sonochemical degradation of PFOS.

Frequency (kHz)	r_{\max} ($\mu\text{M F}^{-1} \text{ min}^{-1}$)	$r_{\max, \text{PFOS}}$ (nM PFOS min^{-1})	K_s (M^{-1})	[PFOS] _{bubble} (mM)	Reference
385	–	230	121,000	–	[35]
500	6.7 ^a	370.3 ^a	12,234.4 ^a	8.1 ^b	This study
1000	5.6 ^c	327.2 ^c	–	8.1 ^b	This study

^a r_{\max} and K_s at 500 kHz were obtained from the linear fitting of $dt/d[\text{F}^{-}]$ vs. $1/[\text{PFOS}]$ (Fig. S1) or $dt/d[\text{PFOS}]$ vs. $1/[\text{PFOS}]$, and using Eq. (10).

^b [PFOS]_{bubble} at 500 kHz was calculated using Eq. (7) and K_s .

^c r_{\max} at 1 MHz was directly obtained from the experimental data, using the PFOS defluorination or degradation rate for 100–460 μM .

and, consequently:

$$\frac{d[\text{F}^{-}]}{dt} = r_{\max} \cdot K_s \cdot [\text{PFOS}] \quad (8)$$

Thus, the reaction becomes pseudo-first order as the rate is only dependent on the PFOS concentration since r_{\max} and K_s are constant for fixed sound field and solution temperature conditions.

At high PFOS concentrations, the degradation rate will be independent of the PFOS concentration, as observed in the 1 MHz experiments and predicted by the model, since $K_s \cdot [\text{PFOS}] \gg 1$, $\theta = 1$, and:

$$\frac{d[\text{F}^{-}]}{dt} = r_{\max} \quad (9)$$

The saturation concentration at the bubble surface, [PFOS]_{bubble}, can be defined as the lowest PFOS concentration that will provide the maximum defluorination rate, or, the concentration at which θ becomes ≈ 1 .

$$[\text{PFOS}]_{\text{bubble}} = \frac{\theta}{(1-\theta) \cdot K_s} = \frac{0.99}{0.01 \cdot K_s} \quad (10)$$

The kinetics parameters, r_{\max} and K_s , sonochemical partitioning coefficient for the degradation of PFOS under a given frequency, can be calculated by inverting Eq. (6) [34]:

$$\frac{dt}{d[\text{F}^{-}]} = \frac{1}{r_{\max}} + \frac{1}{r_{\max} \cdot K_s} \frac{1}{[\text{PFOS}]} \quad (11)$$

The experiments performed at 500 kHz were under-saturated at the highest concentration investigated in this study (460 μM), and when $dt/d[\text{F}^{-}]$ vs. $1/[\text{PFOS}]$ was plotted in Fig. S1 in the Supplementary information (SI), the experimental data fit to a linear model ($R^2 = 0.9998$).

At 500 kHz, the maximum defluorination, r_{\max} , will occur at 6.7 $\mu\text{M F}^{-1} \text{ min}^{-1}$. Using Eq. (1), PFOS degradation rate was calculated and a similar kinetic analysis was performed. The maximum PFOS degradation rate, $r_{\max, \text{PFOS}}$, under 500 kHz was 370.3 nM PFOS min^{-1} , which is comparable to the value obtained by Vecitis et al. [35]. The K_s value determined at 500 kHz (12,234.4 M^{-1}) is an order of magnitude lower compared to the value by Vecitis et al. [35] at 385 kHz (120,000 M^{-1}). This difference could be due to the limitations of the model that assumes a uniform adsorption of the molecules on the interfacial sites, no interaction between the molecules, and lack of adsorption of the degradation products on the adsorption sites [36]. The [PFOS]_{bubble}, under 500 kHz frequency, 8.1 mM, was calculated using Eq. (10) and the experimental K_s .

Linearization of the data obtained at 1 MHz using Eq. (11) was not possible since saturation conditions were reached; therefore, the maximum defluorination rate (5.6 \pm 0.6 $\mu\text{M F}^{-1} \text{ min}^{-1}$ or 327.2 \pm 25.5 nM PFOS min^{-1}) was determined for the two highest concentrations tested. This r_{\max} is of the same order of magnitude as the values calculated in this study at 500 kHz and reported by Vecitis et al. [35] at 358 kHz.

Table 1 summarizes the kinetics parameters obtained in this study for the sonochemical degradation of PFOS at initial concentrations ranging 10–460 μM under 500 kHz and 1 MHz. These results

are compared with the parameters obtained by Vecitis et al. [35] in sonochemical experiments with PFOS (20–160 nM) under 358 kHz sound field.

4. Conclusions

- This research has demonstrated that high PFOS concentrations are effectively treated using ultra- and mega-sonic field.
- There was a positive correlation between PFOS degradation and PFOS initial concentration (10–460 μM) when the sound frequency was 500 kHz, with faster degradation rates at higher concentrations.
- PFOS degradation rate was controlled by saturation kinetics under a 1 MHz sound field, since an increase in concentration did not improve PFOS degradation after reaching a maximum concentration (100 μM).
- The megasonic frequency (1 MHz) offered superior PFOS degradation for under saturated conditions when compared to the ultrasonic frequencies (25–500 kHz).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2015.07.077>

References

- [1] M.M. Schultz, D.F. Barofsky, J.A. Field, Fluorinated alkyl surfactants, *Environ. Eng. Sci.* 20 (2003) 487–501.
- [2] A.B. Lindstrom, M.J. Strynar, E.L. Libelo, Polyfluorinated compounds: past, present, and future, *Environ. Sci. Technol.* 45 (2011) 7954–7961.
- [3] J. Yu, J.Y. Hu, S. Tanaka, S. Fujii, Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) in sewage treatment plants, *Water Res.* 43 (2009) 2399–2408.
- [4] C. Eschauzier, E. Beerendonk, P. Scholte-Veenendaal, P. De Voegt, Impact of treatment processes on the removal of perfluoroalkyl acids from the drinking water production Chain, *Environ. Sci. Technol.* 46 (2012) 1708–1715.
- [5] K.J. Hansen, H.O. Johnson, J.S. Eldridge, J.L. Butenhoff, L.A. Dick, Quantitative characterization of trace levels of PFOS and PFOA in the Tennessee River, *Environ. Sci. Technol.* 36 (2002) 1681–1685.
- [6] P.C. Rumsby, C.L. McLaughlin, T. Hall, Perfluorooctane sulphonate and perfluorooctanoic acid in drinking and environmental waters, *Philos. Trans. R. Soc. A – Math. Phys. Eng. Sci.* 367 (2009) 4119–4136.
- [7] D. Chen, S.K. Sharma, A. Mudhoo, *Handbook on Applications of Ultrasound: Sonochemistry for Sustainability*, CRC, Press, Taylor and Francis Group, Boca Raton, Florida, USA, 2011.
- [8] H. Park, C.D. Vecitis, J. Cheng, W. Choi, B.T. Mader, M.R. Hoffmann, Reductive defluorination of aqueous perfluorinated alkyl surfactants: effects of ionic headgroup and chain length, *J. Phys. Chem. A* 113 (2009) 690–696.
- [9] J.P. Giesy, K. Kannan, Global distribution of perfluorooctane sulfonate in wildlife, *Environ. Sci. Technol.* 35 (2001) 1339–1342.
- [10] C. Lau, K. Anitole, C. Hodes, D. Lai, A. Pfahles-Hutchens, J. Seed, Perfluoroalkyl acids: a review of monitoring and toxicological findings, *Toxicol. Sci.* 99 (2007) 366–394.
- [11] E.A. Emmett, H. Zhang, F.S. Shofer, D. Freeman, N.V. Rodway, C. Desai, L.M. Shaw, Community exposure to perfluorooctanoate: relationships between

- serum levels and certain health parameters, *J. Occup. Environ. Med.* 48 (2006) 771–779.
- [12] G.L. Kennedy, J.L. Butenhoff, G.W. Olsen, J.C. O'Connor, A.M. Seacat, R.G. Perkins, L.B. Biegel, S.R. Murphy, D.G. Farrar, The toxicology of perfluorooctanoate, *Crit. Rev. Toxicol.* 34 (2004) 351–384.
- [13] S. Fujii, C. Polprasert, S. Tanaka, N.P.H. Lien, Y. Qiu, New POPs in the water environment: distribution, bioaccumulation and treatment of perfluorinated compounds—a review paper, *J. Water Supply Res. Technol.* 56 (2007) 313–326.
- [14] S. Rayne, K. Forest, Perfluoroalkyl sulfonic and carboxylic acids: a critical review of physicochemical properties, levels and patterns in waters and wastewaters, and treatment methods, *J. Environ. Sci. Heal. A* 44 (2009) 1145–1199.
- [15] C.D. Vecitis, Y.J. Wang, J. Cheng, H. Park, B.T. Mader, M.R. Hoffmann, Sonochemical degradation of perfluorooctanesulfonate in aqueous film-forming foams, *Environ. Sci. Technol.* 44 (2010) 432–438.
- [16] H.F. Schroder, R.J.W. Meesters, Stability of fluorinated surfactants in advanced oxidation processes—a follow up of degradation products using flow injection-mass spectrometry, liquid chromatography–mass spectrometry and liquid chromatography–multiple stage mass spectrometry, *J. Chromatogr. A* 1082 (2005) 110–119.
- [17] C.D. Vecitis, H. Park, J. Cheng, B.T. Mader, M.R. Hoffmann, Treatment technologies for aqueous perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA), *Front. Environ. Sci. Eng. China* 3 (2009) 129–151.
- [18] Q. Zhuo, S. Deng, B. Yang, J. Huang, B. Wang, T. Zhang, G. Yu, Degradation of perfluorinated compounds on a boron-doped diamond electrode, *Electrochim. Acta* 77 (2012) 17–22.
- [19] A. Anglada, A. Urriaga, I. Ortiz, Contributions of electrochemical oxidation to waste–water treatment: fundamentals and review of applications, *J. Chem. Technol. Biotechnol.* 84 (2009) 1747–1755.
- [20] P.R. Gogate, A.B. Pandit, A review of imperative technologies for wastewater treatment I: oxidation technologies at ambient conditions, *Adv. Environ. Res.* 8 (2004) 501–551.
- [21] M. Keswani, S. Raghavan, P. Deymier, Characterization of transient cavitation in gas sparged solutions exposed to megasonic field using cyclic voltammetry, *Microelectron. Eng.* 102 (2013) 91–97.
- [22] C.D. Vecitis, H. Park, J. Cheng, B.T. Mader, M.R. Hoffmann, Kinetics and mechanism of the sonolytic conversion of the aqueous perfluorinated surfactants, perfluorooctanoate (PFOA), and perfluorooctane sulfonate (PFOS) into inorganic products, *J. Phys. Chem. A* 112 (2008) 4261–4270.
- [23] H. Moriwaki, Y. Takagi, M. Tanaka, K. Tsuruho, K. Okitsu, Y. Maeda, Sonochemical decomposition of perfluorooctane sulfonate and perfluorooctanoic acid, *Environ. Sci. Technol.* 39 (2005) 3388–3392.
- [24] B.J. Place, J.A. Field, Identification of novel fluorochemicals in aqueous film-forming foams used by the US military, *Environ. Sci. Technol.* 46 (2012) 7120–7127.
- [25] C.A. Moody, J.A. Field, Perfluorinated surfactants and the environmental implications of their use in fire-fighting foams, *Environ. Sci. Technol.* 34 (2000) 3864–3870.
- [26] M. Keswani, S. Raghavan, R. Govindarajan, I. Brown, Measurement of hydroxyl radicals in wafer cleaning solutions irradiated with megasonic waves, *Microelectron. Eng.* 118 (2014) 61–65.
- [27] G.J. Price, F.A. Duck, M. Digby, W. Holland, T. Berryman, Measurement of radical production as a result of cavitation in medical ultrasound fields, *Ultrason. Sonochem.* 4 (1997) 165–171.
- [28] A.J. Colussi, H.M. Hung, M.R. Hoffmann, Sonochemical degradation rates of volatile solutes, *J. Phys. Chem. A* 103 (1999) 2696–2699.
- [29] M. Lim, Y. Son, J. Khim, Frequency effects on the sonochemical degradation of chlorinated compounds, *Ultrason. Sonochem.* 18 (2011) 460–465.
- [30] T.Y. Campbell, C.D. Vecitis, B.T. Mader, M.R. Hoffmann, Perfluorinated surfactant chain-length effects on sonochemical kinetics, *J. Phys. Chem. A* 113 (2009) 9834–9842.
- [31] H.M. Hung, M.R. Hoffmann, Kinetics and mechanism of the sonolytic degradation of chlorinated hydrocarbons: frequency effects, *J. Phys. Chem. A* 103 (1999) 2734–2739.
- [32] G. Mark, A. Tauber, R. Laupert, H.-P. Schuchmann, D. Schulz, A. Mues, C. von Sonntag, OH-radical formation by ultrasound in aqueous solution—Part II: terephthalate and fricke dosimetry and the influence of various conditions on the sonolytic yield, *Ultrason. Sonochem.* 5 (1998) 41–52.
- [33] M. Ashokkumar, M. Hodnett, B. Zeqiri, F. Grieser, G.J. Price, Acoustic emission spectra from 515 kHz cavitation in aqueous solutions containing surface-active solutes, *J. Am. Chem. Soc.* 129 (2007) 2250–2258.
- [34] K. Okitsu, K. Iwasaki, Y. Yobiko, H. Bandow, R. Nishimura, Y. Maeda, Sonochemical degradation of azo dyes in aqueous solution: a new heterogeneous kinetics model taking into account the local concentration of OH radicals and azo dyes, *Ultrason. Sonochem.* 12 (2005) 255–262.
- [35] C.D. Vecitis, H. Park, J. Cheng, B.T. Mader, M.R. Hoffmann, Enhancement of perfluorooctanoate and perfluorooctanesulfonate activity at acoustic cavitation bubble interfaces, *J. Phys. Chem. C* 112 (2008) 16850–16857.
- [36] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, *J. Am. Chem. Soc.* 40 (1918) 1361–1403.