Efficient PFOS decomposition in an alkaline ultrasonic system

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Abstract. Perfluorooctane sulfonate (PFOS) has attracted increasing attention due to its global distribution, high chemical stability and environmental persistence. An alkaline ultrasonic system was explored and used for PFOS decomposition in this study. $k_{obs}$ of PFOS decomposition in the investigated system was 0.0196 min⁻¹, which was remarkably efficient than that in sole ultrasonic system. $e_{aq-}$ induced reductive decomposition and pyrolysis decomposition based on the collapse of cavitation bubble were found to be two main reasons contributing to PFOS decomposition. PFOS decomposition kinetics was boosted by increasing alkaline dosage and reaction temperature, but suppressed when increasing initial PFOS concentration.

1. Introduction

Perfluorooctyl acids (PFAAs) are a class of organofluorine compounds which consists of a fully fluorinated carbon chain and ionic headgroup. The total substitution of C-H bond with C-F bonds in the carbon chain gives PFAAs unique physical and chemical properties, such as excellent chemical and thermal stability, low surface tension, olephobic-hydrophobic properties, thus PFAAs have been applied in numerous industrial activities[1]. PFAAs inevitably released into the environment because of their extensive use, and the industrial wastewater discharge was determined as the main source responsible for PFAAs releasing into the environment[2]. Toxicologic studies revealed PFAAs had neurotoxicity, reproductive toxicity, and potential carcinogenicity towards living organisms[3]. Therefore, the production and manufacturing of one dominant PFAAs, perfluorooctane sulfonate (PFOS) has been legally restricted in most developed countries since 2009. However, PFOS continued to be detected in water, air and biota, especially nearby the fluorochemical manufacturing facilities[4]. Therefore, development of PFOS decomposition techniques are still needed.

The high chemical stability of C-F bond makes PFAAs inert to conventional oxidation and biological treatment methods. Advance reduction processes (ARPs) have drawn increasing concern on account of their high efficiency in remediation of halogenated organic pollutants[5]. Multiple vigorous species involving hydrogen atom (H·), hydrated electron ($e_{aq-}$) and sulfite radical (SO₃²⁻) are produced in ARPs. $e_{aq-}$ was found almost owing the strongest nucleophilicity with standard reduction potential of -2.9 V [6]. UV or VUV relevant photolysis methods (i.e. direct UV or VUV photolysis, UV/sulfite photolysis, UV/KI photolysis) have been widely explored for $e_{aq-}$ generation [7], nevertheless little attention was paid to ultrasonic system. During the ultrasonic process, water molecular inside the cavitation bubbles suffers from extremely high temperature and pressure once the cavitation bubbles are collapsed, which results in the homolysis of water molecules, and thus some radicals (i.e. ·H, ·OH)
are generated (eq 1), and most of them recombines to reform H₂O, H₂ or H₂O₂. If high concentration of OH⁻ is introduced in the system, ·H can be quickly transformed to eaq⁻ through eq 2 [8].

\[
\text{H}_2\text{O} \rightarrow \cdot\text{H} + \cdot\text{OH} \quad (1)
\]

\[
\cdot\text{H} + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{eaq}^- \quad (2)
\]

In this study, eaq⁻ generation in an alkaline ultrasonic system was demonstrated, and this system was used for PFOS decomposition. Relevant influential factors including alkaline dosage, initial PFOS concentration and reaction temperature on PFOS decomposition were investigated. Findings in this study can provide a new strategy for recalcitrant organic pollutants decomposition.

2. Materials and Methods

2.1. Chemicals
Potassium perfluorooctane sulfonate (PFOS, 98%), sodium hydroxide (NaOH, 96%), potassium ferricyanide (K₃[Fe(CN)₆], 99%), sodium nitrite (NaNO₂, 99%) were purchased from Sigma-Aldrich, and used directly without further treatment. Argon with high purity (≥99.99%) was provided by Shenzhen Changlida Gas company.

2.2. Batch experiments for PFOS decomposition
PFOS ultrasonic experiments were performed in a KAIJO QUAVA mini (QR-003) ultrasonic apparatus which consisting of an ultrasonic generator and an oscillator operating at 100 W and 430 kHz. A PVC trough was coupled to the oscillator, and connected with a cooling jacket circulation system. 100 mL mixed solution containing 9.29 μM PFOS and 300 mM sodium hydroxide was filled into a quartz cylinder reactor and fixed at the central of the PVC trough (50 mm from the oscillator). The liquid level in the reactor was well matched with the surrounding water level in PVC trough. Reaction temperature was kept constant around 298 K unless otherwise specified. High purity argon was continuously bubbled into the reactor at least 30 min prior to and during the decomposition experiments. PFOS decomposition was studied at varying sodium hydroxide concentrations from 300 mM to 800 mM. When investigating the influence of initial PFOS concentration, PFOS concentrations was changed from 4.65 μM to 18.58 μM. The influence of reaction temperature was evaluated with temperature varying from 288 K to 308 K.

2.3. Analysis
PFOS concentration was analyzed by UPLC/MS-MS, which was operated under multiple reaction monitoring (MRM) and ESI mode. Ammonium acetate (5 mM) and methanol were used as mobile phase. The elution flow rate was kept unchanged at 0.3 mL/min. Fluoride ion concentration was detected by a fluoride ion selective electrode (INESA, Shanghai). Samples were firstly neutralized by dropwise addition of hydrochloric acid before fluoride ion analysis. UV absorbance spectra of potassium ferricyanide was measured by an ultraviolet spectrophotometer (UV2450, Shimadzu).

3. Results and discussion

3.1. PFOS decomposition in the alkaline ultrasonic system
As shown in Figure 1, efficient PFOS decomposition was achieved in the alkaline ultrasonic (alkaline US) system. At alkaline dosage of 300 mM, 97% PFOS was decomposed from its initial concentration of 9.29 μM within 120 min, and the defluorination efficiency reached 72%. Compared to sole ultrasonic system, the introduction of alkaline apparently enhanced PFOS decomposition and defluorination. PFOS decomposition kinetics can be well described by a pseudo-first-order model (R² > 0.98) in the alkaline ultrasonic system., and the observed rate constants (kobs) was 0.0196 min⁻¹, which was remarkably higher than that in sole ultrasonic system, where kobs was 0.01 min⁻¹. These results
were in agreement with a report from Vecitis et al, which described a phenomenon the reaction order varied from pseudo-first-order ([PFOS]₀ < 20 μM) to zero-order ([PFOS]₀ > 40 μM) along with the increasing initial PFOS concentration in the ultrasonic decomposition experiments[9].

![Figure 1. PFOS decomposition and defluorination in the strongly alkaline sonolysis system.](image)

As an efficient one-electron acceptor, Fe(CN)₆³⁻ was introduced in the alkaline ultrasonic system to examine the existence of eaq⁻ (eq 3). The UV spectra of Fe(CN)₆³⁻ solution before and after 30 min sonication in the studied system were presented in Figure 2 (a). The maximum absorbance of Fe(CN)₆³⁻ solution appeared at wavelength around 415 nm, which was consistent with previous studies [8,10]. After 30 min sonication, the maximum absorbance obviously declined. Besides, NO₂⁻ was used as the eaq⁻ scavenger and added into the studied system, the results showed the co-presence of 10 mM NO₂⁻ caused nearly 20% suppression on PFOS decomposition after 120 min reaction (Figure 2 (b)). These results not only demonstrated eaq⁻ was generated in the alkaline ultrasonic system and responsible for PFOS decomposition, but also indicated there are other reason resulting in PFOS decomposition. As well known, pyrolysis and ·OH based oxidation are two main reasons contributed to pollutants destruction in ultrasonic process. Previous studies have confirmed ·OH based oxidation had little effectiveness on PFAAs decomposition, thus pyrolysis with a high temperature around 4000 K during collapse of cavitation bubble was also attributed for PFOS decomposition in the studied system, similar results were reported by Vecitis et al and Moriwaki et al[9,11], which could explain the partial suppression of NO₂⁻ on PFOS decomposition.

![Figure 2. (a) UV absorbance of [Fe(CN)₆]³⁻ before and after 30 min sonication, (b) PFOS decomposition with 10 mM NO₂⁻](image)
Fe(CN)$_6^{3-}$ + e$_{aq}^-$ → Fe(CN)$_6^{4-}$  

(3)

3.2. Main influential factors for PFOS decomposition

3.2.1. Influence of alkaline dosage

The influence of alkaline dosage on PFOS decomposition was investigated and results were presented in Figure 3 (a). PFOS decomposition efficiency was enhanced from 97% to 100% within 120 min reaction when alkaline dosage increased from 300 mM to 800 mM. PFOS decomposition kinetics at various conditions was well fitted with pseudo-first-order model (Table 1), and $k_{obs}$ of PFOS decomposition increased with increasing alkaline dosage. $e_{aq}^-$ generation through eq 2 is theoretically proportional to OH$^-$ concentration, and higher alkaline dosage resulted in higher OH$^-$ concentration, thus led to faster PFOS decomposition kinetics. This conclusion was similar to a report from Dharmaratne et al[8], where methyl viologen (MV$^{2+}$Cl$^-$_2) was used as the $e_{aq}^-$ probe in an alkaline ultrasonic system, and concentration of the formed MV$^+$ continuously raised as alkaline dosage increased from 0 to 1200 mM.

3.2.2. Influence of initial PFOS concentration

The level of PFAAs content in industrial wastewater was also a significant factor impacting its decomposition, thus the role of initial PFOS concentration on the extent and rate on its ultrasonic decomposition was studied (Figure 3 (b) and Table 1). The rate of PFOS decomposition decreased with increasing initial PFOS concentration. The decomposition rate averaged 0.0282 min$^{-1}$, 0.0196 min$^{-1}$ and 0.0141 min$^{-1}$ when initial PFOS concentration were 4.65, 9.29 and 18.58 μM, respectively. The increasing PFOS decomposition rate observed at lower initial PFOS concentration can be explained by the following reasons. Firstly, higher initial PFOS concentration resulted in more generation of intermediate products, which consumed $e_{aq}^-$ with much faster rate constants [12], and therefore restrained the reaction between $e_{aq}^-$ and PFOS. Secondly, more PFOS molecule would absorb at the liquid-bubble interface and cause an increase in electrostatic repulsion between the cavitation bubbles, thus preventing the bubbles from coalescing and subsequently enhance the number density of cavitation bubbles when higher initial PFOS concentration was used [13]. The enhancement of cavitation may remarkably increase the generation of oxidative species such as OH and H$_2$O$_2$, which would bring about severe $e_{aq}^-$ quenching reactions. The rate constant between OH and $e_{aq}^-$ was 3.0×10$^{10}$ M$^{-1}$s$^{-1}$, which was at least three magnitude higher than that with PFAAs [6,14]. Nevertheless, the total amount of PFOS decomposed was increased from 4.65 μM to 15.98 μM as the initial PFOS concentration changed from 4.65 μM to 18.58 μM.
Figure 3. PFOS decomposition with different (a) alkaline dosage, (b) initial PFOS concentration and (c) reaction temperature in the studied system.

Table 1. Comparison of PFOS decomposition in this study with other reported ultrasonic treatments.

| NO. | Alkaline dosage (mM) | Temperature (K) | Initial PFOS concentration (μM) | k_{obs} (min^{-1}) | R^2 |
|-----|----------------------|-----------------|---------------------------------|--------------------|-----|
| 1   | 300                  | 298             | 9.29                            | 0.0196             | 0.9876 |
| 2   | 500                  | 298             | 9.29                            | 0.0216             | 0.9800 |
| 3   | 800                  | 298             | 9.29                            | 0.0268             | 0.9809 |
| 4   | 300                  | 288             | 9.29                            | 0.0076             | 0.9773 |
| 5   | 300                  | 308             | 9.29                            | 0.0287             | 0.9608 |
| 6   | 300                  | 298             | 4.65                            | 0.0282             | 0.9880 |
| 7   | 300                  | 298             | 18.58                           | 0.0141             | 0.9954 |

3.2.3. Influence of reaction temperature
PFOS decomposition at reaction temperature ranging from 288 K to 308 K was investigated and presented in Figure 3 (c). The decomposition of PFOS was boosted with increasing reaction temperature, \( k_{obs} \) at 308 K was almost three times higher than that at 288 K. On one hand, the diffusion motion of PFOS molecular and \( e_{aq} \) was enhanced with increasing temperature\[9\], thus their collision probability was raised and thus behaved faster decomposition kinetics. On the other hand, PFOS easily migrates from bulk solution to liquid-bubble interface at higher reaction temperature, which was also beneficial for PFOA ultrasonic decomposition. Nevertheless, surface tension and gas solubility were found decrease with the increasing reaction temperature, thus resulting in weakening of the cavitation collapse intensity\[15\]. Therefore, the influence of reaction temperature on ultrasonic PFOS decomposition was complicated.

4. Conclusion
Based on the above investigations, the alkaline ultrasonic system was found capable of efficiently decomposing PFOS. \( k_{obs} \) of PFOS decomposition in the investigated system was 0.0196 min^{-1}, which was remarkably efficient than that in sole ultrasonic system. \( e_{aq} \) induced reductive decomposition and pyrolysis decomposition based on the collapse of cavitation bubble were found two main reasons contributing to PFOS decomposition and defluorination. PFOS decomposition kinetics was boosted by enhancing alkaline dosage and reaction temperature, but suppressed when increasing initial PFOS concentration.
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