



# Enhancing decomposition rate of perfluorooctanoic acid by carbonate radical assisted sonochemical treatment



Lan-Anh Phan Thi <sup>a</sup>, Huu-Tuan Do <sup>b</sup>, Shang-Lien Lo <sup>a,\*</sup>

<sup>a</sup> Graduate Institute of Environmental Engineering, National Taiwan University, 71 Chou-Shan Rd., Taipei, Taiwan, ROC

<sup>b</sup> Faculty of Environmental Sciences, College of Science, Vietnam National University, Hanoi, 334 Nguyen Trai Street, Thanh Xuan Dist., Ha Noi, Viet Nam

## ARTICLE INFO

### Article history:

Received 3 January 2014  
Received in revised form 26 March 2014  
Accepted 26 March 2014  
Available online 4 April 2014

### Keywords:

Perfluorooctanoic acid  
Sonochemical  
Ultrasonic reaction  
Carbonate radical anion

## ABSTRACT

Perfluorooctanoic acid (PFOA) is a recalcitrant organic pollutant in wastewater because of its wide range of applications. Technologies for PFOA treatment have recently been developed. In this study, PFOA decomposition by sonochemical treatment was investigated to determine the effects of  $\text{NaHCO}_3$  concentrations,  $\text{N}_2$  saturation, and pH on decomposition rates and defluorination efficiencies. The results showed that PFOA decomposition by ultrasound treatment only (150 W, 40 kHz), with or without saturated  $\text{N}_2$ , was <25% after 4 h reaction. The extent and rate of PFOA decomposition and defluorination efficiencies of PFOA, however, greatly increased with the addition of carbonate radical reagents. PFOA was completely decomposed after 4 h of sonochemical treatment with a carbonate radical oxidant and saturated  $\text{N}_2$ . Without saturated  $\text{N}_2$ , PFOA was also decomposed to a high (98.81%) degree. The highest PFOA decomposition and defluorination efficiencies occurred in  $\text{N}_2$  saturated solution containing an initial  $\text{NaHCO}_3$  concentration of 30 mM. Sonodecomposition of PFOA with  $\text{CO}_3^-$  radical was most favorable in a slightly alkaline environment (pH = 8.65). There isn't any shorter-chain perfluorinated carboxylic acids detected except fluorine ions in final reaction solution.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

Perfluorocarboxylic acids ( $\text{C}_n\text{F}_{2n+1}\text{COOH}$ , PFCAs), including perfluorooctanoic acid (PFOA), are a family of anthropogenic fluorinated organic compounds with a wide range of applications [1]. They have been used in various commercial and industrial applications such as surface treatment, surfactant, polymers, metal coating and fire retardant [2]. The extremely strong carbon–fluorine bonds (C–F, 116 kcal/mol) [1] in their structure gives the material high thermal and acid resistance. Because of the widespread use of these chemicals and the resistance to degradation, PFCAs have been detected in drinking water [3] and wastewater treatment plant effluents [4]. In addition, recent studies indicated that these compounds are toxic and carcinogenic to animals such as rats, fishes, monkeys, and even humans [5]; they are listed as persisted organic pollutants (POPs) [6].

Technologies for PFOA treatment include photolysis, photochemical reaction, photocatalysis [7–10], sonochemical treatment [11], electrochemical treatment [12], and adsorption [13,14].

Among these treatment methods, sonochemical treatment is an innovative technique that can enhance the degradation rate of environmental contaminants in water. The effectiveness of sonochemical treatment can be further enhanced by combining it with additives such as microwave [15], photocatalytic compounds [16], persulfate [17–19], and carbonate [20].

The effects of sonochemical treatment are generally due to the cavitation phenomenon; the formation, growth, and the sudden collapse of cavitation bubbles in liquid gives rise to localized, transient high temperatures and high pressures [21,22]. The sonochemical decomposition of organic contaminants via reaction with hydroxyl radicals ( $\text{OH}^\cdot$ ) formed from pyrolysis of water or via direct pyrolysis. The ultrasonic reaction is powerful, but it is relatively inefficient with respect to total input energy and is therefore not economical when used alone. With additive-assisted sonochemical treatment, the total input energy may be reduced and the pollutant decomposition rate accelerated.

The carbonate radical anion ( $\text{CO}_3^-$ ) is a secondary radical formed by one-electron oxidation of carbonate or bicarbonate ions by  $\text{OH}^\cdot$  radical or sulfate radical ( $\text{SO}_4^-$ ). It is a powerful oxidant with a one-electron reduction potential of 1.59 V at pH of 12.5 and 1.78 V at pH of 7 [23]. The radical is a strong acid ( $\text{p}K_a < 0$ ) [24]. In comparison to  $\text{OH}^\cdot$  radical,  $\text{CO}_3^-$  radical is more selective, but could migrate towards the bulk solution and induce the decomposition

\* Corresponding author. Address: Graduate Institute of Environmental Engineering, National Taiwan University, 71 Chou-Shan Rd., Taipei 106, Taiwan, ROC. Tel.: +886 2 2362 5373; fax: +886 2 2392 8821.

E-mail address: [sll@ntu.edu.tw](mailto:sll@ntu.edu.tw) (S.-L. Lo).

of non-volatile pollutants [25]. It is hypothesized that carbonate radicals are important in reducing the persistence of chemical pollutants, especially those that are electron-rich. In previous research [26],  $\text{CO}_3^-$  radical has been used successfully to decompose PFOA under photolysis condition. In this study, we investigated the decomposition of PFOA in aqueous solutions by sonochemically induced  $\text{CO}_3^-$  radical, and compared the efficiencies of decomposition and defluorination of PFOA under various conditions such as pH values,  $\text{NaHCO}_3$  concentrations,  $\text{N}_2$  saturation, and reaction time.

## 2. Materials and methods

### 2.1. Instruments and chemicals

The perfluorooctanoic acid (PFOA,  $\text{C}_7\text{F}_{15}\text{COOH}$ , 96% purity) was from Aldrich; the perfluoroheptanoic acid (PFHpA,  $\text{C}_6\text{F}_{13}\text{COOH}$ , 98% purity), perfluoropentanoic acid (PFPeA,  $\text{C}_4\text{F}_9\text{COOH}$ , 97% purity), and perfluorobutyric acid (PFBA,  $\text{C}_3\text{F}_7\text{COOH}$ , 99% purity) were from Alfa Aesar. The perfluorohexanoic acid (PFHxA,  $\text{C}_5\text{F}_{11}\text{COOH}$ , 97% purity) and perfluoropropionic acid (PFPrA,  $\text{C}_2\text{F}_5\text{COOH}$ , 97% purity) were purchased from Fluka, and the trifluoroacetic acid (TFA,  $\text{CF}_3\text{COOH}$ ) was from Riedel-deHaen. Sodium carbonate ( $\text{Na}_2\text{CO}_3$ , 100% purity) was from Nacalai Tesque, sodium bicarbonate ( $\text{NaHCO}_3$ , 99.6% purity) was from J.T. Baker, and nitrogen gas ( $\text{N}_2$ , 99.99% purity) was from Chin-Fon, Co., Ltd., Taipei, Taiwan. The fluorine standard was purchased from High-Purity Standards.

### 2.2. Reaction procedures

PFOA, at a concentration of 100 ppm, and  $\text{NaHCO}_3$ , at a concentration of 0.5 N, were prepared and stored at 4 °C. In each experiment, solution containing 50 ppm of PFOA and different initial concentrations of  $\text{NaHCO}_3$  was mixed by a magnetic stirrer. A 1-liter closed double-layered glass reactor containing 1 L solution was connected with circulating water bath (B204, Firstek Scientific Co., Ltd., Taipei, Taiwan) to control the reactor's temperature at  $25 \pm 1$  °C. Air volume controller was connected with  $\text{N}_2$  tank and

the reactor to saturate  $\text{N}_2$  with the aqueous solution at 200 cc/min in 30 min. pH values were adjusted by using 1 N NaOH and/or 1 N HCl solutions. The reactor was then placed in a cabinet. A sonicator's probe 22 mm diameter (Branson, 2000LPt, 150 W, 40 kHz, USA) was put into the aqueous solution to generate ultrasound. The experimental setup is shown in Fig. 1. The samples were taken at various intervals and filtered by Millipore syringe filters with a 0.22  $\mu\text{m}$  pore size. The PFOA concentration in the filtrate was determined by a HPLC and the  $\text{F}^-$  concentration was measured by an IC system, respectively.

### 2.3. Samples analysis

The samples were taken at various intervals and filtered by Millipore syringe filters with a 0.22  $\mu\text{m}$  pore size. The PFOA concentration in the filtrate was determined by a high-performance liquid chromatography (HPLC) (Dionex, UltiMate 3000, USA) equipped with a conductivity detector (ED-50, Dionex, USA) and an anion self-regenerating suppressor (ASRS 300 2-mm, USA). The PFOA and other PFCAs (C3–C8) were extracted by a  $150 \times 2.1$  mm, 3.5  $\mu\text{m}$  column (Acclaim® Polar Advantage II, C18, Dionex, USA) maintained at 30 °C. The ternary solution that included 70:30 (v/v) acetonitrile/Milli-Q water (solution A), Milli-Q water (solution B) and 9 mM NaOH and 100 mM  $\text{H}_3\text{BO}_3$  in Milli-Q water (solution C) was employed as an eluent at a flow rate of 0.3 mL/min. The gradient was operated at 20% solution A, 40% solution B, and 40% solution C for the first 5 min. For the next 15 min, it was operated at 20–60% solution A, 40–0% solution B, and 40% solution C. For the last 15–20 min, solution A was maintained at 60% and solution B at 0%. All calibration curves for PFCAs were linear over the 0.5–50 ppm range. The decomposition ratio of PFOA was calculated according to the following equation:

$$\text{Degradation (\%)} = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

where  $C$  is the PFOA concentration (ppm), and  $C_0$  is the initial PFOA concentration (ppm). The other byproducts of PFOA were calculated based on the external calibration curves.

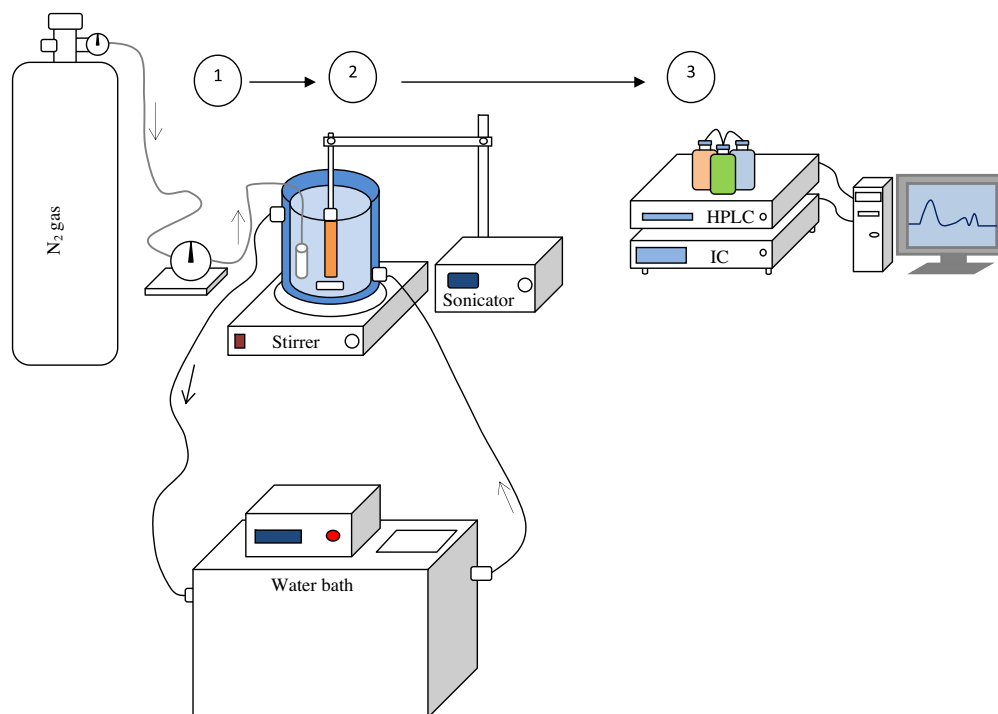


Fig. 1. The sonochemical experiment setup schematic.

Download English Version:

<https://daneshyari.com/en/article/1266114>

Download Persian Version:

<https://daneshyari.com/article/1266114>

[Daneshyari.com](https://daneshyari.com)