

Autocatalytic degradation of perfluorooctanoic acid in a permanganate-ultrasonic system

Yi-bo Hu, Shang-Lien Lo*, Yueh-Feng Li, Yu-Chi Lee, Meng-Jia Chen, Jo-Chen Lin

Graduate Institute of Environmental Engineering, National Taiwan University, 71 Chou-Shan Rd., Taipei, 106, Taiwan

ARTICLE INFO

Article history:

Received 12 January 2018

Received in revised form

17 April 2018

Accepted 18 April 2018

Available online 21 April 2018

Keywords:

Perfluorooctanoic acid

Permanganate

Ultrasonic irradiation

Autocatalysis

ABSTRACT

An autocatalytic system, permanganate-ultrasonic (PM-US) system, was applied to degrade perfluorooctanoic acid (PFOA) in aqueous solutions. After a 120-min ultrasonication, a PM dosage of 6 mM increased the pseudo first-order rate constant (k_1) for PFOA decomposition from 3.5×10^{-3} to $13.0 \times 10^{-3} \text{ min}^{-1}$ and increased the pseudo zeroth-order rate constant (k_2) for PFOA defluorination from 1.5×10^{-3} to $7.9 \times 10^{-3} \text{ mM} \cdot \text{min}^{-1}$, respectively. The PFOA degradation rates increased proportionally with the enhanced production rates of MnO_2 particles. An initial pH 4 condition was optimal for the PFOA degradation compared to highly acidic and neutral conditions. PFOA degradation could be significantly facilitated by increasing power density of ultrasonication from 60 to $180 \text{ W} \cdot \text{L}^{-1}$. While increasing solution temperature to 50°C only slightly promoted the PFOA decomposition and defluorination to 1.15 and 1.07 times of that at 30°C , respectively. The solution saturated with argon was more favorable for the PFOA degradation in the PM-US system than that saturated with air and oxygen. Co-dissolved Cu(II) , Fe(II) and Fe(III) ions inhibited the PFOA degradation by forming metal-PFOA complexes. Based on the experimental results and intermediates analysis, mechanisms and pathways of PFOA decomposition and defluorination in the PM-US system were proposed.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

Since 1950s, perfluorooctanoic acid (PFOA) has been extensively used in production of nonstick coatings, semi-conductors and fire-fighting foam due to its chemical stability and capacity of lowering surface tension (Lindstrom et al., 2011; Zareitalabad et al., 2013). Around 260 tons of PFOA produced annually in the world resulted in its wide presence in surface waters, groundwater and sediments in many countries, with concentrations ranging from $\text{ng} \cdot \text{L}^{-1}$ to $\text{mg} \cdot \text{L}^{-1}$ level (Schultz et al., 2004; Zareitalabad et al., 2013). The fact that people living in industrialized countries have PFOA in their serum with mean values of $2\text{--}8 \mu\text{g} \cdot \text{L}^{-1}$ (Vestergren and Cousins, 2009) indicates widespread exposure of human to PFOA. PFOA is classified as possibly carcinogenic to humans (Benbrahim-Tallaa et al., 2014), and a toxicant for liver, thyroid, developmental and immune systems (Lau et al., 2007; Melzer et al., 2010). Hence, removing PFOA from the environment is of increasing importance to abate health risks of humans and wildlife.

However, due to the strong bond energy of the C-C bond ($410 \text{ kJ} \cdot \text{mol}^{-1}$) and C-F bond ($530 \text{ kJ} \cdot \text{mol}^{-1}$) (Vecitis et al., 2008), using ozonation or Fenton reaction alone could not efficiently degrade aqueous PFOA (Post et al., 2012; Trojanowicz et al., 2018). Considerable efforts have been expended to break the strong bonds in order to degrade PFOA to harmless species. Photocatalysis (Li et al., 2012), electrochemical oxidation (Zhao et al., 2013), and microwave-induced decomposition (Lee et al., 2009) are recently investigated as effective techniques to remove PFOA. Nevertheless, perfluorinated carboxylic acids (PFCAs) with shorter chains were produced as intermediates by those techniques.

Ultrasonication (US) technique is a promising process for complete mineralization of PFOA (Cheng et al., 2008; Vecitis et al., 2008; Lin et al., 2015). Under ultrasonic irradiation, cavitation bubbles could be formed and collapsed in the aqueous phase, leading to release transient high temperature and reactive oxygen species (ROS) (eqs. (1) and (2)) for pyrolytic and chemical decomposition of organics. In addition, the ultrasonic irradiation with a range from 20 to 40 kHz could be facily provided by a hand-held probe, which has been widely used to degrade PFOA (Panchangam et al., 2009; Zhao et al., 2013; Lin et al., 2016) and other organic pollutants (Guo et al., 2015; Ince, 2018) for water decontamination in recent years.

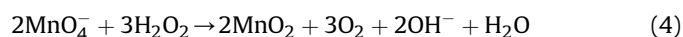
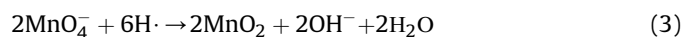
* Corresponding author.

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



In order to further enhance mineralization efficiency of PFOA with this physicochemical technique and reduce energy consumption, ozone (Song et al., 2007), persulfate (Hori et al., 2012) and Fenton process (Fe/H₂O₂) (Segura et al., 2012) have been applied to enhance PFOA degradation under ultrasonic irradiation due to the generation of additional oxidizing radicals. Permanganate is a strong and environmental-friendly oxidant commonly used to oxidize a wide range of organic pollutants (Jiang et al., 2009; Hu et al., 2011; Zhang et al., 2014) for drinking water treatment (Rodríguez-Álvarez et al., 2013) and groundwater remediation (Nelson et al., 2001). Permanganate has also been studied as an oxidant to decompose perfluorinated compounds, with rate constants at 10⁻² d⁻¹ level (Liu et al., 2012).

Under ultrasonic irradiation, permanganate could be reduced to colloidal MnO₂ particles (Okitsu et al., 2009; Abulizi et al., 2014) (eqs. (3) and (4)).



The formed MnO₂ solids can act as a catalyst promoting permanganate oxidation of hydrophobic pollutants (Zhang and Huang, 2003; Jiang et al., 2009; Perez-Benito, 2009). Moreover, MnO₂ has been used as a cavitation nucleus to enhance ultrasonic cavitation effects via decreasing the cavitation nucleation threshold (Zhao et al., 2014).

In view of the above synergistic effects, the present study was conducted to assess the effectiveness of a permanganate-ultrasonic (PM-US) system for degradation of PFOA using a low-frequency ultrasonic system by altering permanganate dosages and ultrasonic power. Additionally, effects of solution conditions (i.e., initial pH, temperature and atmosphere) on system performance were evaluated systematically. Moreover, the degradation pathways of PFOA in the PM-US system were discussed. The results in this study implied that the PM-US system is a cost-effective technology, which can be applied in treating wastewater polluted with PFOA or other persistent organics pollutants.

2. Experimental

2.1. Chemicals

Perfluorooctanoic acid (PFOA, C₇F₁₅COOH, 96%) was purchased from Sigma Aldrich; humic acids, perfluoroheptanoic acid (PFHpA, C₆F₁₃COOH, 98%), perfluoropentanoic acid (PFPeA, C₄F₉COOH, 97%) and heptafluorobutyric acid (PFBA, C₃F₇COOH, 99%) were obtained from Alfa Aesar; undecafluorohexanoic acid (PFHeA, C₅F₁₁COOH, 97%) and pentafluoropropionic acid (PFPrA, C₂F₅COOH, 97%) were purchased from Fluka; trifluoroacetic acid (TFA, CF₃COOH, 98%) was obtained from Riedel-de Haën; potassium permanganate (KMnO₄) (99.0%) and tert-butyl alcohol (TBA) (A.C.S. Reagent) were purchased from J. T. Baker; iron sulfate (Fe₂(SO₄)₃·xH₂O, 97% and FeSO₄·7H₂O, 99%) and copper sulfate (CuSO₄·5H₂O) were purchased from Sigma-Aldrich and Crown, respectively. 18 MΩ cm Milli-Q water prepared by Millipore was used to prepare stock and reaction solutions throughout this study.

2.2. Experimental procedures

Ultrasonic irradiation of PFOA solution was performed in a cylindrical jacketed glass reactor (inside diameter = 8 cm, height = 17.8 cm) mounted on a magnetic stirring apparatus (Fargo MS-90). The ultrasonic irradiation was provided by an ultrasonic apparatus (Branson Lpt, 150 W, 40 kHz), which consists of an ultrasonic drive device and a handpiece. The handpiece contained an ultrasonic oscillator and a probe (length = 9 cm, diameter = 3.5 cm, aluminum alloy). For a typical run, the reactor was filled with a 500 mL aqueous solution containing 132 μM PFOA. Then, the PM powder was dissolved in the PFOA solution to obtain a pre-determined concentration of PM. Finally, the ultrasonic probe providing a power density of 180 W·L⁻¹ was inserted into the solution at a depth of 5.8 cm and the solution was irradiated continuously for 120 min. The solution temperature was kept at 30 ± 1 °C by cooling water flowing through the jacket during the 120-min reaction. A suspension of 2 mL was collected from the reactor at a 10-min interval. Centrifugation of the suspension at 8000 rpm, followed by filtration with a 0.22-μm membrane, was applied to remove MnO₂ particles. To study the capacity of MnO₂ production by ultrasonic reduction of PM, experiments were conducted under the same conditions in the presence or absence of PFOA. The concentration of PM was adjusted to range from 1 to 20 mM to study the effects of PM dosage and MnO₂ production on the degradation of PFOA. TBA of 0.1 mM was added to quench HO· radicals produced under ultrasonication (Nagata et al., 1996) to study the contribution of the HO· radicals in the PM-US system. Power output ratio of US was set from 20 to 60% to obtain ultrasonic power densities from 60 to 180 W·L⁻¹. The initial pH value of the solution was adjusted from 2.0 to 7.0 with 1.8 M H₂SO₄ and 0.05 M NaOH solutions. The temperature of the solution was elevated stepwise to 50 ± 1 °C by increasing the temperature of the cooling water. Argon or oxygen gas (99.99%) was bubbled into the solutions from the reactor bottom during ultrasonication at a flow rate of 500 mL min⁻¹ to study the effects of the atmosphere. Humic acids with a concentration of 20 mg·L⁻¹ was added to evaluate the effects of background organics on the PFOA degradation rates. Fe²⁺, Cu²⁺ or Fe³⁺ was added, when needed, to obtain a concentration of 0.2 mM before ultrasonication. The solubility of PFOA in the presence of co-dissolved transition metal cations was measured without the ultrasonication. All the experiments were conducted in duplicate.

2.3. Analytical procedures

Concentrations of PFOA and PFCAs with shorter chains were analyzed by a high-performance liquid chromatography (HPLC) (Dionex, Ultimate 3000, U.S.A.), equipped with an Agilent column (Eclipse XDB-C18, U.S.A.), a conductivity detector and an anion self-regenerating suppressor (ASRS 300 2 mm U.S.A.). Concentrations of PFPrA, TFA and fluoride ion were measured with an ion-chromatograph (IC) system (Dionex, Ics-3000, U.S.A.), equipped with a separation column (Ion Pac As4a-SC Analytical Column, Dionex) and a conductivity detector. The detailed information of mobile phase and limit of detection for the measurements with the HPLC and IC are presented in the supplemental information (SI). Decomposition and defluorination efficiency of PFOA were defined as follows (eqs. (5) and (6)):

$$\text{Decomposition efficiency (\%)} = \frac{[\text{PFOA}]_0 - [\text{PFOA}]}{[\text{PFOA}]_0} \times 100\% \quad (5)$$

Download English Version:

<https://daneshyari.com/en/article/8873830>

Download Persian Version:

<https://daneshyari.com/article/8873830>

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