VIETNAM JOURNAL OF
HYDROMETEOROLOGY

Research Article

Degradation of perfluorooctanoic acid in aqueous solution with sulfate radicals generated in the UV/sodium sulfate system

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Received: 12 May 2021; Accepted: 19 July 2021; Published: 25 August 2021

Abstract: Perfluorooctanoic acid ($C_7F_{15}COOH$, PFOA) is a persisted organic pollutant widely used in industry in recently. It is widespread occurrence in the environment and because of its ability to bioaccumulate. PFOA is reported toxic and carcinogenic to animals such as rats, fishes, monkeys, and even humans. Photodegradation PFOA solution in presence Na_2SO_4 was studied in this study. PFOA was photodegraded about 93% after 24 h by using a combination of UV 254nm irradiation and Na_2SO_4 30mM, while under only UV irradiation, 43% of PFOA was photodegraded. Na_2SO_4 30mM was the concentration that photodegradation PFOA reached highest efficiency. The optimal temperature for PFOA degradation is 25^{o}C.

Keywords: Perfluorooctanoic acid; Photodegradation; Treatment; Radical scavenger.

1. Introduction

Perfluorooctanoic acid ($C_7F_{15}COOH$, PFOA) is a contaminant widely used in industry in recently. It is very stable in the natural environment due to its strong C–F bonds (110 kcal/mol) [1–2]. It contains both hydropholic and hydropholic polar structure, so it is used as a surface treatment agent in photolithography, an emulsifying agent in polymer synthesis, a fire retardant, and is one component of paper coating [3]. PFOA has been detected in aquatic environments and animals, and has been demonstrated to exhibit bioaccumulative and biomagnificative effects [4]. They are toxic and carcinogenic to animals such as rats, fishes, monkeys, and even humans [3–6]. Therefore, there is interest in developing methods for PFOA removal.

The treatment technologies of PFOA are interested recently. Some advanced oxidation processes (AOPs) in critical conditions have been developed to degrade PFOA. The noticeable treatment technologies are either photo–based approaches, such as: photolysis, photochemical and photocatalysis [7–11] sonochemical treatment [12–15] or microwave–hydrothermal treatment [16–17]. The key factor in these treatment reactions are one–electron oxidants such as persulfate [8–16] periodate [10], or photocatalysts such as heteropolyacid [7], TiO_2 [9, 11], have been used to decompose PFCAs under UV–irradiation.

This study explored the effect of the presence of sulfate radicals on the degradation rate of PFOA undergoing UV–irradiation. The effects of sulfate concentration, solution temperature and the radical scavengers on the degradation rate of PFOA were investigated.

2. Materials and methods

2.1. Materials

The perfluorooctanoic acid (PFOA, $C_7F_{15}COOH$, 96% purity) was from Aldrich. Sodium Sulfate Anhydrous (Na_2SO_4, 100% purity) was from Nacalai Tesque. Acetic acid 99%, ammonium acetate 97%, methanol, and tert–BuOH was from Merck, Germany.

2.2. Experimental procedures

A stock solution of 250 ppm PFOA was prepared by diluting the chemicals into the desired volume of Milli–Q water. This solution was stored in a 4°C refrigerator and used for all following experiments; the solution concentration was adjusted accordingly. The Na_2SO_4 solution was prepared at a concentration of 100mM and stored at 4°C. The photodegradation experimental was setup in a dark close carton box. A 1 L closed double–layered glass reactor with a low–pressure mercury vapor quartz lamp (254 nm, 11 W, Aquapro, Taiwan) was placed in the middle of reactor. The reaction temperature was controlled at 25°C by a circulating water bath (B204, Firstek Scientific Co. Ltd., Taiwan). The Na_2SO_4 solutions were mixed well with PFOA solution by a magnetic stirrer. The samples were taken at various intervals and filtered by Millipore syringe filters with a 0.22 µm pore size (Millipore, Ireland) to analyze the concentration of PFOA remain.

2.3 Samples analysis

The LC–MS/MS (8040 Shimadzu, Japan) system was equipped with a column (Poroshell 120, EC.C18 (2.1 mm I.D. × 150 mm L, 2.7 µm) and guard column EC–C18, Agilent, USA was used to analyze samples. The mobile phase consisted of a binary mixture of A (2 mM.L–1 ammonium acetate in water with methanol in a ratio of volume is 9 and 1) and solvent B (methanol) at flow rate of 0.25 ml.min–1. The gradient, the start with 50%B in 2 min increased to 95% B for 18 min and linearly at 95% B for 4 min then ramped to 50%A for 3 min. Total running time was 27 min. The inject volume was 2µL. The MS system was running with an electrospray ionization source in negative mode (ESI) at 3.5kV. The PFOA degradation efficiency was calculated via following equation:

$$\text{PFOA degradation (\%)} = \frac{C}{C_0} x100 \quad (1)$$

where C and C_0 are the PFOA concentration at the sampling and the initial time (ppm), respectively.

3. Results and Discussion

3.1. Photodegradation of PFOA

The photodegradation of PFOA was carried out with 1ppm PFOA in DI water. The photodegradation efficiencies of direct photolysis and photolysis in the solution with Na_2SO_4 were compared in figure 1. Red circle shows the experimental results of PFOA photodegradation in Na_2SO_4 (30mM) solution and black square for case without Na_2SO_4. When the solution with 50 ppm PFOA was decomposed with direct photolysis under 254 nm irradiation for 24 h, the decomposition efficiency of PFOA reached 41.3%. Na_2SO_4 (30mM) containing solution showed higher PFOA degradation efficiency. The PFOA photodegradation reached 92.3% under UV irradiation assisted Na_2SO_4. This result implies that Na_2SO_4 act as an efficient oxidant for PFOA degradation when combined with the effects of H_2O_2 and UV irradiation.

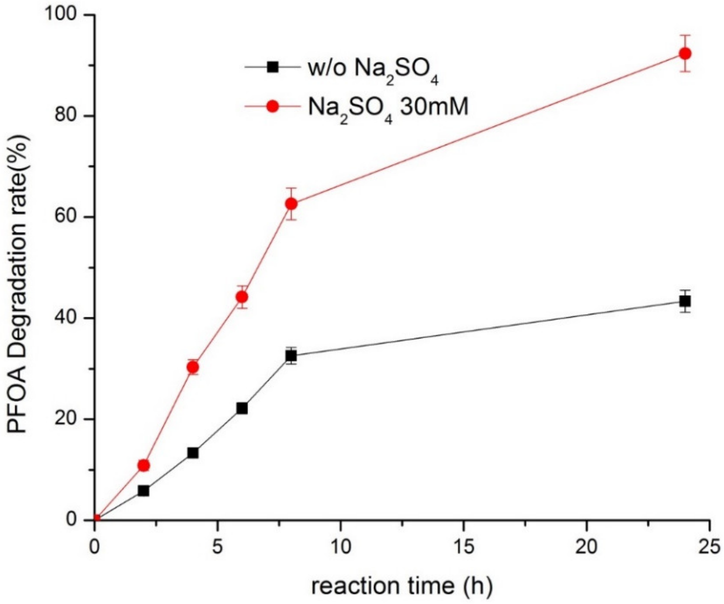

Figure 1. Photodegradation of PFOA with and without Na_2SO_4.

3.2. Degradation of PFOA by different Na_2SO_4 concentration

Degradation of PFOA by different Na_2SO_4 concentration, from 20 mM to 50 mM Na_2SO_4 used to investigate the effluence on degradation efficiency. Figure 2 shows the degradation efficiencies of PFOA at different initial Na_2SO_4 concentrations. The highest degradation efficiency reaches at 40 mM Na_2SO_4 solution. The degradation efficiency increased with increasing Na_2SO_4 concentrations from 20 mM to 40 mM and decreased at 50 mM Na_2SO_4 solution.

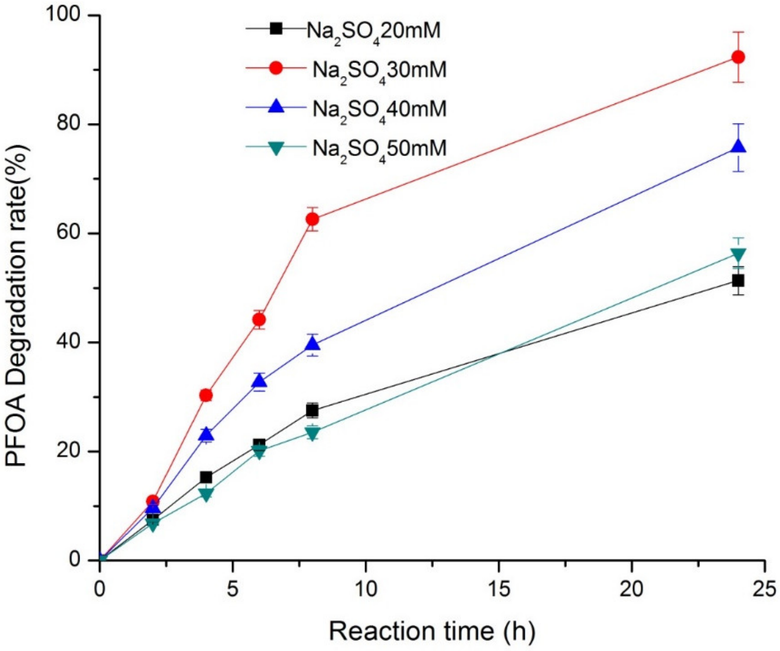

Figure 2. Photodegradation of PFOA by different Na_2SO_4 concentration.

3.3. Degradation of PFOA by Na_2SO_4 presence of t–BuOH

To investigate $SO_4^{\bullet-}$ radical affection on PFOA photodegradation, tert–butanol (t–BuOH), a typical hydroxyl radical inhibitor, was added in PFOA/Na_2SO_4 decomposition solution. t–BuOH, a typical •OH inhibitor, has been used to inhibit the activity of •OH. The effect of radical scavenger t–BuOH on PFOA decomposition was illustrated in figure 3. With UV/Na_2SO_4, the degradation of PFOA in the presence of t–BuOH was considerably reduced to about 45% after 24 hours irradiation. The reaction rate without t–BuOH was 1.5 times faster that with t–BuOH in the UV/Na_2SO_4 system. Comparison with previous literatures [12–13], this results are in a fair agreement with those conclusion. That confirms t–BuOH is an effective radical scavenger in the UV/Na_2SO_4 system.

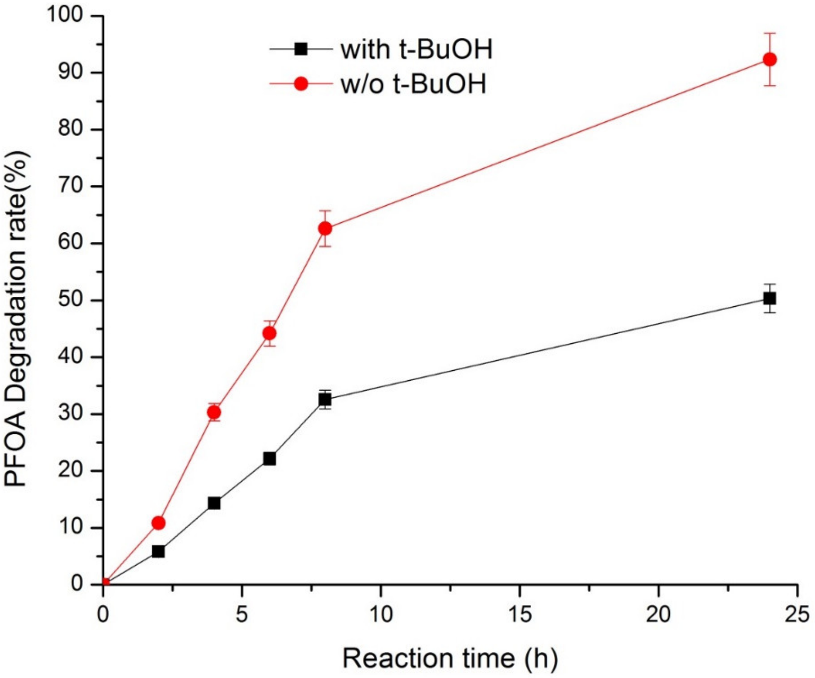

Figure 3. Photodegradation of PFOA effluent by radical scavenger t–BuOH.

3.4. Degradation of PFOA affected by reaction temperature

Solution temperature was controlled by water bath cycle at 15, 25, 35, and 45°C to evaluate the effects of solution temperature on the photodegradation of PFOA.

The result of photodegradation of PFOA affected by reaction temperature was shown in figure 4. UV/Na_2SO_4 system, the highest photodegradation rate was observed at 25°C. At 15°C, 35°C and 45°C, the photodegradation efficienies of PFOA were lower than those at 25°C. These results imply that the sulfate assisted UV treatment works best under ambient temperatures (25°C), while higher temperatures have an adverse effect irrespective of sulfate addition.

4. Conclusion

This study investigated the efficiency of PFOA photodegradation by UV/Na_2SO_4 system with different Na_2SO_4 concentrations, solution temperature levels, and presence of radical scavenger t–BuOH. The rate of PFOA degradation depend heavily on Na_2SO_4 dose. The effficiency of PFOA degradation in UV/Na_2SO_4 solution showed higher than it in UV irradiation only. The highest PFOA degradation efficiency obtains at Na_2SO_4 30mM, 25°C. The degradation of PFOA in the presence of t–BuOH was reduced. Photodegradation shows promised technique in treatment PFOA and other POPs, the presence of oxidants like SO_4^{2-}

(Na_2SO_4) will improve the efficiency of photodegradation. This study demonstrated that PFOA degradation can be effectively achieved through sulfate-assisted photochemical treatment at room temperature.

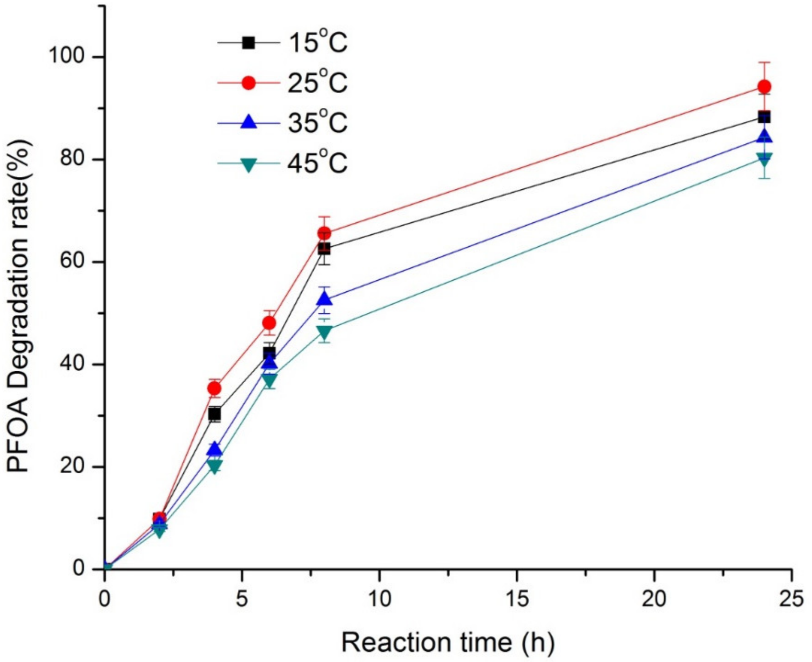

Figure 4. Photodegradation of PFOA at different temperature levels.

Acknowledgement

This research is funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 104.99–2018.37.

Author Contributions: The experiment was conducted by H.T.D., L.A.P.T., T.H.P.; the paper was written by H.T.D., L.A.P.T.

Conflicts of Interest: The authors declare no conflict of interest.

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