Separation and Purification Technology 91 (2012) 46–51

Contents lists available at SciVerse ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Effect of temperature on oxidative transformation of perfluorooctanoic acid (PFOA) by persulfate activation in water

C.S. Liu [a,b], C.P. Higgins [c], F. Wang [a], K. Shih [a,*]

[a] Department of Civil Engineering, The University of Hong Kong, Pokfulam Road, Hong Kong, PR China
[b] Guangdong Institute of Eco-Environmental and Soil Sciences, Guangzhou 510650, PR China
[c] Environmental Science and Engineering Division, Colorado School of Mines, Golden, CO 80401, USA

ARTICLE INFO

Article history:
Available online 2 October 2011

Keywords:
Perfluorochemicals
Oxidative degradation
Degradation mechanism
Sulfate radical
$S_2O_8^{2-}$

ABSTRACT

Perfluorooctanoic acid (PFOA) is an emerging environmental pollutant attracting significant attention due to its global distribution, high persistence, and bioaccumulation properties. In this study, the degradation of aqueous PFOA at different temperatures was examined using heat-activated persulfate. Using this approach, 93.5% of PFOA was degraded after 30 h at 85 °C with 43.6% of F^- yield, and the shorter chain length compounds (PFHpA ($C_6F_{13}COOH$), PFHxA ($C_5F_{11}COOH$), PFPeA (C_4F_9COOH), and PFBA (C_3F_7COOH)) were observed as degradation intermediates. The sequential degradation mechanism of losing one CF_2 unit from PFOA and its intermediates on a step-by-step basis were observed. Controlled temperature kinetics studies yielded an activation energy of approximately 60 kJ/mol for the degradation of PFOA by heat-activated persulfate. However, at elevated temperatures, excess persulfate is needed for efficient PFOA degradation, presumably due to more intensive $SO_4^{\cdot-}$ scavenging. Lower reaction pH was generally found to inhibit PFOA degradation, presumably due to the more prevalent radical-to-radical interactions.

1. Introduction

Due to the unique high surface activity, thermal and acid resistance, and hydro- and lipophobic properties, Perfluorochemicals (PFCs) have been used extensively in the electronics, engineering, chemical, and medical industries [1]. Recently, the global distribution of PFCs has received attention from both environmental and public health communities, as PFC accumulation in humans has led to increasing concerns over potential adverse human health outcomes [2–4]. Toxicology studies have suggested neurotoxic and immunotoxic effects [5,6], and the occurrence of some PFCs in source waters led the US Environmental Protection Agency (EPA) to issue Provisional Health Advisory (PHA) values for PFOA and perfluorooctane sulfonate (PFOS) in January of 2009 [7].

In the past 10 years, the development of technologies for the degradation of PFCs has received increased attention. However, PFCs are highly recalcitrant because the complete substitution of carbon–hydrogen bonds with carbon–fluorine bonds impart significant thermal stability (i.e., bond strengths for C_2F_5–F of 127 kcal/mol *vs.* C_2H_5–H of 101 kcal/mol, and CF_3–CF_3 of 99 kcal/mol *vs.* CH_3–CH_3 of 89 kcal/mol) with higher resistance to oxidation (i.e., $F + e^- \rightarrow F^-$, $E_0 = 3.6$ eV) [8]. This unique physicochemical property of PFCs makes them difficult to treat using most conventional advanced oxidation technologies (AOTs) [9,10].

Perfluorooctanoic acid (PFOA) is one of the most important PFCs that released from a wide range of commercial products [3], and no natural decomposition process for PFOA has been reported to date [11]. Advanced oxidation technologies (AOTs), including photocatalysis [12], UV photolysis [13], sonochemical decomposition [14], electrochemical decomposition [15], are currently the only potential approaches capable of degrading PFOA. However, due to the high degradation resistance of PFOA, different forms of very strong and exogenous energies have been needed in the processes to initiate or accelerate the decomposition [16]. Furthermore, most of these previous degradation investigations are characterized by very high PFOA concentrations (50 μM–67.3 mM; 20–27,000 mg/L) and extreme reaction conditions (e.g. highly acidic pH, under high pressure, etc.) [17]. However, PFOA concentrations in contaminated waters and wastewaters commonly range from ng/L to mg/L levels [17], and extreme reaction conditions may be useful only in some special cases. Therefore, the further exploration of treatment methods to effectively decompose PFOA under natural conditions will be more beneficial in the removal of environmental PFOA from our natural resources.

Persulfate ($S_2O_8^{2-}$) is a strong oxidant ($E_0 = 2.1$ eV) which is relatively stable during storage and handling and can also be activated to generate free sulfate radicals ($SO_4^{\cdot-}$) to achieve an even higher oxidative potential (2.6 eV) by various agents [18]. Due to this unique advantage, persulfate is now widely applied in *in situ* chemical oxidation (ISCO) remediation of contaminated environment with a wide range of organic pollutants [19–21]. Also

---

* Corresponding author. Tel.: +852 2859 1973; fax: +852 2559 5337.
E-mail address: kshih@hku.hk (K. Shih).

1383-5866/$ - see front matter
doi:10.1016/j.seppur.2011.09.047

because of its high reactivity, persulfate has been used in the attempts of degrading PFOA with activation methods of photolysis [22] and microwave [23]. However, substantial energy and extreme reaction conditions were adopted in these investigations and high PFOA initial concentrations (higher than mg/L level) were commonly used to achieve efficient decomposition. Heat-activated persulfate has been explored for PFOA degradation in a previous study [24], but the degradation mechanism(s) of PFOA by persulfate under different reaction conditions still needs further investigation, especially with a low PFOA concentration similar to the cases in natural environment.

In this study, we systematically investigated the oxidative degradation of aqueous PFOA by persulfate at elevated temperatures. The primary aim is to explore the PFOA transformation behavior by heat-activated persulfate at low PFOA concentrations. To achieve this goal, experiments were conducted to: (i) assess the influence of heat in the degradation process; (ii) identify major degradation byproducts and confirm the transformation pathway of PFOA; and (iii) evaluate the oxidative degradation of PFOA by activated persulfate under different reaction conditions.

2. Materials and methods

2.1. Chemicals

Sodium persulfate ($Na_2S_2O_8$, 98+% purity) and five perfluoroalkyl carboxylates, including perfluorooctanoic acid (PFOA, $C_8F_{15}HO_2$, 98%), perfluoroheptanoic acid (PFHpA, $C_6F_{13}COOH$, 98%), perfluorohexanoic acid (PFHxA, $C_5F_{11}COOH$, 98%), perfluoropentanic acid (PFPeA, C_4F_9COOH, 98%), and perfluorobutanoic acid (PFBA, C_3F_7COOH, 98%), were obtained from Sigma–Aldrich Co. (St. Louis, MO). All of the other chemicals were of analytical grade and purchased from BDH Chemicals (Poole, UK). All of the chemicals were used as received. The 18 MΩ cm water obtained from a Milli-Q water purification system was used to prepare the reaction solutions and the mobile phase for the chromatography analyses.

2.2. Experimental setup

Stock solutions of PFOA (5.0 μM; 2.1 mg/L) and sodium persulfate (20 mM) were prepared with 18 MΩ cm water and stored at 4 °C before used. The reactions were conducted in batch experiments in sealed polypropylene (PP) test tubes (40 mL), which were chosen for their superiority of less PFC sorption [17]. The reaction solution was prepared by introducing an appropriate amount of PFOA stock solution into water, controlling the initial PFOA concentration at 0.5 μM. The reaction pH was adjusted by adding 0.5 M NaOH or 0.5 M HCl as needed. After being heated to the preset target temperature, the reaction was initiated by adding the corresponding amount of sodium persulfate into the solution and then kept at constant temperature in oven. When investigating the effect of ferrous ions on PFOA degradation by persulfate, 1.0 mM ferrous sulfate was additionally introduced into the same reaction solution in the experimental procedure.

At the designated sampling time, a test tube was sampled and quickly cooled to room temperature by immersion in cold water (4 °C). For PFOA and intermediate measurements, a 1.5 mL sample solution was mixed with 3.5 mL methanol for better recovery in the ultra-performance liquid chromatography (UPLC) technique as indicated in previous work [17]. The mixture was then filtered through a 0.02 μm Whatman inorganic membrane (Kent, UK) and stored in a freezer of −20 °C before UPLC/MS/MS analysis. Control experiments were performed in the absence of persulfate, and each experiment was conducted in triplicate with the mean data values reported in the results.

The concentrations of PFOA were measured with a Waters Acquity UPLC/MS/MS system equipped with a 50 mm × 2.1 mm Waters BEH C18 column (1.7 μm particle size) and tandem quadrupole mass spectrometers (Milford, MA). Further details of the system modification and measurement procedures, such as PEEK tubes being substituted for transferring the solvents and samples in the UPLC system, the installation of an in-line isolator column, column temperature, mobile phase, and flow rate, etc., are provided in our previous work [17]. PFOA recoveries under the different analytical conditions have also been reported in another previous work [25]. The determination of possible intermediates was also conducted by the same UPLC/MS/MS system with their corresponding standard chemicals for calibration. The generations of fluoride and sulfate ions were determined by a Dionex ICS-90 IC (Sunnyvale, CA), with a mobile phase of 1.0 mM $NaHCO_3$–8.0 mM Na_2CO_3 aqueous solution at a flow rate of 1.0 mL/min, in which the quantitative detection limits of fluoride and sulfate ions were found to be 8.0 μg/L and 5.0 μg/L, respectively. Such results were obtained from the equation of $C_{\min} = C_s\,(3H_n/H)$, where $C_{\min}$ is the detection limit; C_s is the detected concentrations of targeted ions; H_n is the reference noise; and H is the peak height of the targeted ions. The concentration of persulfate ions were determined by a UV spectrophotometric method based on modification of the iodometric titration method [26]. Samples used for measuring fluoride and sulfate ions were cooled and directly filtered through a 0.2 μm Whatman inorganic membrane and stored in 4 °C refrigerator prior to analysis. All fluoride and sulfate ion analyses were conducted in duplicate.

3. Results and discussion

3.1. The degradation process of PFOA by activated persulfate in hot water

Among the various activation methods for persulfate, heat activation may be the easiest method for controlling the generation of radicals and was found to be more effective than iron for activation, which is a method widely studied and considered to be highly effective [18]. Without persulfate at 85 °C or with persulfate at 25 °C, PFOA concentrations were stable with no discernable degradation occurring throughout the testing period as indicated by Fig. 1a. As expected, F^- concentration was also not detected in the system as shown in Fig. 1b. When persulfate was present, PFOA degradation was observed with 93.5% of initial PFOA removed after 30 h. The decomposition of PFOA under this condition followed pseudo-first-order kinetics, with a rate constant of $9.15 \times 10^{-2}\ h^{-1}$ ($R^2 = 0.998$). Accompanied with the removal of PFOA, the mineralization product of F^- was detected, with increasing F^- levels as the reaction progressed. After 30 h, the amount of F^- was accumulated up to 3.27 μM, which corresponds to a 43.6% F^- yield (moles of F^- detected/moles of fluorine in initial PFOA).

In accordance with the observed degradation of PFOA, persulfate is expected to be thermally activated to form sulfate radical ($SO_4^{\cdot-}$), which may be consequently reduced and then accumulated as SO_4^{2-}. In Fig. 1c, the concentration of $S_2O_8^{2-}$ was found to decrease with the accumulation of SO_4^{2-} observed in the system, and such a trend was also followed closely by the decomposition of PFOA and the formation of F^- in the same reaction period. The sulfur balance of about 20 mM in total was well-maintained in the solution. After 30 h, the concentration of $S_2O_8^{2-}$ was reduced from initial 10 mM to 1.07 mM, and the concentration of SO_4^{2-} reached 16.79 mM: more than 80% of the sulfur content in the initial persulfate was transformed to sulfate ions. As the amount of generated $SO_4^{\cdot-}$ was about five orders of magnitude more than that of the transformed PFOA, this may be reflective of significant