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Reductive defluorination of perfluorooctanoic acid by hydrated electrons in a sulfite-mediated UV photochemical system

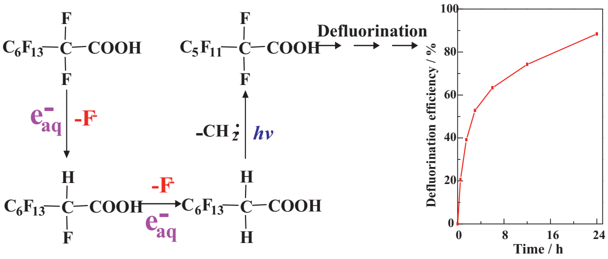
Zhou Song[a,b], Heqing Tang[a,*], Nan Wang[b,**], Lihua Zhu[b]

[a] Key Laboratory of Catalysis and Materials Science of the State Ethnic Affairs Commission and Ministry of Education, College of Chemistry and Materials Science, South-Central University for Nationalities, Wuhan 430074, PR China
[b] College of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, PR China

HIGHLIGHTS

- A new reductive method for PFOA defluorination was established by sulfite-mediated photolysis.
- The defluorination of PFOA was dependent on sulfite concentration and solution pH.
- A defluorination ratio of PFOA as high as 88.5% was achieved after reaction of 24 h.
- A few of perfluorinated sulfonates were detected as intermediates during the degradation of PFOA.
- A mechanism was proposed for the reductive defluorination of PFOA by hydrated electrons.

GRAPHICAL ABSTRACT



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ABSTRACT

A method for reductive degradation of perfluorooctanoic acid (PFOA) was established by using a sulfite/UV process. This process led to a PFOA removal of 100% at about 1 h and a defluorination ratio of 88.5% at reaction time of 24 h under N_2 atmosphere, whereas the use of either UV irradiation or $SO_3{}^{2-}$ alone induced little defluorination of PFOA under the same conditions. It was confirmed that the reductive defluorination of PFOA was achieved by hydrated electrons being generated from the photo-conversion of $SO_3{}^{2-}$ as a mediator. Theoretical reaction kinetic analysis demonstrated that the generation of hydrated electrons was promoted by increasing either $SO_3{}^{2-}$ concentration or solution pH, leading to the acceleration of the PFOA defluorination. Accompanying the reduction of PFOA, a small amount of short-chain perfluorocarboxylic acids, less fluorinated carboxylic acids and perfluorinated alkyl sulfonates were generated, all of which were able to be further degraded with further releasing of fluoride ions. Based on the generation, accumulation and distribution of intermediates, hydrated electrons induced defluorination pathway of PFOA was proposed in a sulfite-mediated UV photochemical system.

1. Introduction

Perfluorooctanoic acid ($C_7F_{15}COOH$, PFOA), as a main end-product during most perfluorinated compounds (PFCs) degradation through natural processes [1], has been recognized as a persistent organic pollutant and hence received much attention [2]. PFOA and its perfluorinated precursors are widely used as fire retardants, photolithographic film, carpet cleaners and paper coatings due to

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* Corresponding author. Tel.: +86 27 67843323; fax: +86 27 67843323.
** Corresponding author. Tel.: +86 27 87543632; fax: +86 27 87543632.
E-mail addresses: tangheqing@mail.scuec.edu.cn, hqtang62@aliyun.com (H. Tang), nwang83@sina.com (N. Wang).

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their unique hydrophobic and oleophobic properties [3–5]. As the use of PFCs has increased, some of them (typically, PFOA) have been detected in the environment across the globe [6,7]. Therefore, much effort has been devoted to eliminate its adverse effect on human health and ecosystem [3,7].

Several oxidative processes including direct photolysis [8,9], photochemical oxidation [9–12], and photocatalytic oxidation [13–17] have been employed to degrade PFOA. Although it was reported that photogenerated holes in In_2O_3 were efficient for decomposing PFOA, many of the reported processes showed slow defluorination rates of PFOA, probably because the electronegative fluorine substituents envelope completely the carbon skeleton and shield it from the chemical attack of $^{\bullet}OH$. In contrast, the strong electronegativity of fluorine atom(s) may act as the reductive reaction center(s) for defluorination. Moreover, since the toxicity and persistent of PFOA is closely related to the fluorine atoms, the cleavage of C—F bond is the critical step for eliminating its adverse effect. Thus, a reduction process may be a better alternative for the removal of PFOA.

Hydrated electron (e_{aq}^-) is a powerful reducing agent with a standard reduction potential of −2.9 V, and it can react rapidly with halogenated organic compounds [18]. Huang et al. [19] demonstrated the feasibility of the reaction between e_{aq}^- and PFOA by using the laser flush photolysis of $K_4Fe(CN)_6$ in aqueous solution, and estimated the second-order rate constant to be $1.7 \times 10^7\ M^{-1}\ s^{-1}$ for the reaction of e_{aq}^- with PFOA. Qu et al. [20] and Park et al. [21] investigated the e_{aq}^--induced photo-reductive defluorination of PFOA using KI as a mediator. However, these methods suffer from some problems such as the limited applications of laser flush photolysis in the practical treatment of massive PFOA and the potential insalubrious effect of iodides on humans [22]. Thus, it is required to find more economical, eco-friendly and massively operable reductive processes for the PFOA defluorination.

In the present work, we are focused on $SO_3{}^{2-}$-mediated photolysis, because it may function as an alternative source of e_{aq}^-. Fischer and Warneck reported that the photooxidation of hydrogen sulfite in aqueous solution could generate e_{aq}^- for hydrogen production [23]. Li et al. used a sulfite/UV process for the reductive dechlorination of monochloroacetic acid [24]. In this work, we firstly employed the sulfite/UV process to reduce PFOA, and achieved a defluorination ratio as high as 88.5% at reaction time of 24 h. Along with the investigation of the important reaction parameters, the mechanism of the PFOA degradation was also explored in detail.

2. Materials and methods

2.1. Materials

PFOA ($C_7F_{15}COOH$, 96%), heptafluorobutyric acid (PFBA, C_3F_7COOH, 99%) and pentafluoropropionic acid (PFPrA, C_2F_5COOH, 97%) were purchased from Acros (New Jersey, USA). Perfluoroheptanoic acid (PFHpA, $C_6F_{13}COOH$, 98%) was purchased from Alfa Aesar (Lancs, UK). Undecafluorohexanoic acid (PFHeA, $C_5F_{11}COOH$, 98%) and perfluoropentanoic acid (PFPeA, C_4F_9COOH, 98%) were purchased from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan). Trifluoroacetic acid (TFA, CF_3COOH, 99.0%) was purchased from Aladdin (Shanghai, China). Tridecafluorohexane-1-sulfonic acid potassium salt (PFHS, $C_6F_{13}SO_3K$, ≥98.0%), potassium nonafluoro-1-butanesulfonate (PFBS, $C_4F_9SO_3K$, 98.0%) and heptadecafluorooctanesulfonic acid potassium salt (TFOH, CF_3SO_3K, ≥98.0%) were purchased from Sigma–Aldrich (St. Louis, MO, USA). Analytical-grade reagents of sodium sulfite, ammonia solution, trisodium citrate, sodium nitrite and sodium nitrate were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All the reagents were used as received without further purification. Deionized water was used in the present work. N_2 gas with high purity of 99.99% was obtained from Minghui Gas Technology Co., Ltd. (Wuhan, China).

Table 1
The chosen *m*/*z* values for PFOA and its possible intermediates quantified by LC/MS in SIM mode.

Compound	*m*/*z*	Compound	*m*/*z*	Compound	*m*/*z*
$C_7F_{15}COOH$	413	$C_7F_{14}HCOOH$	395	$C_7F_{15}SO_3{}^-$	449
$C_6F_{13}COOH$	363	$C_7F_{13}H_2COOH$	377	$C_6F_{13}SO_3{}^-$	399
$C_5F_{11}COOH$	313	$C_6F_{12}HCOOH$	345	$C_5F_{11}SO_3{}^-$	349
C_4F_9COOH	263	$C_6F_{11}H_2COOH$	327	$C_4F_9SO_3{}^-$	299
C_3F_7COOH	213	$C_5F_{10}HCOOH$	295	$C_3F_7SO_3{}^-$	249
C_2F_5COOH	163	$C_5F_9H_2COOH$	277	$C_2F_5SO_3{}^-$	199
CF_3COOH	113	C_4F_8HCOOH	245	$CF_3SO_3{}^-$	149
		$C_4F_7H_2COOH$	227		
		C_3F_6HCOOH	195		
		$C_3F_5H_2COOH$	177		
		C_2F_4HCOOH	145		
		$C_2F_3H_2COOH$	127		
		CF_2HCOOH	95		
		CFH_2COOH	77		

2.2. Degradation experiment

The photolytic experiments were conducted in a cylindrical quartz photoreactor with an inner diameter of 58 mm and a length of 158 mm. A 10 W low-pressure mercury lamp (Philips) with emission at 254 nm was used to provide UV irradiation. The reaction temperature was kept at 25 °C by using a cooling water jacket around the reactor. After pH was adjusted with ammonia solution (1:1, V/V) or sulfuric acid ($0.1\ mol\ L^{-1}$), 200 mL of $20.0\ \mu mol\ L^{-1}$ PFOA aqueous solution was filled into the reactor. The reaction solution was purged with N_2 gas for 30 min to achieve oxygen-free condition. After adding the required amount of sodium sulfite, the solution pH was recorded and regarded as initial pH. Then, the degradation reaction was initiated by switching on the UV lamp. Samples were taken from the reaction solution at predetermined time intervals, followed by analysis. All degradation experiments were conducted in duplicate and the averaged values were presented as the results.

2.3. Analytical methods

PFOA and its degradation intermediates were analyzed by Waters 2695 HPLC system coupled with Waters Acquity TQD MS system. The sample separation was performed with a ZORBAX SB-C18 (150 mm × 4.6 mm, 5 μm). Mobile phase was composed of methanol and $5\ mmol\ L^{-1}$ ammonium acetate (pH 6.0) aqueous solution operated by increasing methanol from 40% to 80% in 10 min, holding on 5 min and then reverting to initial conditions within 2 min. Between two successive samples, the equilibration time was 5 min. The flow rate and injected volume were $0.2\ mL\ min^{-1}$ and 10 μL, respectively. Column temperature was kept at 40 °C. The electron-spray ionization conditions in the negative ion mode were as follows: capillary voltages 2.5 kV, the cone voltage 12 V, source temperature 120 °C, desolvation temperature 350 °C, and desolvation gas flow $550\ L\ h^{-1}$. Selected ion monitoring (SIM) mode was used for the quantitation of PFOA and its degradation products. The chosen *m*/*z* values were shown in Table 1.

H_2O_2 was measured by using a N,N-diethyl-p-phenylenediamine sulfate (DPD) method [25]. The DPD method is a spectrophotometric method for determination of H_2O_2 concentration in the solution, where DPD is oxidized by H_2O_2 in the presence of Horseradish peroxidase to form a colored product $DPD^{\bullet +}$, which has an absorption maximum at 551 nm wavelength. The concentration