



Nitrogen dioxide radicals mediated mineralization of perfluorooctanoic acid in aqueous nitrate solution with UV irradiation



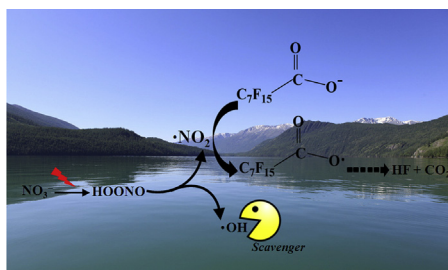
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HIGHLIGHTS

- An attractive strategy of $\cdot\text{NO}_2$ -mediated complete mineralization of PFOA developed.
- $\cdot\text{NO}_2$ generated by the photolysis of nitrate aqueous solution (UV/Nitrate).
- The feasibility of PFOA removal with $\cdot\text{NO}_2$ confirmed by DFT calculations.
- Prompted roles of hydroxyl radical scavengers explored for the degradation of PFOA.
- Near-stoichiometry of fluorides release and high TOC removal efficiencies realized.

GRAPHICAL ABSTRACT



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ABSTRACT

Effective decomposition of perfluorooctanoic acid (PFOA) has received increasing attention in recent years because of its global occurrence and resistance to most conventional treatment processes. In this study, the complete mineralization of PFOA was achieved by the UV-photolysis of nitrate aqueous solution (UV/Nitrate), where the in-situ generated nitrogen dioxide radicals ($\cdot\text{NO}_2$) efficiently mediated the degradation of PFOA. In particular, when the twinborn hydroxyl radicals were scavenged, the production of more $\cdot\text{NO}_2$ radicals realized the complete mineralization of PFOA. DFT calculations further confirm the feasibility of PFOA removal with $\cdot\text{NO}_2$. Near-stoichiometric equivalents of fluoride released rather than the related intermediates were detected in solution after decomposition of PFOA, further demonstrating the complete degradation of PFOA. Possible PFOA degradation pathways were proposed on the basis of experimental results. This work offers an efficient strategy for the complete mineralization of perfluorinated chemicals, and also sheds light on the indispensable roles of nitrogen dioxide radicals for environmental pollutants removal.

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1. Introduction

Perfluorooctanoic acid ($\text{C}_7\text{H}_{15}\text{COOH}$, PFOA) is a new environmentally persistent toxic and bioaccumulative pollutant, posing potential health and environment risks (Post et al., 2012). Over the last 60 years, PFOA has been extensively used in a variety of fields such as stain repellents, food packaging, and fire retardants (Hori

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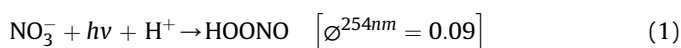
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et al., 2004; Key et al., 1997; Renner, 2001; Schultz et al., 2003), resulting in widespread contamination of various environmental and biological matrices including water, sediments, human blood, and wildlife (Asher et al., 2012; Houde et al., 2006; Lindstrom et al., 2011). Recent studies reveal that PFOA is associated with carcinogenicity, infertility, birth defects, and reduced immune function even at parts per million (ppm) levels (Betts, 2007a, 2007b; St Paul, 2002; Takagi et al., 1991). Owing to the strong electronegative property of fluorine and the abundant tightly-bonded fluorine atoms to carbon with high bond strength (i.e., 530 kJ mol⁻¹), PFOA could not be efficiently removed with most conventional degradation technologies, and even Fenton's reagents because of slow reaction rates between PFOA and hydroxyl radicals (Schroder and Meesters, 2005; Wardman, 1989; Vecitis et al., 2009; Das et al., 2013). Recently, Naidu et al. gave a comprehensive review on recent research of treatment technologies for aqueous perfluorooctanesulfonate and perfluorooctanoate, especially emphasizing field testing (Arias Espana et al., 2015). Non-hydroxyl radicals based advanced oxidation processes (AOPs), such as photochemical, sonochemical, electrochemical, and catalyzed hydrogen peroxide propagation approaches (Hori et al., 2005; Qian et al., 2016; Thi et al., 2013; Qu et al., 2010; Lyu et al., 2015; Zhang et al., 2014; Cheng et al., 2010; Lin et al., 2012; Xiao et al., 2011; Mitchell et al., 2014; Luo et al., 2015), have received much attention, because these processes could generate highly reactive species such as SO₄^{•-} (Hori et al., 2005; Qian et al., 2016), CO₃^{•-} (Thi et al., 2013), hydrated electron (e_{aq}⁻) (Qu et al., 2010; Lyu et al., 2015; Zhang et al., 2014), and perhydroxyl radical (HO₂[•]) (Mitchell et al., 2014), which were very effective to degrade PFOA. However, the generations of these reactive species have limitations mainly due to the harsh reaction conditions and/or complex procedures (Hori et al., 2005; Cheng et al., 2010; Lin et al., 2012; Xiao et al., 2011; Luo et al., 2015). Meanwhile, some undesired recalcitrant by-products might be generated from the reactions between these reactive species and PFOA. Therefore, it is still a great challenge to develop an economical and green chemical strategy for the complete degradation of PFOA.

Nitrogen dioxide radicals (•NO₂), a kind of commonly existing free radical, can be produced by combustion, microbial process, or the photolysis of nitrate aqueous solution. As nitrate usually exists in surface water (Byun et al., 1999; Carpenter et al., 1998), upon UV irradiation of surface water, some reactive nitrogen species (e.g. ONOO⁻, •NO₂, •NO) can be generated as follows (Eqs. (1)–(5)) (Mark et al., 1996; Vione et al., 2001, 2005).



Among the above reactive nitrogen species, nitrogen dioxide radicals (•NO₂) possess a strong oxidation ability. They can migrate towards the bulk solution and eventually lead to the decomposition of the pollutants, mainly through electron transfer (Vione et al., 2001), hydrogen abstraction (Cerón-Carrasco et al., 2015), or radical addition (Cerón-Carrasco et al., 2010). For example, nitrogen

dioxide radical (•NO₂) could oxidize oxyhemoglobin into methemoglobin (Unnikrishnan and Rao, 1995), or induce the lipid peroxidation (Byun et al., 1999), or prompt the phenol nitration (Vione et al., 2001), or participate in the relevant photo transformations of ionophore antibiotics (Sun et al., 2014), xenobiotics (Shankar et al., 2007), and nicotine (Passananti et al., 2014). Despite these advances, the reactions between •NO₂ and PFOA have never been studied before.

In this work, we utilize the UV-photolysis of nitrate aqueous solution (UV/Nitrate) to produce •NO₂, and then investigate the reactions between •NO₂ and PFOA systematically, aiming to develop a novel PFOA removal strategy. The influence of twinborn hydroxyl radicals during the photolysis of nitrate on the decomposition of PFOA is studied and the fluorine ions generated during the PFOA degradation are also monitored.

2. Experimental section

2.1. Chemicals and materials

PFOA (96% purity) was purchased from Aladdin Industrial Co. (Shanghai, China). Sodium nitrate, methanol, isopropanol, tert-butanol, and *p*-benzoquinone were from Sinopharm Chemical Reagent Company. High-performance liquid chromatography (HPLC) grade acetonitrile, methanol and ammonium acetate were from Fisher Scientific. Sodium carbonate anhydrous (99.8%) and sodium bicarbonate (99%) used for ion chromatography were obtained from Aladdin Industrial Corporation.

2.2. Reaction systems

An 80-mL quartz tube reactor equipped with a low-pressure mercury UV lamp (18 W, 254 nm) was used for the degradation of PFOA (5 ppm, 50 mL). The initial concentration of sodium nitrate aqueous solution was 100 mM and its initial pH value was 6.3. Control experiments were carried out with using deionized water instead of sodium nitrate aqueous solution. 2 mL of degradation solution was drawn at designed intervals for the subsequent analysis. *p*-benzoquinone (0.1 g/L) was added into the degradation solution to scavenge superoxide anion radical, and 600 μL of isopropanol, methanol or tert-butanol was used to remove hydroxyl radical. All the reactions were conducted at room temperature.

2.3. Instrumental analysis

The concentration of PFCAs was measured by Agilent 1290 high-performance liquid chromatography coupled with an Agilent 6410 triple-quadrupole mass spectrometer (Agilent Technologies, USA). 10 μL of the eluent was injected into an Agilent 1290 HPLC equipped with an Agilent ZORBAX Eclipse Plus C18 column (100 mm × 3.0 mm, 3.5 μm particle size). The column temperature was set at 40 °C. The flow rate was maintained at 0.3 mL/min; the mobile phase consisted of eluent A (10 mM ammonium acetate in deionized water) and B (acetonitrile). The eluent gradient started with 70% A for 1 min, then 10% A for 13 min and followed by another 14 min, ultimately back to 70% A for 15 min. The mass spectrometer was equipped with an electrospray ionization (ESI) source, operating in the negative ion mode with a capillary voltage of 4000 eV, 45 psi N₂ nebulizer gas at a flow of 6 L min⁻¹, N₂ collision gas, a temperature of 325 °C and a nozzle voltage of 500 V. Multiple reaction monitoring (MRM) mode was used to maximize the instrument performance. The parent ion, daughter ion, and collision energy (eV) for PFCAs detection were: PFOA (413 > 369, 5), PFHpA (363 > 319, 5), PFHxA (313 > 269, 3), PFPeA (263 > 219, 2),

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