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Hydrated electron based decomposition of perfluorooctane sulfonate (PFOS) in the VUV/sulfite system

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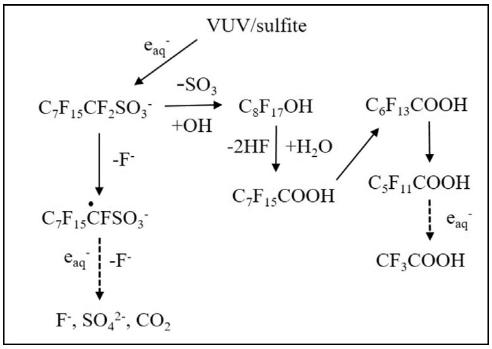
HIGHLIGHTS

- Fast reductive PFOS decomposition was achieved using the VUV/sulfite system.
- This system enhanced PFOS decomposition at weak acidic and alkaline conditions.
- Effective sulfite concentration was vital for PFOS decomposition efficiency.
- Two attacking ways were involved in the decomposition mechanisms.

GRAPHICAL ABSTRACT



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ABSTRACT

As one of the most reactive species, hydrated electron (e_{aq}^-) is promising for reductive decomposition of recalcitrant organic pollutants, such as perfluorooctane sulfonate (PFOS). In this study, PFOS decomposition using a vacuum ultraviolet (VUV)/sulfite system was systematically investigated in comparison with sole VUV and ultraviolet (UV)/sulfite systems. A fast and nearly complete (97.3%) PFOS decomposition was observed within 4 h from its initial concentration of 37.2 μM in the VUV/sulfite system. The observed rate constant (k_{obs}) for PFOS decomposition in the studied system was 0.87 ± 0.0060 h^{-1}, which was nearly 7.5 and 2 folds faster than that in sole VUV and UV/sulfite systems, respectively. Compared to previously studied UV/sulfite system, VUV/sulfite system enhanced PFOS decomposition in both weak acidic and alkaline pH conditions. In weak acidic condition (pH 6.0), PFOS predominantly decomposed via direct VUV photolysis, whereas in alkaline condition (pH > 9.0), PFOS decomposition was mainly induced by e_{aq}^- generated from both sulfite and VUV photolytic reactions. At a fixed initial solution pH (pH 10.0), PFOS decomposition kinetics showed a positive linear dependence with sulfite dosage. The co-presence of humic acid (HA) and NO_3^- obviously suppressed PFOS decomposition, whereas HCO_3^- showed marginal inhibition. A few amount of short chain perfluorocarboxylic acids (PFCAs) were detected in PFOS decomposition process, and a high defluorination efficiency (75.4%) was achieved. These results suggested most fluorine atoms in PFOS molecule ultimately mineralized into fluoride ions, and the mechanisms for PFOS decomposition in the VUV/sulfite system were proposed.

1. Introduction

Perfluorinated compounds (PFCs) are one of the anthropogenic organic chemicals those are characterized by a perfluorinated carbon

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chain attached with various functional groups (Jin et al., 2015). PFCs have been extensively applied in the manufactory of industrial and consumer products because of their excellent physicochemical properties, such as high surface activity, high thermal and chemical stability (Lindstrom et al., 2011). Perfluorooctane sulfonate (PFOS), one of the predominant families of PFCs, has received most environmental attention for its bioaccumulation, persistence and toxicity in the recent decade (Lee et al., 2017; Suh et al., 2017). Its production and use have been restricted in developed countries since 2000. Nevertheless, due to the incomplete restriction and increasing demands of PFCs related products, PFOS involved production and manufacturing are moving to and keeping rising in some developing countries (e.g. China) (Xie et al., 2013). As a consequence, PFOS has been widely detected in various environmental media, especially in wastewater which is an important conduit for the entry of PFOS into the environment (Higgins et al., 2005). PFOS concentrations were observed increasing in the water environment adjacent to PFOS involved industrial activities (Liu et al., 2017). Therefore, effective methods for onsite PFOS decomposition are of vital importance to alleviate its increasing release into the environment.

PFOS exhibits strong recalcitrance to biological and conventional oxidation treatments due to the high electronegativity of the fluorine atoms and the high strength of C—F bonds in its molecule (Jin et al., 2015). Some advanced treatment techniques, such as photochemical (Song et al., 2017), sonochemical (Moriwaki et al., 2005), electrochemical (Schaefer et al., 2017), subcritical Fe^0 reductive (Hori et al., 2006), and mechanochemical destruction (Zhang et al., 2013), have been employed to decompose PFOS. Amongst them, photochemical decomposition process is the most favored one because of its operational simplicity. However, direct ultraviolet (UV) photolytic PFOS decomposition showed slow kinetics because of its very weak absorption at 254 nm when using the traditional UV irradiation (Jin et al., 2014; Tian et al., 2016). Compared with UV irradiation ($\lambda = 254$ nm), vacuum ultraviolet (VUV) with a wavelength of 185 nm is considered more effective in pollutants decomposition due to the production of high-energy photons (647 kJ/mol) (Lee et al., 2012). Besides by direct VUV photolysis, organic pollutants can also be decomposed by the active species generated in water homolysis and ionization (Eqs (1)–(2)) (Gonzalez et al., 2004; Liu et al., 2016). One of the generated species, hydrated electron (e_{aq}^-), possesses high standard reduction potential of −2.9 V (Buxton et al., 1988), and is capable of efficiently decomposing halogenated organic pollutants (Gu et al., 2017; Li et al., 2012; Liu et al., 2014). It can act as a nucleophile when reacting with organic compounds. The reactivity can be greatly enhanced when organic molecules contain halogen atoms, leading to the cleavage of C-X bond and the release of halide ion (Buxton et al., 1988). Nevertheless, VUV photolysis showed marginal promotion on PFOS decomposition compared to UV photolysis (Yang et al., 2013). This shall be due to the small percentage of 185 nm light in the overall ultraviolet range (about 10%). Another responsible reason might be the easy absorption of VUV by water or the generated reactive species (Gonzalez et al., 2004). Besides through direct VUV photolysis, e_{aq}^- can also be produced by inorganic anions mediated UV photolysis (e.g. ferrous ion, iodide and sulfite) (Airey and Dainton, 1966; Qu et al., 2010; Song et al., 2013). UV/sulfite system was found comparatively a more efficient way to generate e_{aq}^- (Vellanki et al., 2013) (Eq. (3)). The reported e_{aq}^- quantum yield by 254 nm UV light was about 0.116 mol/einstein (Li et al., 2012). Since the UV/sulfite system already showed effective decomposition for PFOS (Gu et al., 2016) and the 185 nm VUV light also displayed appreciable decomposition for PFOS in alkaline condition, especially for branched PFOS (Jin and Zhang, 2015), the system combined with VUV and sulfite is supposed to can enhance e_{aq}^- generation and consequently achieves more efficient pollutant decomposition by making full use of both 185 and 254 nm UV light.

$$H_2O + h\nu \rightarrow {}^{\cdot}H + {}^{\cdot}OH \quad (1)$$

$$H_2O + h\nu \rightarrow H^+ + e_{aq}{}^- + {}^{\cdot}OH \quad (2)$$

$$SO_3{}^{2-} + h\nu \rightarrow SO_3{}^{\cdot -} + e_{aq}{}^- \quad \Phi = 0.116\ \text{mol/einstein} \quad (3)$$

In the presented study, a VUV/sulfite system configured with a low-pressure VUV lamp as the irradiation source was applied for decomposing PFOS. PFOS decomposition in the studied system was examined and compared with sole UV, sole VUV, and UV/sulfite treatments. Additionally, PFOS decomposition in the studied VUV/sulfite system was compared with VUV/persulfate and VUV/iodide treatments using the same VUV lamp. Studies on the effects of initial solution pH, sulfite dosage and some common co-present constituents (e.g. humic acid, NO_3^- and HCO_3^-) on PFOS decomposition were carried out. The role of e_{aq}^- was elucidated and possible decomposition mechanisms were explored. The outcomes of this study would be helpful for facilitating future applications of e_{aq}^- induced reduction techniques for efficient recalcitrant pollutants decomposition.

2. Materials and methods

2.1. Materials

Potassium perfluorooctane sulfonate ($C_8F_{17}SO_3K$, PFOS, 98%), perfluorooctanoic acid ($C_7F_{15}COOH$, PFOA, 96%), perfluoroheptanoic acid ($C_6F_{13}COOH$, PFHpA, 99%), perfluorohexanoic acid ($C_5F_{11}COOH$, PFHxA, 98%), potassium persulfate ($K_2S_2O_8$, >99%), methanol (CH_3OH, 99.5%), sodium bicarbonate ($NaHCO_3$, 99.8%), humic acid (HA, 90%), sodium sulfite (Na_2SO_3, 98%), sodium nitrate ($NaNO_3$, >99%), sodium hydroxide (NaOH, 96%), sulfuric acid (H_2SO_4, 98%) and potassium iodide (KI, >99%) were purchased from commercial sources (Sigma-Aldrich and Aladdin). N_2 and O_2 (>99.9%) used for purging in the reactions were obtained from Shenzhen Changlida Gas company. All the chemicals were used without further purification, and ultrapure water (Millipore Milli-Q) was used in all experiments.

2.2. Photochemical reaction procedures

The photo-decomposition experiments were conducted in a tubular glass reactor with inner diameter of 70 mm and height of 370 mm. A low-pressure mercury lamp (10 W, Philips) with λ_{max} at 254 nm and a minor emission at 185 nm (VUV) was placed in the center of the reactor with a quartz envelope (external diameter 25 mm). The other low-pressure mercury lamp (11 W, Philips) that emits only UV light at 254 nm (UV) with almost the same power was used for comparison. A magnetic stirrer was located at the bottom of the reactor to make good mixing (Fig. S1). The reaction temperature was maintained at 25 °C by a thermostatic water recirculation system. N_2 or O_2 was continuously purged into the reactor through a thin glass tube immersed into the solution at a flow rate of 1.0 L/min all the time.

In a typical photo-decomposition experiment, 800 mL mixture of PFOS (37.2 μM) and Na_2SO_3 (20 mM) was filled into the reactor. The initial PFOS concentration falls in a typical concentration range present in the untreated perfluorinated organic pollutants bearing industrial wastewater (Rayne and Forest, 2009). Besides the VUV/sulfite treatment, another four experiments were conducted. The first experiment was conducted with the presence of sulfite (20 mM) but without UV or VUV irradiation. Another two experiments were conducted with sole UV irradiation or sole VUV irradiation but without sulfite. The last experiment was conducted with both UV irradiation and 20 mM sulfite addition in the solution. Initial solution pH was 10.0 and not adjusted unless specified. For comparing the effectiveness of the studied VUV/sulfite system with other photo-oxidative or -reductive treatments, two experiments employing persulfate as the photochemical oxidant and iodide as the e_{aq}^- photo-exciting agent, respectively, were conducted using the same VUV lamp. The detailed solution conditions were described in Text S1.