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EB degradation of perfluorooctanoic acid and perfluorooctane sulfonate in aqueous solution

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Abstract Electron beam (EB) degradation of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) in aqueous solutions was studied. It suggested that PFOA and PFOS degradation followed the pseudo-first-order kinetics, and degradation rates increased with increasing initial pH. Radical scavengers' experiments indicated that hydrated electron and hydrogen radical were important in the electron beam degradation of PFOA and PFOS, especially hydrated electron. The decomposition efficiencies were 95.7% for PFOA and 85.9% for PFOS, by EB irradiation in an anoxic alkaline solution (pH = 13). The potential degradation pathways of PFOA and PFOS by electron beam irradiation through defluorination and the removal of CH_2 unit were proposed.

Keywords Perfluorooctanoic acid (PFOA) · Perfluorooctane sulfonate (PFOS) · Electron beam irradiation · Degradation · Defluorination

1 Introduction

Perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) are among the perfluorinated compounds (PFCs) that received a great deal of concern in recent years. Because of their extraordinary stability, hydrophobicity, oleophobicity and excellent surfactant performance, many PFCs have been widely applied to industrial and domestic production for over sixty years. PFOA and PFOS have been found almost ubiquitously in various environmental media including waters [1–4], air [5–7], sediments [8, 9], wildlife [10, 11] and human [12, 13]. Moreover, toxic and bioaccumulative effects of contaminants also have been confirmed by extensive studies [14–17]. These indicate that the toxic pollutants can accumulate in human body and may pose a risk to human health. As a result, PFOS was listed as a persistent organic pollutant under the Stockholm Convention in 2009, calling for restricted production and use worldwide.

Recently, the degradation of PFOA and PFOS has received increasing attention. Various techniques including adsorption [18, 19], photolytic methods [20–23], photo-electrocatalysis [24], ultrasonic irradiation [25, 26], thermolysis [27], gamma irradiation [28], etc. [29–33], were used to remove PFOA and PFOS. However, PFCs are chemically inert due to the unique properties of fluorine and relatively strong carbon–fluorine bond (C–F, 116 kcal/mol) making them resistant to conventional advanced oxidation processes. Therefore, new techniques are desirable to efficiently decompose PFOA and PFOS.

Electron beam (EB) irradiation has been recognized as effective method to treat organic pollutants [34–38]. Water is degraded into hydroxyl radicals ($^{\cdot}OH$), hydrogen radical ($H^{\cdot}$) and hydrated electron (e^{-}_{aq}) with different G-values

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(μmol/J) under EB irradiation as Eq. (1). The radicals react with the pollutants and cause their degradation [39]. While hydroxyl radical can oxidize the organic compounds in aqueous solutions, hydrogen radical and hydrated electron have reductive ability to reduce the targeted organic compounds [40, 41]. Hydrated electron is a strong reducing agent, reacting rapidly with halogenated organic compounds [41–44].

$$H_2O \rightarrow (0.28)e^-_{aq} + (0.06)H\cdot + (0.27)OH\cdot + (0.27)H^+ + (0.05)H_2 + (0.07)H_2O_2. \tag{1}$$

In the present study, the degradation kinetics of EB-irradiated PFOA and PFOS were determined. The effects of initial concentrations and initial pH on the degradation of contaminants were discussed. The roles of oxidative or reductive species in PFOA and PFOS degradation were investigated by selectively adding specific promoters or inhibitors, such as O_2, N_2 and tert-butanol (t-BuOH). Possible mechanisms of the radiolysis degradation of PFOA and PFOS were proposed. Our findings may bring an efficient and environmentally friendly technique for PFCs degradation.

2 Materials and methods

2.1 Materials

Perfluorooctanoic acid (PFOA, $C_8F_{15}HO_2$, 95.5%) and perfluorooctane sulfonate (PFOS, $C_8F_{17}SO_3K$, 98.0%) were supplied by Dr. Ehrenstorfer (Augsburg, Germany). Ammonium acetate (LC grade, 99%), fluoride standard (99.99%) and methanol (HPLC grade, 99.99%) were provided by Shanghai Anpel scientific instrument corporation. Sodium carbonate (Na_2CO_3), sodium bicarbonate ($NaHCO_3$), hydrogen chloride (HCl), sodium hydroxide (NaOH) and tert-butanol (t-BuOH) were purchased from Sinopharm Chemical Reagent Co., Ltd. All aqueous solutions were prepared by a Millipore Milli-Q system (resistance [18.2 MΩ]).

2.2 The samples and their irradiation

Four initial concentrations of PFOA and PFOS solutions in 100 mL polypropylene vessels were stored at 4 °C before use. Samples pouched in high-density polyethylene (HDPE) bags were irradiated to 100–500 kGy at ambient temperatures by 1.8 MeV electron beams of up to 10 mA. The samples were placed about 30 cm away under the beam-scan horn.

2.3 Analytical methods

Concentrations of PFOA, PFOS and their degradation products were determined by liquid chromatography–tandem mass spectrometry (LC–MS/MS) using an Agilent 1260 LC chromatograph coupled to an Agilent 6460 mass spectrometer with electron spray ionization (ESI) interface and a heated nebulizer. HPLC separation was carried out by ZORBAX SB-C18 reversed-phase column (4.6 × 50 mm, 5 μm, Agilent) and EC-C18 (3.0 × 100 mm, 2.7 μm, Agilent) at 40 °C using a gradient composition of solvent *A* (methanol) and solvent *B* (water containing 2 mmol/L of ammonium acetate). The injection volume was 5 μL. The gradient (%*A*) was as follows: 0–0.75 min, a linear increase from 5 to 60%; 0.75–5 min, increase to 92% *A*; 5–5.1 min, further increase to 100% *A*; 5.1–8.5 min, being held at 100% *A*; 8.5–9.0 min, the mobile phase returning to the initial conditions; and 9–10 min, being held at 5% *A*. The flow rate was 0.4 mL/min. Quantification was performed using multiple reaction monitoring (MRM) of the transitions m/z 499 → 80.1 (PFOS) and m/z 413 → 368.9 (PFOA). Mass spectrometry full scanning analysis (m/z 100–550) was used to identify the intermediate products of PFOS and PFOA after irradiation. The instrument conditions were as follows: capillary voltage, 4.0 kV; drying gas flow, 3 L/min; drying gas temperature, 350 °C; and source gas flow, 10 L/min; nebulizer pressure, 38 psi and nozzle voltage of 1 kV.

An ion-chromatograph system (Dionex ICS-1100, USA) was used to determine the concentration of F^-. It consisted of an automatic sample injector (sample injection volume 25 μL), a degasser, a pump, a guard column (Dionex AG22, 4 × 50 mm, USA), a separation column (Dionex AS22, 4 × 250 mm, USA), a column oven (30 °C) and a conductivity detector with a suppressor device. The mobile phase was composed of 4.5 mmol/L Na_2CO_3 and 1.4 mmol/L $NaHCO_3$, and the flow rate was set at 1.0 mL/min. The lowest detection limit of F^- was 0.02 mg/L.

3 Results and discussion

3.1 Kinetic studies of PFOA and PFOS under electron beam radiolysis

PFOA and PFOS aqueous solutions in initial concentrations of 10–40 mg/L were irradiated to 100–500 kGy. As shown in Fig. 1a, the PFOA and PFOS contents decreased with increasing doses. At initial concentrations of 10, 20, 30 and 40 mg/L, the PFOA degradation rates at 500 kGy were 63.6, 51.4, 48.2 and 41.7%, respectively; and the PFOS degradation rates were 57.1, 42.4, 35.5 and

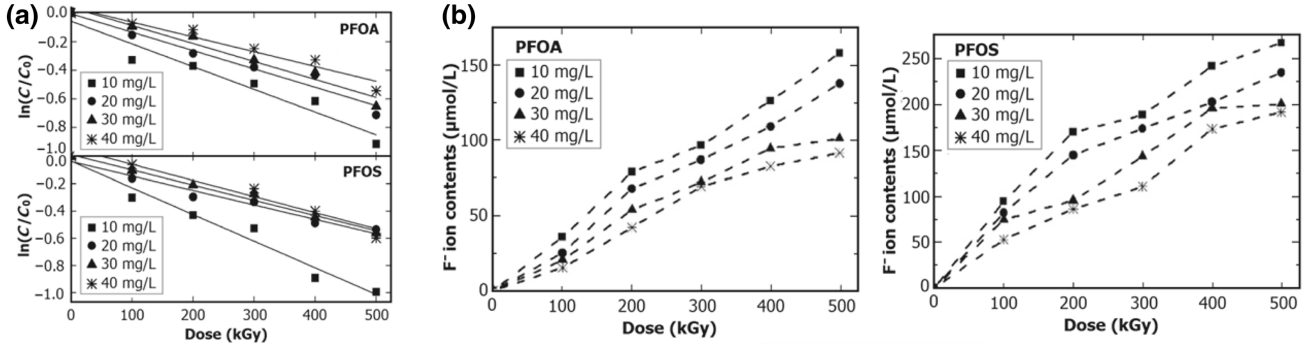

Fig. 1 Degradation kinetics (**a**) and fluoride ion release (**b**) of PFOA and PFOS in initial contents of 10–40 mg/L irradiated to 100–500 kGy

32.4%, respectively. These results indicate that PFOA and PFOS degradation rates decreased with increasing initial concentrations. The PFOA and PFOS concentration changing rate was plotted in natural logarithm versus the irradiation dose, and each of the data sets could be fitted linearly with $R^2 > 0.90$, suggesting that the EB degradation of PFOA and PFOS followed pseudo-first-order kinetics at different initial concentrations. Also, as shown in Fig. 1b, certain amounts of fluoride ions were detected at different doses, implying that the EB degradation of PFOA and PFOS was mainly through the defluorination.

3.2 Effect of initial pH on PFOA and PFOS degradation

Initial pH is an important factor in the degradation processes, as hydroxyl radicals, hydrated electron and hydrogen radical may react with OH^- and H^+ in aqueous solution. PFOA and PFOS aqueous solutions (20 mg/L) in initial pH 3–13 were irradiated to 100–500 kGy. The degradation (Fig. 2a) and the fluoride release (Fig. 2b) increased with the pH value. At pH13 and 500 kGy, the degradation rates of PFOA and PFOS were 88.1 and 63.4%, respectively; and the concentration of fluoride ions increased rapidly to 239.5 and 352.6 μmol/L with the corresponding defluorination percentage of 37.5 and 51.8%, respectively. Decomposition of PFOS is more difficult than that of PFOA, as oxidation of sulfonate to sulfate is more difficult. However, the generated fluoride ions concentrations of PFOS were slightly higher than those of PFOA. This can be attributed to hydrogen radical, which can be inverted into hydrated electron in alkaline condition, and the loss of hydrated electron in acidic condition, as shown in Eqs. (2) and (3). Thus, the solutions in alkaline conditions may be helpful to the degradation of PFOA and PFOS.

$$H\cdot + OH^- \rightarrow e_{aq}^- + H_2O, \tag{2}$$

$$e_{aq}^- + H^+ \rightarrow H\cdot. \tag{3}$$

3.3 Effect of radical scavengers on PFOA and PFOS degradation

In order to investigate which active species played the leading role in degradation of PFOA and PFOS, the aqueous solutions (20 mg/L) were saturated by N_2, O_2 and 0.1 mol/L tert-butanol with N_2. In N_2-saturated solution, hydroxyl radicals, hydrated electron and hydrogen radical were all existed and should be considered in the reactions process. It is well known that the reducing radicals hydrated electron and hydrogen radical can react with O_2 through Eqs. (4) and (5) and turn into activated radicals $O_2^{-\cdot}$ and HO_2. Hydroxyl radicals were the main reactive species in O_2 saturated solution. However, both hydrated electron and hydrogen radical existed in N_2-saturated solution containing 0.1 mol/L tert-butanol, because hydroxyl radicals were scavenged by tert-butanol, as shown in Eq. (6).

$$e_{aq}^- + O_2 \rightarrow O_2^-\cdot, \tag{4}$$

$$H\cdot + O_2 \rightarrow HO_2\cdot. \tag{5}$$

$$(CH_3)_3COH + OH\cdot \rightarrow H_2O + \cdot CH_2(CH_3)_2COH. \tag{6}$$

Figure 3 shows the degradation and fluoride release of PFOA and PFOS under the different conditions. At 500 kGy, the degradation rates were higher in N_2-saturated solutions, being 81.6% for PFOA and 71.3% for PFOS, and in N_2-saturated solution containing 0.1 mol/L tert-butanol, being 87.4% for PFOA and 76.9% for PFOS, while the degradation rates were low in O_2-situated solutions, being just 11.0% for PFOA and 8.7% for PFOS. For PFOA, the higher concentrations of fluoride ions were observed in N_2-situated solution (200.3 μmol/L) and N_2-saturated solution containing 0.1 mol/L tert-butanol (232.9 μmol/L) at 500 kGy, while it reached 27.5 μmol/L in O_2-saturated solution. Similarly, the formation of fluoride ions of PFOS showed the same trends as that of PFOA. Lower degradation rates and fluoride ions concentrations of PFOA and PFOS were observed in O_2-saturated solution indicated that

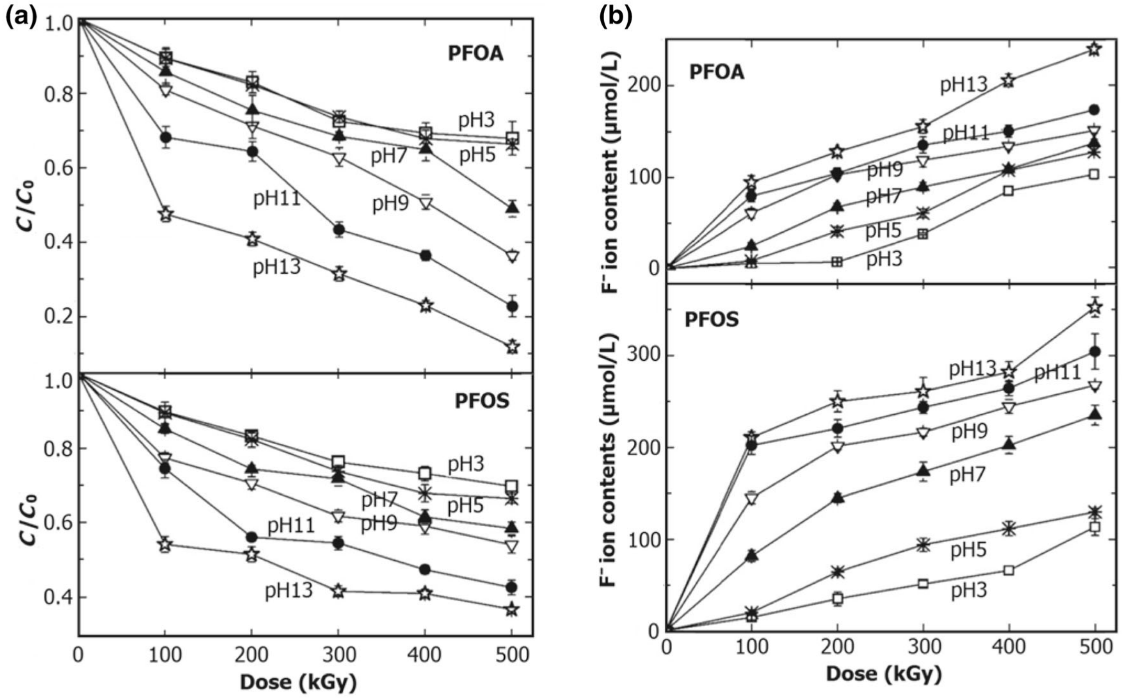

Fig. 2 Effects of initial pH on the decomposition (**a**) and fluoride release (**b**) of EB- irradiated PFOA (20 mg/L) and PFOS (20 mg/L)

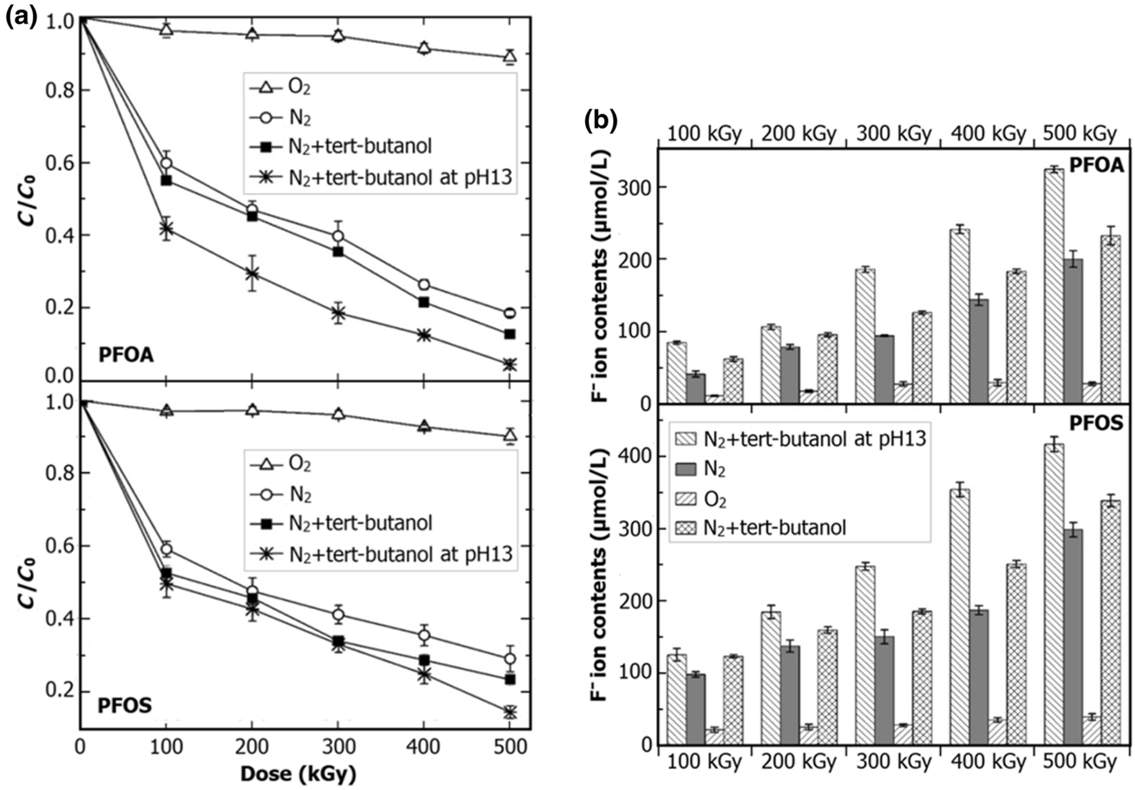

Fig. 3 Effects of scavenger on the decomposition (**a**) and fluoride release (**b**) of EB-irradiated PFOA (20 mg/L) and PFOS (20 mg/L)

hydroxyl radicals were not favorable for degrading PFOA and PFOS under electron beam irradiation. Consequently, higher degradation rates and concentrations of fluoride ions occurred in N_2-saturated solution and N_2-saturated solution containing 0.1 mol/L tert-butanol. Due to the strong reductive property and the relatively higher concentration of hydrated electron [41–43], we considered that hydrated electron, and hydrogen radical especially, played key roles in electron beam degradation of PFOA and PFOS.

Furthermore, the quantum yield of hydrated electron increases greatly in alkaline solutions as the transformation of hydrogen atoms into hydrated electrons, i.e., Eq. (2). As the results show, the PFOA and PFOS degradation rates and concentrations of fluoride ions are higher in alkaline condition. Thus, the effect of pH on PFOA and PFOS decomposition further implies that hydrated electrons play the key role in the decomposition of PFOA and PFOS.

In order to investigate the optimal EB degradation condition of PFOA and PFOS, the aqueous solutions (20 mg/L) were saturated by N_2 and adjusted to pH 13. The results are shown in Fig. 3. At 500 kGy, the degradation rates of PFOA and PFOS in nitrogen atmosphere were 95.7 and 85.9%, and their fluoride ion concentrations increased rapidly to 324.6 and 416.9 μmol/L, respectively, indicating that PFOA and PFOS in an anoxic alkaline solution are efficiently decomposed by EB irradiation.

3.4 Mechanism of PFOA and PFOS degradation by irradiation

PFOA, PFOS and their degradation products in the aqueous solutions were identified using LC–MS/MS method. The results are shown in Fig. 4. $C_7F_{14}HCOOH$, $C_6F_{12}HCOOH$, $C_5F_{10}HCOOH$, C_4F_9COOH, C_3F_7COOH, C_2F_5COOH, $C_7F_{14}HSO_3^-$, $C_6F_{12}HSO_3^-$, $C_5F_{11}SO_3^-$, $C_3F_7SO_3^-$, $C_2F_5SO_3^-$ and other intermediate products appeared after irradiation.

3.4.1 Mechanism of PFOA degradation by irradiation

Based on these results, a mechanism for PFOA degradation by EB irradiation is proposed in Fig. 5a. Under nitrogen atmosphere, the hydrated electrons attack PFOA, induce the fluoride elimination and react with hydrogen radical to yield the $C_6F_{13}CHFCOOH$ radical via Eqs. (7–9) [45, 46]. The electrophilic radicals are attacked by hydrated electrons to cause an intramolecular defluorination and react further with hydrogen radical to yield $C_6F_{13}CH_2COOH$, via Eqs. (10–12) [47, 48]. The generated $C_6F_{13}CH_2COOH$ can transform to $C_6F_{13}COOH$, via Eqs. (13) and (14) [46]. Other short-chain perfluorocarboxylic acid such as PFHxA, PFPA and PFBA is formed successively by similar reaction.

$$e_{aq}^- + C_7F_{15}COO^- \rightarrow C_7F_{15}COO\cdot^{2-}, \quad (7)$$

$$C_7F_{15}COO\cdot^{2-} \rightarrow C_6F_{13}C\cdot FCOO^- + F^-, \quad (8)$$

$$C_6F_{13}C\cdot FCOO^- + H\cdot \rightarrow C_6F_{13}CHFCOO^-, \quad (9)$$

$$C_6F_{13}CHFCOO^- + e_{aq}^- \rightarrow C_6F_{13}CHFCOO\cdot^{2-}, \quad (10)$$

$$C_6F_{13}CHFCOO\cdot^{2-} \rightarrow C_6F_{13}C\cdot HCOO^- + F^-, \quad (11)$$

$$C_6F_{13}C\cdot HCOO^- + H\cdot \rightarrow C_6F_{13}CH_2COO^-, \quad (12)$$

$$C_6F_{13}CH_2COOH \rightarrow C_6F_{13}\cdot + :CH_2 + COOH\cdot, \quad (13)$$

$$C_6F_{13}\cdot + COOH\cdot \rightarrow C_6F_{13}COOH. \quad (14)$$

3.4.2 Mechanism of PFOS degradation by irradiation

On the basis of the intermediate products identified, the possible degradation pathway of PFOS is proposed in Fig. 5b. The degradation pathway of PFOS is similar to that of PFOA. Reaction of PFOS with hydrated electron yields the radical anion $C_8F_{17}SO_3\cdot^{2-}$ via Eq. (15). The radical anion is decomposed by fluoride elimination and

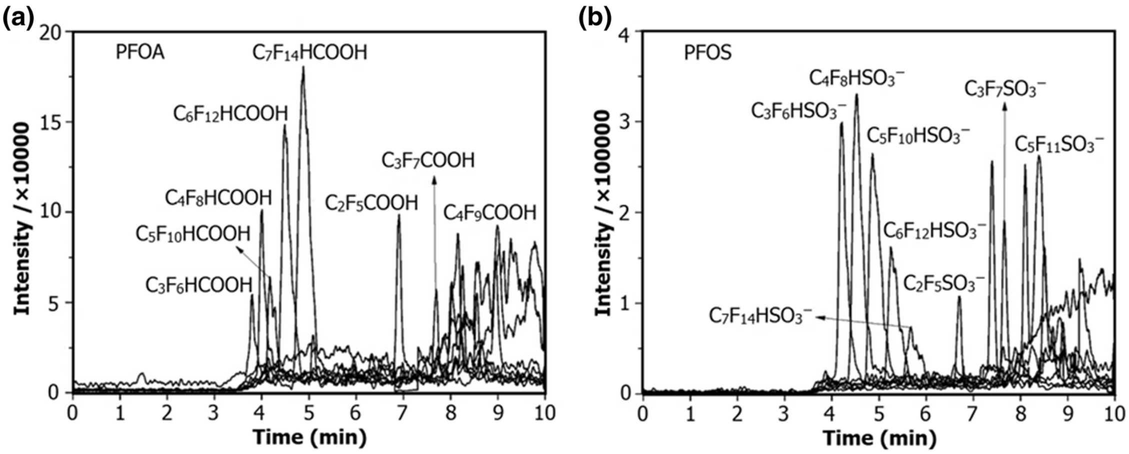

Fig. 4 MS of the intermediate products in PFOA (**a**) and PFOS (**b**) degradation by EB-generated e_{aq}^- radicals in aqueous solution

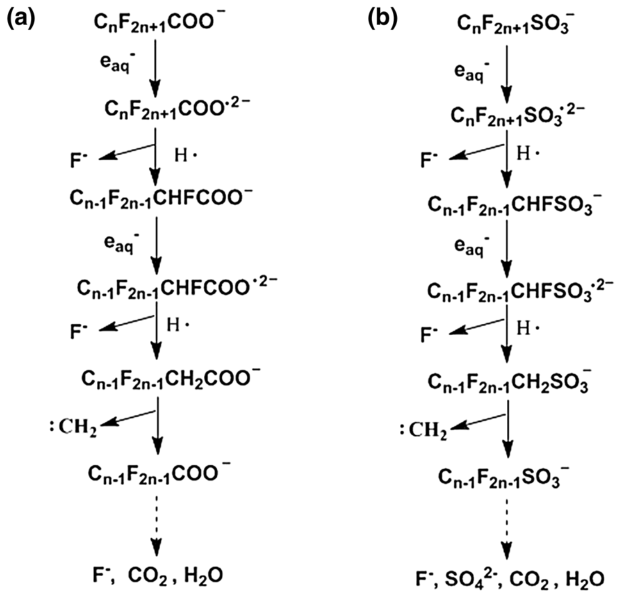

Fig. 5 Mechanism for decomposition of **a** PFOA and **b** PFOS by electron beam irradiation

reacts further with hydrogen radical to yield $C_7F_{15}CHFSO_3^-$ via Eqs. (16–19). The $C_7F_{15}CHSO_3{\cdot}^-$ may react with hydrogen radical to form $C_7F_{15}CH_2SO_3^-$, via Eq. (20) [48, 49]. The generated $C_7F_{15}CH_2SO_3^-$ transforms to $C_7F_{15}SO_3^-$ via Eqs. (21) and (22) and finally complete degradation.

$$e_{aq}^{-} + C_8F_{17}SO_3^{-} \rightarrow C_8F_{17}SO_3{\cdot}^{2-}, \tag{15}$$

$$C_8F_{17}SO_3{\cdot}^{2-} \rightarrow C_7F_{15}C{\cdot}FSO_3^{-} + F^{-}, \tag{16}$$

$$C_7F_{15}C{\cdot}FSO_3^{-} + H \rightarrow C_7F_{15}CHFSO_3^{-}, \tag{17}$$

$$C_7F_{15}CHFSO_3^{-} + e_{aq}^{-} \rightarrow C_7F_{15}CHFSO_3{\cdot}^{2-}, \tag{18}$$

$$C_7F_{15}CHFSO_3{\cdot}^{2-} \rightarrow C_7F_{15}C{\cdot}HSO_3^{-} + F^{-}, \tag{19}$$

$$C_7F_{15}C{\cdot}HSO_3^{-} + H{\cdot} \rightarrow C_7F_{15}CH_2SO_3^{-}, \tag{20}$$

$$C_7F_{15}CH_2SO_3^{-} \rightarrow C_7F_{15}{\cdot} + \ddot{C}H_2 + SO_3{\cdot}^{-}, \tag{21}$$

$$C_7F_{15}{\cdot} + SO_3{\cdot}^{-} \rightarrow C_7F_{15}SO_3^{-}. \tag{22}$$

The proposed degradation mechanisms of PFOA and PFOS were different from previous studies [23, 28, 30, 50]. The present degradation mechanisms have two main differences from those in Ref. [50]. One is the main reactive species. While the hydroxyl radical took part in the mineralization process, hydrated electron and hydrogen radical played key roles in the EB degradation, especially hydrated electron. Another is the main reaction pathway. In electrolysis system, ·OH-initiated process was the main degradation pathway, and decarboxylation reaction occurred on anode first in electrolysis system. However, direct defluorination was the important pathway in electron beam degradation.

4 Conclusion

Electron beam radiolysis of PFOA and PFOS was performed. The degradation of PFOA and PFOS followed the pseudo-first-order kinetics. At 500 kGy, the degradation rates of PFOA and PFOS in N_2 atmosphere were 95.7 and 85.9% at pH13, and the fluoride ion concentration rapidly increased to 324.6 and 416.9 μmol/L with corresponding defluorination rates of 46.8 and 71.4%, respectively. The results showed that PFOA and PFOS could be efficiently decomposed by EB irradiation in an anoxic alkaline solution. The work with radical scavengers demonstrated hydrated electron, and hydrogen radical especially, played key roles in EB degradation of PFOA and PFOS. Based on effects of the radicals and detected intermediate products, the EB degradation pathways of PFOA and PFOS were proposed. Further work may include adding catalyst to improve the degradation efficiencies at low dose, and toxicity of PFCs by-products.

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