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Complete mineralization of perfluorooctanoic acid (PFOA) by γ-irradiation in aqueous solution

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Decomposition of perfluorooctanoic acid ($C_7F_{15}COOH$, PFOA) has been gaining increasing interests because it is a ubiquitous environmental contaminant and resistant to the most conventional treatment processes. In this work, the rapid and complete mineralization of PFOA and simultaneous defluorination were achieved by γ-ray irradiation with a ^{60}Co source. The degradation rate of PFOA by γ-ray irradiation would be high, and a pseudo-first-order kinetic rate constant of 0.67 h^{-1} could be achieved in the N_2 satured condition at pH 13.0. The experimental results and quantum chemical calculation confirmed that two radicals, i.e., hydroxyl radical ($\cdot OH$) and aqueous electrons (e_{aq}^-), were responsible for the degradation of PFOA, while only either e_{aq}^- or $\cdot OH$ might not be able to accomplish complete mineralization of PFOA. The synergistic effects of $\cdot OH$ and e_{aq}^- involved in the cleavage of C-C and C-F bonds, and therefore complete mineralization of PFOA were achieved. The intermediate products were identified and the degradation pathway was also proposed. The results of this study may offer a useful, high-efficient approach for complete mineralizing fluorochemicals and other persistent pollutants.

A class of fully fluorinated hydrocarbons known as perfluorocarboxylic acids (PFCAs, $C_nF_{2n+1}COOH$) has been widely applied in various ranges for several decades. They are receiving increasing attention because of their easy bioaccumulation and persistent toxic environment impact. Perfluorooctanoic acid ($C_7F_{15}COOH$, PFOA), as a PFCA has already been detected in environment waters, human bodies and wildlife[1–4]. As a ubiquitous environmental contaminant, PFOA has the following features: extremely resistant degradation, bioaccumulation in food chains, and long half-lives in human bodies, all of which present characteristics of persistent organic pollutants[5–6]. The major human exposure sources to PFOA and other PFCs include drinking water[7] and edible fish[8] etc, and can lead to several chronic and developmental problems, such as children attention deficit/hyperactivity disorder[9] and lowered immune response to vaccinations[10]. Statistic survey shows that its concentration in human bodies and wildlife continues to increase in certain location globally[11].

However, PFOA is very stable and considered almost non-biodegradable under natural environments because of the strong C-F bonds (116 kcal/mol). Besides, some researchers reported that PFCAs could almost not be degraded by advanced oxidation process. The principal reason may be that C-F bonds can't be destroyed effectively by hydroxyl radicals ($\cdot OH$)[12–13]. Various treatments for PFCAs including adsorption[14], photocatalysis[15–16], photolysis[17], thermolysis[18], sonochemical[19] and other methods[20–21] have been tested for decomposing PFCAs. However, harsh reaction conditions at high temperatures and high pressures are usually needed[18–19]. Furthermore, the mineralization and defluorination of PFCAs always could not be achieved completely, and toxic by-products might be formed during the decomposing processes[12]. Thus, it is highly desirable not only to decompose the PFCAs, but also to defluorinate the toxic by-products for complete mineralization of PFCAs. A novel method for PFCAs mineralization with high efficiency is still highly desired.

It is well-known that γ-ray irradiation can also degrade persistent organic pollutants efficiently owning to the production of active species, e.g., $\cdot OH$ and e_{aq}^-, which make γ-ray irradiation a promising method for wastewater and sludge treatment[22–23]. Also, it has several unique advantages, and especially it needs no additional chemicals to fully complete mineralization of pollutants[24–26]. When aqueous solutions are irradiated with γ-ray, water will absorb most of the radiation and produce several activated species, in which $\cdot OH$ and e_{aq}^- are predominant, as shown in Eq. 1. The numbers in brackets are the yields (μmol/J) of those species per unit of radiation at pH 7.0[27]. However, it has not been reported whether PFCs could be mineralized efficiently by γ-ray irradiation or not.

$$H_2O \rightarrow e_{aq}^- (0.27) + \cdot OH(0.28) + H_2O_2(0.07)$$
$$+ H\cdot(0.06) + H_2(0.05) \tag{1}$$
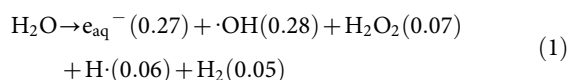
Therefore, in this work, the efficiency of the radiation-induced degradation and defluorination of PFOA in aqueous solution by a [60]Co γ-source was explored. The mineralization mechanisms of PFOA and the crucial roles of $\cdot$OH and e_{aq}^- generated were also investigated. To be the best of our knowledge, this might be the first report about the degradation of PFOA by γ-ray irradiation. The results would bring an efficient and environmentally friendly technique for PFCAs degradation.

Results and Discussion

Mineralization of PFOA by γ-ray irradiation. The degradation of PFOA by irradiation at various pH values is shown in Figure 1. The degradation efficiency of PFOA increased with the increasing pH value. At pH < 7.0, PFOA could not be decomposed efficiently. However, at pH 13.0 the degradation efficiency could reach almost 100% after 6-h irradiation. Also, the defluorination efficiency was also nearly 100% at pH 13.0 (Figure 1B). Furthermore, the released F$^-$ concentration also decreased with the decreasing pH. At pH < 7.0, almost no F$^-$ could be detected. This might be attributed to the loss of e_{aq}^- through Eq. 2:

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

e_{aq}^- ($E^0 = -2.9$ eV) was a much stronger reducing agent than H$\cdot$ ($E^0 = -2.1$ eV), and might play a more important role in the degradation of PFOA rather than H$\cdot$.
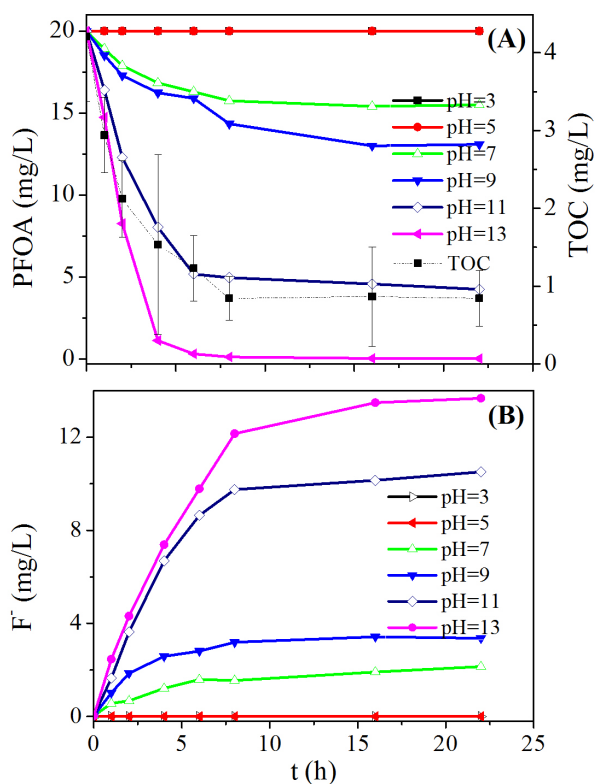
Total organic carbon (TOC), as an important index of mineralization, decreased from 4.2 mg/L to 0.6 mg/L after 22-h irradiation at pH 13.0 (Figure 1A). The mineralization degree of PFOA was around 86%, meanwhile the defluorination ratio was nearly 100%, indicating that most of the PFOA was degraded to CO_2, fluorine ion and water. The high efficiency of defluorination and TOC removal implies that nearly all the C-F and C-C bonds in PFOA could be broken by γ-ray irradiation.

High degradation kinetics of PFOA by γ-ray irradiation. To compare the degradation rate of PFOA by γ-ray irradiation at various conditions, a pseudo-first-order kinetic model was used to describe the degradation kinetics:

$$dC/dt = -kC \tag{3}$$

$$\ln(C/C_0) = -kt \tag{4}$$

where C and C_0 are the representative PFOA concentrations at time t and at initial. k is the apparent first-order rate constant. The linear regression between $\ln(C/C_0)$ vs t under various conditions is shown in Figure 2. The high correlation coefficiencies at various pHs indicate that the pseudo-first-order kinetic model was appropriate to describe the degradation of PFOA by γ-ray irradiation.

The degradation of PFOA could be promoted in an alkaline medium. As Table 1 shows, the linear fit of the kinetic plots gives $k_7 = 0.034$ h^{-1}, $k_9 = 0.043$ h^{-1}, $k_{11} = 0.199$ h^{-1} and $k_{13} = 0.654$ h^{-1} at pH 7.0, 9.0, 11.0 and 13.0, respectively. The high PFOA degradation rate constant at pH 13.0 was about 20 times of that at pH 7.0, and 15 times of that at pH 9.0. Furthermore, the degradation rate constants in this study were much higher than those reported previously by other methods[28–30], indicating that the γ-ray irradiation is efficient for the PFOA decomposition.

Roles of e_{aq}^- and $\cdot$OH in the PFOA degradation. Preliminary experimental results show that PFOA is degraded and defluorinated efficiently in alkaline solution under N_2-saturated conditions. The most likely active species responsible for the degradation of PFOA are $\cdot$OH and e_{aq}^- according to Eq. (1). To investigate the contributions of the activated species produced by the γ-ray on the degradation of PFOA, PFOA samples were irradiated with the dose of radical scavengers (e.g., t-BuOH and H_2O_2), under N_2- or O_2-saturated conditions respectively (Table 2). The dose of scavenger was able to confirm which
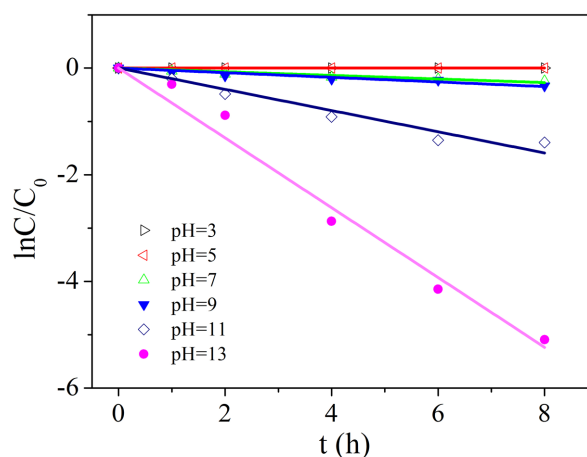

Figure 1 | (A) PFOA degradation by γ-ray at various pHs. The dotted line shows the change of TOC of the solution during irradiation at pH 13.0; and (B) Concentrations of F$^-$ released into the solution at various pHs.

Figure 2 | **PFOA degradation kinetics at different pHs.** The lines were regressed using the pseudo-first-order kinetic model.

Table 1 | The pseudo-first-order apparent degradation rate constants and half times of PFOA by γ-ray irradiation at various pH values

pH	k (h^{-1})	$\tau_{1/2}$ (h)	R^2
7.0	0.034	20.39	0.887
9.0	0.043	16.12	0.900
11.0	0.199	3.48	0.951
13.0	0.654	1.06	0.981

Figure 3 | **Effects of addition of t-BuOH on the degradation and defluorine of PFOA.** The samples were irradiated for 12 hours in N$_2$-saturated atmosphere and at pH 13.0.

activated species was crucial in the PFOA decomposition or defluorination. As shown in Table 2, after 22-h reaction, in the presence of H$_2$O$_2$ or O$_2$, PFOA seemed to be resistant to γ-ray irradiation, and no degradation or defluorination of PFOA could be detected after irradiation. This implies that the radicals eliminated by H$_2$O$_2$ or O$_2$ were essential for the degradation and defluorination of PFOA. It is well known that the reducing radicals e$_{aq}^-$, would react with O$_2$ and H$_2$O$_2$ through Eqs. 5 and 6, and turned into weak activated radicals O$_2^-$· and HO$_2$·. Consequently, e$_{aq}^-$ should be the crucial radical for the cleavage of both C-C and C-F bonds, and PFOA can't be degraded by ·OH radical only.

$$e_{aq}^- + O_2 \rightarrow O_2^- \cdot \tag{5}$$

$$e_{aq}^- + 2H_2O_2 \rightarrow HO_2 \cdot + H_2O + OH^- \tag{6}$$
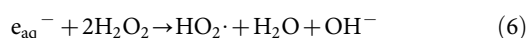
t-BuOH, a ·OH scavenger, was added to the PFOA solutions before irradiation. As shown in Figure 3, with the increasing t-BuOH concentration, less F$^-$ was released. With the addition of 100 mmol/L t-BuOH, little F$^-$ could be detected after irradiation. However, it was surprising to find that the degradation efficiency of PFOA was nearly 100% no matter how much t-BuOH was dosed. These results imply that C-F bond could not be broken efficiently in the absence of ·OH. With the decrease in t-BuOH dosage, the amount of ·OH in the aqueous sample gradually increased, and more F$^-$ could be found in the solution after irradiation. These results show that both ·OH and e$_{aq}^-$ were responsible for the degradation of PFOA by γ-ray irradiation.

Mechanism of PFOA decomposition by irradiation. The decomposition products of PFOA in the aqueous solutions were identified using LC-MS method, and the results are shown in Figure 4, while the mass spectra of various intermediated products are shown in Figure S1. It was observed that the concentrations of PFHpA (C$_6$F$_{13}$COOH), PFHxA (C$_5$F$_{11}$COOH) and other intermediate products increased at initial after irradiation, but decreased gradually. After 22-h degradation, all these intermediate products were degraded.

On the basis of the products identified, the possible degradation pathway of PFOA was proposed and is illustrated in Figure 5. DFT simulations were used to investigate the thermodynamic perform-
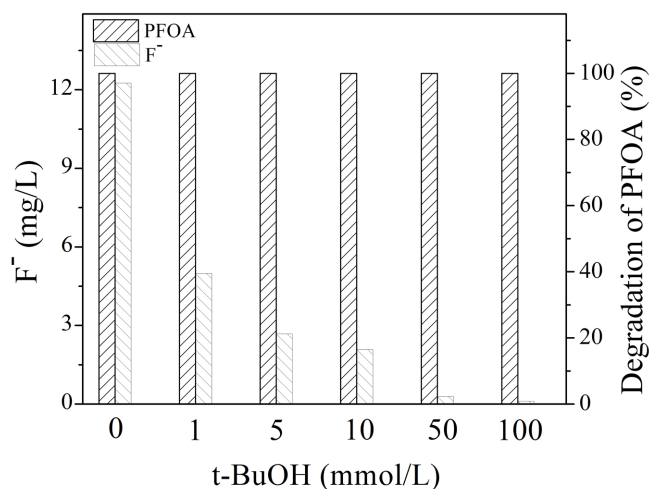
ance for the reactions of e$_{aq}^-$ and ·OH at different sites on PFOA molecule. Configurations of the initial reactants and intermediate products are shown in Figure S2. And the structural parameters of the reactive sites through the degradation process are presented in Table S1. PFOA (C$_7$F$_{15}$COO$^-$) was considered to be degraded to short-chain PFHpA (C$_6$F$_{13}$COO$^-$), through a series of reactions (Table 3). At the beginning, the e$_{aq}^-$-mediated reduction occurs at the carbonyl group with a subsequent loss of HO$^-$ and CO, yielding an alkyl radical, or in this case a fluoroalkyl radical (C$_6$F$_{13}$CF$_2$·, Table 3). The negative Gibbs free energy change ($\Delta G^\theta = \Delta G_1^\theta + \Delta G_2^\theta + \Delta G_3^\theta = -3.059$ eV) of the initial three steps indicates that the generation of C$_6$F$_{13}$CF$_2$· from C$_7$F$_{15}$COO$^-$ is thermodynamically favored according to the DFT calculations (Table 3). The bond lengths of C$_7$-F$_{14}$ and C$_7$-F$_{15}$ decrease with the bond angle of F$_{14}$-C$_7$-F$_{15}$ increasing (Table S1). Following this, the radical C$_6$F$_{13}$CF$_2$· in aqueous solution will react with ·OH to form unstable alcohol C$_6$F$_{13}$CF$_2$OH, which undergoes HF elimination to form C$_6$F$_{13}$COF with ΔG_5^θ of -0.116 eV. After that, ·OH will attack and cleave the C = O bond to form another radical C$_6$F$_{13}$CF(OH)O·, which can be easily attacked by e$_{aq}^-$. Then, PFHpA (C$_6$F$_{13}$COO$^-$) is formed by releasing the HF. The generated PFHpA can also undergo this process to be degraded to PFHxA (C$_5$F$_{11}$COO$^-$), as shown in Figure 5. By repeating this CF$_2$-unzipping cycle, PFOA could be completely decomposed to CO$_2$ and F$^-$.

In the alkaline aqueous solution, ·OH may be converted to O·$^-$ for the pKa value of ·OH is 11.9[31], and H$^+$ was scavenged by OH$^-$. The thermodynamic properties for the reactions of e$_{aq}^-$ and O·$^-$ with PFOA molecules were calculated and listed in Table S2. The steps 2, 4–7 of ·OH degradation pathway in Table 3 were replaced by the

Table 2 | Degradation efficiency of PFOA after 22-h irradiation at different conditions

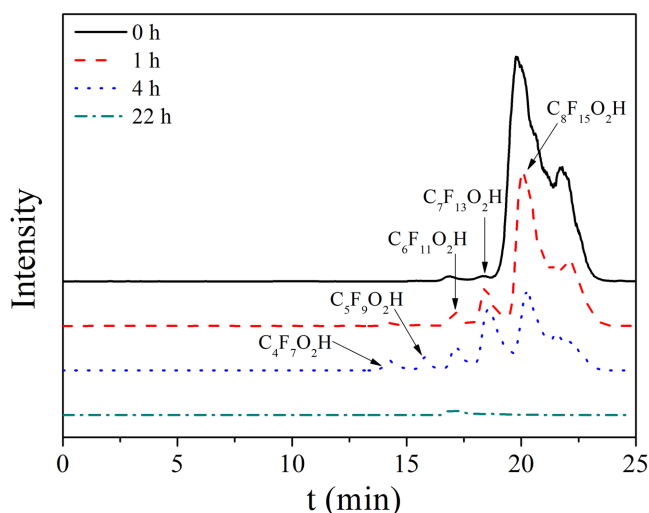|		N$_2$			O$_2$		
	Radical scavenger	pH = 3.6	pH = 7.0	pH = 13.0	pH = 3.6	pH = 7.0	pH = 13.0
Degradation efficiency of PFOA (%)	N/A	0.5	22.5	99.9	0.3	0.1	0.2
	t-BuOH (100 mM)	0.1	20.3	99.3	0.2	0.5	0.0
	H$_2$O$_2$ (100 mM)	0.6	0.7	0.4	0.3	0.5	0.2
Concentration of F$^-$ released (mg/L)	N/A	0.3	2.1	13.7	0.0	0.0	0.0
	t-BuOH (100 mM)	0.0	1.4	3.1	0.0	0.0	0.1
	H$_2$O$_2$ (100 mM)	0.0	0.0	0.0	0.0	0.0	0.0

Figure 4 | LC-MS of the intermediated products of shorter-chain perfluorocarboxyl anions including $C_3F_7COO^-$ (PFBA), $C_4F_9COO^-$ (PFPeA), $C_5F_{11}COO^-$ (PFHxA), and $C_6F_{13}COO^-$ (PFHpA) at various irradiation times.

Figure 5 | Proposed PFOA degradation pathway with synergies of ·OH ($O^{·-}$) and e_{aq}^- generated by γ-ray irradiation.

steps O2, and O4 ~ O7 in Table S2 in the Supplementary information. The DFT calculation indicates that the PFOA degradation could also occur spontaneously in the alkaline solution with the synergistic effects of e_{aq}^- and $O^{·-}$ generated by γ-ray irradiation. The possible degradation pathway of PFOA by $O^{·-}$ and e_{aq}^- is also illustrated in Figure 5.

Furthermore, some possible alternative reactions for PFOA degradation are also investigated, as listed in Table S3. Configurations of the possible intermediate products are shown in Figure S3. The thermodynamic properties of PFOA degradation individually by radical e_{aq}^- or ·OH in aqueous solution were calculated. The results agreed well with the experimental results, i.e., only either e_{aq}^- or ·OH might not be able to accomplish complete mineralization of PFOA.

Limitations and future research. Use of γ-ray irradiation for wastewater and contaminated sludge treatments is a promising treatment technology[22–23]. The disinfection of sludge for beneficial reuse has been demonstrated at full scale using γ-ray irradiation[32]. And a lab scale wastewater treatment system using γ-ray irradiation directly is being developed[33–35]. But people are sensitive about the safety of γ-ray irradiation used for water treatment. The radiation leaks may affect health issues for γ-rays are biologically hazardous. Therefore, protection and safety measures for sources must be made in a way that they can be regularly monitored and verified for safety, and the consummate management ensures the safety of radiation application for wastewater treatment. There are a number of features that make γ-ray irradiation an attractive process to pursue for eventual application. For example, the process requires no additional chemicals and does not leave any hazardous residues (chemical or radioactive). Both oxidizing and reducing reactive species, such as e_{aq}^- and ·OH, are formed in relatively the same proportion in aqueous media. Moreover, the process is rapid and logistically simple, allowing for maximum flexibility in plant design. In future researches, as a promising approach, γ-ray irradiation will be applied to facilitate the degradation of other persistent organic pollutants, such as polychlorinated biphenyls etc. Furthermore, radiation processing using electron beam accelerator or alpha radiation with the same advantages as γ-ray irradiation, but controllable and safe, could be used in the wastewater treatment for achieving practical industrialization.
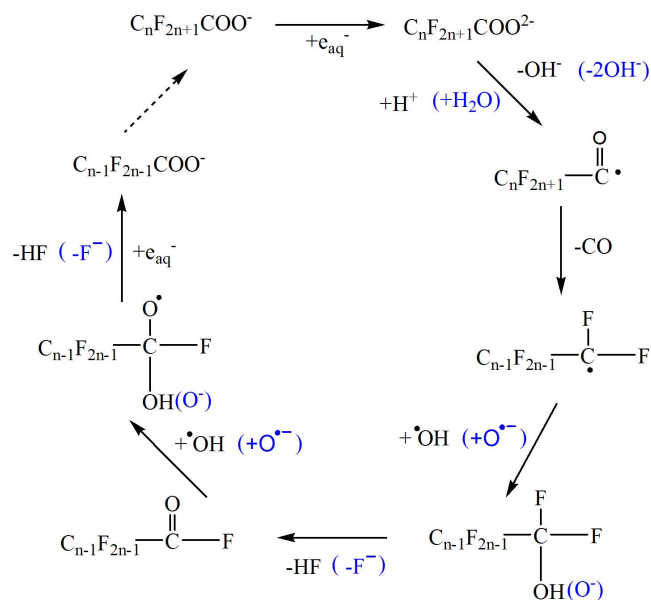
Conclusion

In summary, the complete degradation of PFOA could be achieved by γ-ray irradiation in this work. Results show that the two radicals, ·OH, and e_{aq}^-, played the most important roles in the complete mineralization of PFOA. The proposed mechanism of PFOA degradation by e_{aq}^- and ·OH were elucidated by both experimental measurements and theoretical calculations. The synergistic roles of ·OH and e_{aq}^- involved in the cleavage of C-C and C-F bonds, and therefore complete mineralization of PFOA could be achieved. This work provides a promising approach by virtue of its environmentally friendly and complete mineralization of PFOA, which will facilitate the practical application of PFCAs by γ-ray irradiation in wastewater treatment.

Methods

Reagents. PFOA (>98%) was purchased from Aladdin Corp. H_2O_2, tertiary butanol (t-BuOH) and other chemicals were obtained from Shanghai Chemical Reagent Co., China, which were all analytical grade (>99.7%). All aqueous solutions were prepared with high purity water produced by a Millipore water purification system (Millipore Inc., USA).

Irradiation experiments. PFOA solutions with an initial concentration of 20 mg/L were kept in 100 mL Pyrex glass vessels sealed with teflon caps, and then were irradiated by ^{60}Co-γ-source at an irradiation dose rate of 96 Gy/min. In preliminary experiments, PFOA solutions with three different pHs were prepared and irradiated. The effects of the atmosphere of solutions were also evaluated by saturated with either N_2 or O_2 gas. To identify the contributions of the activated species in PFOA degradation, the radical scavengers (t-BuOH, or H_2O_2) were added to PFOA solutions prior to irradiation. The experimental designs are listed in Table 2. All experiments were conducted at ambient temperature in parallel.

PFOA measurement and other analyses. Concentrations of PFOA and its degradation products were determined by a liquid chromatograph (Accela 600Bar, Thermo Co., USA) coupled with a mass spectrometric system (LTQ-Orbitrap, Thermo Co., USA) (LC-MS). Prior to analysis, each sample was diluted 15 times with methanol to ensure the PFOA concentration below 2 mg/L. The external method was used for the quantitative analysis of PFOA. Solutions with various PFOA concentrations were prepared to make the external calibration curve in the range of 0–2 mg/L. The separation column was a Hypersil GOLD C18 column (2.1 mm i.d. × 100 mm, 3 μm particles), and the column temperature was set at 40°C. The flow rate was maintained at 0.2 mL/min with a mobile phase of eluent A (10 mM ammonium acetate in water) and B (methanol). The eluent gradient started with 40% B for 1 min, and then was linearly increased to 100% B in 6 min, kept for 5 min, and finally returned to the starting conditions within 1 min and held for 2 min for equilibration during injection interval. MS detection was operated in negative mode by using an electrospray ionization source. The parameters were optimized for maximal

Table 3 | Calculated thermodynamic characteristics of the PFOA degradation by radical e_{aq}^- and $\cdot OH$ in aqueous solution generated through γ-ray irradiation

Step	Reactions	ΔG (eV)	ΔH (eV)	ΔS ($\times 10^{-3}$ eV/K)
1	$C_7F_{15}COO^- + e_{aq}^- \rightarrow C_7F_{15}COO\cdot^{2-}$	−2.217	−2.105	0.376
2	$C_7F_{15}COO\cdot^{2-} + H^+ \rightarrow C_7F_{15}CO\cdot + OH^-$	−1.008	−0.978	0.102
3	$C_7F_{15}CO\cdot \rightarrow C_6F_{13}CF_2\cdot + CO$	0.166	0.329	0.547
4	$C_6F_{13}CF_2\cdot + \cdot OH \rightarrow C_6F_{13}CF_2OH$	−0.037	−0.003	0.114
5	$C_6F_{13}CF_2OH \rightarrow C_6F_{13}COF + HF$	−0.116	0.019	0.454
6	$C_6F_{13}COF + \cdot OH \rightarrow C_6F_{13}CF(OH)O\cdot$	−0.071	−0.001	0.232
7	$C_6F_{13}CF(OH)O\cdot + e_{aq}^- \rightarrow C_6F_{13}COO^- + HF$	−7.424	−7.416	0.027

transmission of the PFOA anion (m/z 413) resulting in the following instrument parameters: nitrogen sheath gas flow rate, 20 arbitrary units; Aux/sweep gas flow rate, 5 arbitrary units; spray voltage, 4 kV; heated capillary temperature, 275°C.

The concentration of fluorine ion (F⁻) in aqueous samples was measured by an ion chromatograph system (ICS-1000, Dionex Co., USA), which was equipped with a pump, a degasser, a guard column, and a separation column (Dionex IonPac AS 14A, 4 mm i.d. × 200 mm). The sample injection volume is 25 μL, and the mobile phase was NaHCO₃ (1 mmol/L) and Na₂CO₃ (8 mmol/L). The flow rate was set at 1 mL/min. The suppressor current was set at 124 mA.

TOC was used to evaluate the mineralization degree of PFOA during γ-ray irradiation, which was measured by using a TOC analyzer (V_{CPN}, Shimadzu Co., Japan).

Quantum chemical calculations. Quantum chemistry method can offer an effective and rapid alternative to elucidate the reaction mechanism of refractory organic pollutants[36-39]. The possible PFOA mineralization mechanisms by γ-ray irradiation in aqueous solution were studied using spin-unrestricted DFT computations. In the calculation, an all-electron method within the Perdew, Burke, and Ernzerhof (PBE) form of generalized gradient approximation (GGA)[40] for the exchange-correlation term, and the double precision numerical basis sets including p polarization (DNP)[41] were employed, as implemented in the DMol³ code[42]. The energy in each geometry optimization cycle was converged to within 1×10^{-5} Hartree with a maximum displacement and force of 5×10^{-3} Å and 2×10^{-3} Hartree/Å, respectively. The solvent effect of the water medium was described using the conductor-like screening model (COSMO)[43]. COSMO is a continuum solvent model where the solute molecule forms a cavity within the dielectric continuum of permittivity that represents the solvent.

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Author contributions

Z.Z., X.J.L. and G.P.S. designed the research; Z.Z. conducted the experiments; J.J.C. performed calculations and analyzed the results; Z.Z., J.J.C., X.J.L., H.Y. and G.P.S. wrote and edited the manuscript. G.P.S. was responsible for project planning. All authors contributed to discussion of the results and the manuscript.

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