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Review

Removal of Per- and Polyfluoroalkyl Substances by Electron Beam and Plasma Irradiation: A Mini-Review

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Abstract: The global prevalence and environmental risks of per- and polyfluoroalkyl substances (PFASs) have caused increasing concern regarding their strategic elimination from aqueous environments. It has recently been recognized that advanced oxidation–reduction technologies (AO/RTs) exhibit superior removal performance for these ubiquitous pollutants. However, the detailed mechanisms and product risks have not been well summarized and systematically deciphered. In this mini-review article, the basic operating principles of two typical AO/RTs (electron beam and plasma irradiation) and their reported applications in the abatement of PFASs are described in detail. It is noteworthy that these reductive treatments induced remarkable defluorination efficiency of PFOA and PFOS with the generation of short-chain congeners in water. The reaction mechanisms mainly included desulfonization, decarboxylation, H/F exchange, radical cyclization, and stepwise losses of CF_2 groups. Unexpectedly, partial degradation products manifested high potential in triggering acute and chronic aquatic toxicity, genotoxicity, and developmental toxicity. Additionally, high or even increased resistance to biodegradability was observed for multiple products relative to the parent chemicals. Taken together, both electron beam and plasma irradiation hold great promise in remediating PFAS-contaminated water and wastewater, while the secondary ecological risks should be taken into account during practical applications.

Keywords: advanced oxidation–reduction technology; defluorination performance; reaction mechanisms; product risks

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1. Introduction

The development of modern society has introduced a large number of synthetic chemicals into our daily life as additives for industrial and consumer products, with their inevitable release and ubiquitous prevalence being recorded in global water environments [1–4]. Among these organic compounds, per- and polyfluoroalkyl substances (PFASs) have attracted worldwide concern due to their characteristics of persistence, bioaccumulation, and toxicity (PBT) [1,5–7]. Particularly, perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) constitute the two most important PFAS congeners due to their global occurrence in natural waters, sediments, wildlife, and even human tissues [1,8–11]. The multiple toxic effects of these two PFASs have been widely reported, such as developmental toxicity, hepatotoxicity, carcinogenicity, and immunotoxicity [1,5,7,12,13]. It is known that conventional oxidation processes play a minor role in the effective decomposition of such pollutants due to their intrinsically strong C-F bonds (116 kcal/mol) [14,15]. Therefore, increasing studies have focused on the remediation of contaminated water system using different treatment approaches [12,16–20].

The current literature suggests the use of various treatment technologies (Fenton-like oxidation, photocatalysis, electrochemical oxidation, and reductive treatments) in removing PFASs from water and wastewater [12,14,15,18,21–23]. Due to their high structural resistance to radical-based oxidation (UV/H_2O_2 and UV/persulfate), the hybrid advanced oxidation–reduction technologies (AO/RTs) have exhibited exceptional removal and defluorination performance in treating these PFAS compounds [14,15]. Among them, electron beam and plasma irradiation are the two most widely investigated approaches in the abatement of various organic pollutants, such as PFASs, pharmaceuticals, and personal care products, as well as chlorinated compounds [24–30]. These studies have demonstrated the great promise of both treatment technologies in remediating PFAS-contaminated water and wastewater [25,31–34]. Multiple oxidizing and reducing species were reported to be involved in these treatments, including hydrated electrons (e_{aq}^-), hydroxyl radicals ($^\bullet$OH), and hydrogen radicals ($^\bullet$H) [25,28]. However, the detailed reaction mechanisms of PFASs and secondary environmental risks of the treated water, which are critical for the practical applications of these two AO/RTs, have not been reviewed and described.

In this context, this review is aims to: (1) summarize the state-of-the-art defluorination performance of PFASs from water using electron beam and plasma irradiation; (2) describe the formation of transformation products (TPs), detailed transformation pathways, and reaction mechanisms of two typical PFASs (PFOA and PFOS) in applying these two kinds of AO/RTs; and (3) uncover the possible secondary risks of PFASs during their aqueous abatement using electron beam and plasma irradiation. Overall, the obtained information has pronounced environmental and engineering implications for the strategic modulation of AO/RTs in more environmentally friendly treatments of PFASs from global water environments

2. Brief Introduction of Electron Beam and Plasma Irradiation

As an emerging treatment technology using high-energy electrons, electron beam irradiation could induce ionizing radiation into aqueous systems with low penetration and high dosage rates. The currently reported applications of this approach mainly include the abatement of different classes of refractory organic pollutants, water and surface disinfection, and material modifications [24,35,36]. As shown in Figure 1, a typical electron beam facility with electron accelerators includes an indirectly heated cathode (the most important part of the electron source), control grid, anode, magnetic lens, focusing lens, electron detector, and stage. The electrons generated from the cathode in the electron gun are accelerated under the high-voltage electric field between the cathode and anode. A high-energy electron beam is formed under the action of the magnetic lens and focusing lens. The electron density depends on the operating temperature and cathode compositions. The delivered electrons could attack the water molecules to produce both reducing and oxidizing species (e_{aq}^-, $^\bullet$OH, and $^\bullet$H), which could allow for highly efficient pollutant decomposition and water disinfection [25,35,36]. Due to the high-energy properties of the electron beam, the decontamination is generally accomplished in seconds. It is well recognized that electron beam irradiation has highly efficient removal performance, requires no addition of chemical oxidants, and is eco-safe.

Differing from electron beam technology, the high-energy electrons produced from the plasma system are not produced from the external input but from a series of electromagnetic field conversion and energy transmission processes. Specifically, some substances (usually the carrier gas, such as oxygen, argon, air, or mixed gas) in the aqueous medium are excited to spontaneously generate a large number of highly reactive species, including e^-/e_{aq}^-, $^\bullet$OH, H_2O_2, and O_3. These species could greatly stimulate the decomposition reaction of organic contaminants [29,31,33]. It is worth mentioning that e^-/e_{aq}^- plays an irreplaceable and important role in the highly efficient degradation of various types of PFASs [17,26,33,37]. In terms of the mechanical compositions, the circuit section can be divided into thermal and non-thermal plasma systems according to whether the gas molecules and the electrons can reach thermal equilibrium. Generally, non-thermal plasma requires high-frequency electromagnetic field inputs and an efficient energy transfer system. Figure 2 mainly presents the basic principles and applications of non-thermal plasma technology. The generation power supply types are mainly conventional direct current, high-frequency alternating current, and pulse electricity systems. Their similarities are that they are connected between one high-voltage and one ground electrode to achieve the electrical discharge.

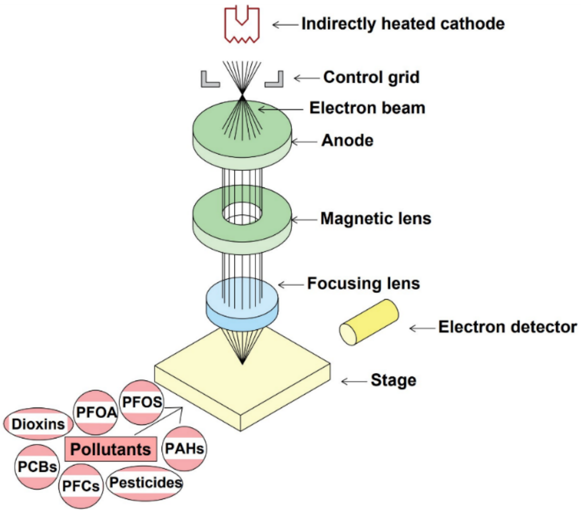

Figure 1. Schematic illustration of electron beam and its applications in treating different organic pollutants.

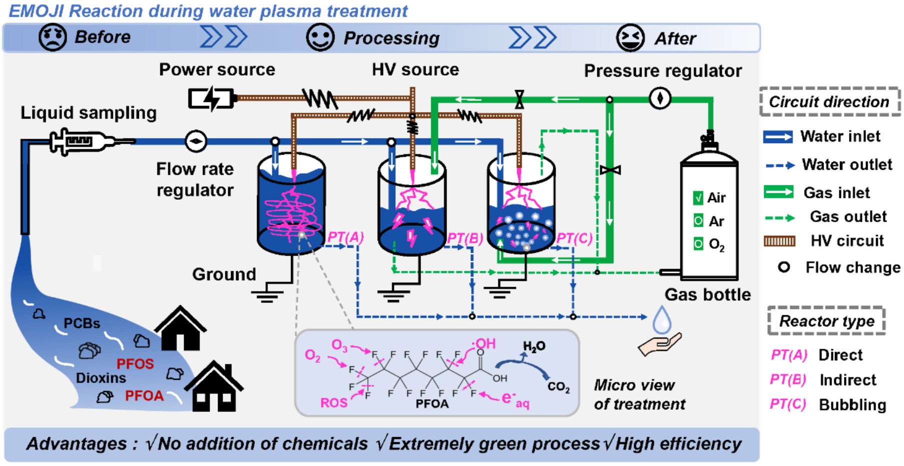

Figure 2. Schematic illustration of plasma technology and its applications in treating different organic pollutants.

3. Removal Performance and Mechanisms of PFASs using Electron Beam and Plasma Irradiation

3.1. Removal Efficiency of PFASs

In this work, the removal–defluorination efficiency and TP formation of PFASs are summarized for their treatments using electron beam and plasma irradiation. As presented in Table 1, the electron beam irradiation exhibited an overall superior removal performance to PFOA, PFOS, and perfluorohepatanoic acid (PFHpA) options, ranging from 53.7% to 100% [32,38–42]. However, very alkaline conditions (i.e., pH 13.0) were commonly used with the high electron beam doses (mostly 500–2000 kGy). For example, Ma et al. [38] reported on the efficient decomposition of PFOA (95.7%) and PFOS (85.9%) using a 500 kGy electron beam in an anoxic alkaline solution (nitrogen atmosphere and pH 13.0). Similarly, our recent study utilized a low-dose electron beam (0–75 kGy) for PFHpA abatement and observed a better removal performance at pH 13.0 than at pH 6.0 [40]. The degradation process of PFOA and PFOS followed the pseudo-first-order kinetics, in which pH-dependent increases in the reaction rates were observed [38]. According to the radical scavenging experiments, both e_{aq}^- and $^•H$ were proposed as the dominant reactive species for the abatement of these two PFASs via defluorination and stepwise CF_2 losses. It is noteworthy that the combined use of electron beam and persulfate could significantly improve the destruction of PFOS, which was ascribed to the synergistic effect of e_{aq}^-, $^•OH$, and sulfate radicals ($SO_4^{•-}$) [32]. On the other hand, rather limited defluorination rates were observed, while the highest efficiency recorded being 71.4% for PFOS treatment using a 500 kGy electron beam at pH 13.0 under Ar gas conditions (Table 1).

Table 1. The removal–defluorination efficiency and TP formation of PFASs after electron beam irradiation in water.

Comp.	Treatment	Reaction Conditions	Removal Efficiency	Defluorination Rate	TPs	Ref.
PFOA	E-beam	[P] = 10 µg/L, E-beam = 2000 kGy, pH 13	53.7%	-	-	[39]
	E-beam	[P] = 20 mg/L, E-beam = 500 kGy, pH 13	88.1%	37.5%	8	[38]
	E-beam	[P] = 40 mg/L, E-beam = 500 kGy, pH 13, Ar	95.7%	46.8%	8	[38]
	E-beam	[P] = 1 mg/L, E-beam = 100 kGy, pH 12.5, Ar, t-butanol = 0.2 M	50.0%	-	6	[41]
	E-beam	[P] = 20 mg/L, E-beam = 500 kGy, pH 13	85.0%	-	-	[24]
PFOS	E-beam	[P] = 10 µg/L, E-beam = 2000 kGy, pH 13	87.9%	-	-	[39]
	E-beam	[P] = 1.0 mg/L, E-beam = 28 kGy, pH 7.0, Ar, t-butanol = 0.2 M	55.0%	49%	4	[42]
	E-beam	[P] = 20 mg/L, E-beam = 500 kGy, pH 13	63.4%	51.8%	8	[38]
	E-beam	[P] = 40 mg/L, E-beam = 500 kGy, pH 13, Ar	85.9%	71.4%	8	[38]
	E-beam	[P] = 20 mg/L, E-beam = 500 kGy, pH 13, t-butanol = 0.1 M	95.0%	-	-	[24]
PFHpA	E-beam	[P] = 100 µg/L, E-beam = 50 kGy, pH 13	100.0%	-	2	[40]

Note: [P]: the concentration of pollutants; E-beam: energy absorption dose of electron beam radiation.

Comparatively, the plasma treatment of PFASs resulted in their almost complete elimination from water under relatively mild conditions (i.e., near-neutral pH values, Table 2) [17,26,31,33,34,37,43–47]. Of these studies, very few have reported the defluorination rates of PFOA and PFOS, of which mesoporous discharge plasma accomplished the maximum defluorination rate of 98% after 60 min of treatment at pH 4.0 under air conditions [37]. Stratton et al. [31] reported that electrical discharge plasma irradiation for 30 min could accomplish higher PFOA abatement (90%) and defluorination (27%) rates than the currently leading alternative technologies, such as sonolysis and electrochemical- and persulfate-based oxidation. Additionally, the destruction of PFOA was largely independent of other coexisting micropollutants (i.e., PFOS) in groundwater, which could also be effectively and simultaneously degraded. Mechanistic insights were gained using quenching experiments, demonstrating e_{aq}^- instead of $^•OH$ and superoxide radicals as the predominant reactive species for PFAS abatement in water [31]. Similarly, the unaffected removal of PFASs by non-PFAS co-contaminants using a pilot-scale plasma reactor was also reported in the liquid-investigation-derived waste [45]. It is noteworthy that PFOA and PFOS could be rapidly decomposed below the USEPA health advisory level (i.e., 70 ng/L) from the real samples within 60 s. These phenomena indicated the viability of plasma irradiation in treating PFASs from natural water matrices. In particular, faster decomposition rates of long-chain PFASs were observed than for the short-chain congeners, suggesting the higher susceptibility of the former during plasma irradiation [45]. Consistently, the comparative removal efficiency of different chains of PFASs ranging from ng/L to mg/L was also reported in an ion-exchange regenerant still-bottom matrix [17] and aqueous film-forming foam-impacted groundwater [44]. Together with the defluorination efficiency of the electron beam irradiation, these results collectively suggested the generation of more recalcitrant TPs than the parent compounds in employing these two typical AO/RTs.

Table 2. The removal–defluorination efficiency and TP formation of PFASs after electron beam irradiation in water.

Comp.	Treatment	Reaction Conditions	Removal Efficiency	Defluorination Rate	TPs	Ref.
PFOA	DC plasma/O_2	[P] = 41.4 μg/L, QO_2 = 100 sccm, I = 10 mA, time = 180 min	98%	94.5%	6	[5]
	laminar jet/Ar	[P] = 20 μM, σ = 1360 μS/cm, Q_{Ar} = 3.9 L/min, U = +25 kV, time = 30 min	~90%	~27.5%	-	[6]
	laminar jet/Ar	[P] = 2.4 nM, σ = 1150 μS/cm, Q_{Ar} = 3.9 L/min, U = +25 kV, time = 30 min	~90%	-	-	[6]
	discharge reactor/Ar	[P] = 8.3 mg/L, V = 1.5 L, Q_{Ar} = 4 L/min, pH 4.6, U = −30 kV, time = 120 min	~100%	-	41	[7]
	discharge reactor/Ar	[P] = 13 ± 27 μg/L, V = ~4 L, Q_{Ar} = 16–18 L/min, pH 5.3–8.0, U = −35 kV, time = 5 min	>93%	-	-	[8]
	discharge reactor/Ar	[P] = 100 ± 20 mg/L, V = ~750 mL, U = −30 kV, time = 120 min	>99%	-	-	[9]
	discharge reactor/Ar	[P] = 180 ± 30 ng/L, V = 56.8 mL, Q_{Ar} = 2.3 L/min, U = −30 kV, time = 12.5 min	100%	-	-	[10]
	Needle-plate pulsed discharge reactor/Ar	[P] = 30 mg/L, V = 200 mL, pH 4.3 ± 0.1, Q_{Ar} = 60 mL/min, P = 38.9 W, time = 120 min	95.3%	50.7%	24	[11]
	mesoporous discharge plasma/air	[P] = 10 mg/L, V = 200 mL, Q_{air} = 2.6 L/min, pH = 4.0, U = +8 kV, time = 60 min	-	98%	18	[12]
PFOS	DC plasma/O_2	[P] = 60 μg/L, QO_2 = 100 sccm, I = 10 mA, time = 480 min	100%	~70%	7	[5]
	laminar jet/Ar	[P] = 0.5 nM, σ= 1150 μS/cm, Q_{Ar} = 3.9 L/min, U = +25 kV, time = 30 min	~100%	-	-	[6]
	discharge reactor/Ar	[P] = 8.3 mg/L, V = 1.5 L, Q_{Ar} = 4 L/min, pH 4.6, U = −30 kV, time = 120 min	100%	-	39	[7]
	discharge reactor/Ar	[P] = 54.3 ± 179 μg/L, V = ~4 L, Q_{Ar} = 16–18 L/min, pH 5.3–8.0, U = −35 kV, time = 5 min	>93%	-	-	[8]
	discharge reactor/Ar	[P] = 90 ± 40 mg/L, V = ~750 mL, U = −30 kV, time = 120 min	>99%	-	-	[9]
	discharge reactor/Ar	[P] = 1100 ± 340 ng/L, V = 56.8 mL, Q_{Ar} = 2.3 L/min, U = −30 kV, time = 12.5 min	~98%	-	-	[10]
	mesoporous discharge plasma/air	[P] = 10 mg/L, V = 200 mL, Q_{air} = 2.6 L/min, pH = 4.0, U = +8 kV, time = 60 min	-	65%	21	[12]
PFOS +PFOA	laminar jet/Ar	[P] = ~1.06 nM, σ= 1150 μS/cm, Q_{Ar} = 3.9 L/min, U = +25 kV, time = 40 min	~100%	-	3	[6]
	non-thermal atmospheric plasma/air	[P] = 0.579 μg/L, pH 6.8–7.1, Q_{air} = 15 L/min, time = 3 min	91.2%	-	-	[13]
	non-thermal atmospheric plasma/O_2	[P] = 0.579 μg/L, pH 6.8–7.1, QO_2 = 20 L/min, time = 7 min	60.1%	-	1	[13]
PFBA	discharge reactor/Ar	[P] = 4 ± 10 μg/L, V = ~4 L, Q_{Ar} = 16–18 L/min, pH 5.3–8.0, U = −35 kV, time = 60 min	~40%	-	-	[8]
	discharge reactor/Ar	[P] = 2 ± 0.5 mg/L, V = ~750 mL, U = −30 kV, time = 120 min	23%	-	-	[9]
	discharge reactor/Ar	[P] = ~230 ng/L, [CTAB] = 0.2 mM, V = 1.5 L, Q_{Ar} = 4.3 L/min, T = 10 °C, U = −30 kV, time = 120 min	~78.26%		-	[10]
PFBS	discharge reactor/Ar	[P] = 7 ± 13 μg/L, V = ~4 L, Q_{Ar} = 16–18 L/min, pH 5.3–8.0, U = −35 kV, time = 60 min	94 ± 13%	-	-	[8]
	discharge reactor/Ar	[P] = 5.0 ± 1.6 mg/L, V = ~750 mL, U = −30 kV, time = 120 min	~99.2%	-	-	[9]
	discharge reactor/Ar	[P] = 180 ng/L, [CTAB] = 0.2 mM, V = 1.5 L, Q_{Ar} = 4.3 L/min, T = 10 °C, U = −30 kV, time = 120 min	~44.44%	-	-	[10]
PFDA	discharge reactor/Ar	[P] = 0.04 ± 0.11 μg/L, V = ~4 L, Q_{Ar} = 16–18 L/min, pH 5.3–8.0, U = −35 kV, time = 60 min	94%	-	-	[8]
	discharge reactor/Ar	[P] = 0.01 ± 0.01 mg/L, V = ~750 mL, U = −30 kV, time = 120 min	>99%	-	-	[9]
PFDS	discharge reactor/Ar	[P] = 5.3 ± 13.9 μg/L, V = ~4 L, Q_{Ar} = 16–18 L/min, pH 5.3–8.0, U = −35 kV, time = 60 min	93%	-	-	[8]

Table 2. *Cont.*

Comp.	Treatment	Reaction Conditions	Removal Efficiency	Defluorination Rate	TPs	Ref.
PFNA	discharge reactor/Ar	[P] = 0.5 ± 1.7 μg/L, V = ~4 L, Q_{Ar} = 16–18 L/min, pH 5.3–8.0, U = −35 kV, time = 60 min	95%	-	-	[8]
	discharge reactor/Ar	[P] = 0.3 ± 0.1 mg/L, V = ~750 mL, U = −30 kV, time = 120 min	>99%	-	-	[9]
	discharge reactor/Ar	[P] = 70 ± 10 ng/L, V = 56.8 mL, Q_{Ar} = 2.3 L/min, U = −30 kV, time = 12.5 min	100%	-	-	[10]
PFNS	discharge reactor/Ar	[P] = 0.07 ± 0.04 mg/L, V = ~750 mL, U = −30 kV, time = 120 min	>99%	-	-	[9]
	discharge reactor/Ar	[P] = 17 ± 9 ng/L, V = 56.8 mL, Q_{Ar} = 2.3 L/min, U = −30 kV, time = 12.5 min	100%	-	-	[10]
PFHpA	discharge reactor/Ar	[P] = 4 ± 10 μg/L, V = ~4 L, Q_{Ar} = 16–18 L/min, pH 5.3–8.0, U = −35 kV, time = 60 min	98%	-	-	[8]
	discharge reactor/Ar	[P] = 7.5 ± 6.1 μg/L, V = ~750 mL, U = −30 kV, time = 120 min	>99%	-	-	[9]
	discharge reactor/Ar	[P] = 240 ± 60 ng/L, V = 56.8 mL, Q_{Ar} = 2.3 L/min, U = −30 kV, time = 12.5 min	~93%	-	-	[10]
PFHpS	discharge reactor/Ar	[P] = 0.8 ± 2 μg/L, V = ~4 L, Q_{Ar} = 16–18 L/min, pH 5.3–8.0, U = −35 kV, time = 60 min	100 ± 0.1%	-	-	[8]
	discharge reactor/Ar	[P] = 2.3 ± 1.9 mg/L, V = ~750 mL, U = −30 kV, time = 120 min	>99%	-	-	[9]
	discharge reactor/Ar	[P] = 30 ± 20 ng/L, V = 56.8 mL, Q_{Ar} = 2.3 L/min, U = −30 kV, time = 12.5 min	100%	-	-	[10]
PFHxA	discharge reactor/Ar	[P] = 25 ± 65 μg/L, V = ~4 L, Q_{Ar} = 16–18 L/min, pH 5.3–8.0, U = −35 kV, time = 60 min	85%	-	-	[8]
	discharge reactor/Ar	[P] = 16 ± 7.8 mg/L, V = ~750 mL, U = −30 kV, time = 120 min	>99%	-	-	[9]
	discharge reactor/Ar	[P] = 360 ng/L, [CTAB] = 0.2 mM, V = 1.5 L, Q_{Ar} = 4.3 L/min, T = 10 °C, U = −30 kV, time = 120 min	100%	-	-	[10]
PFHxS	laminar jet/Ar	[P] = 1.0 nM, σ= 1150 μS/cm, Q_{Ar} = 3.9 L/min, U = +25 kV, time = 30 min	~35%	-	-	[6]
	discharge reactor/Ar	[P] = 33 ± 69 μg/L, V = ~4 L, Q_{Ar} = 16–18 L/min, pH 5.3–8.0, U = −35 kV, time = 60 min	96%	-	-	[8]
	discharge reactor/Ar	[P] = 140 ± 190 mg/L, V = ~750 mL, U = −30 kV, time = 120 min	>99%	-	-	[9]
	discharge reactor/Ar	[P] = 850 ± 390 ng/L, V = 56.8 mL, Q_{Ar} = 2.3 L/min, U = −30 kV, reaction time = 12.5 min	100%	-	-	[10]
PFPeA	discharge reactor/Ar	[P] = 9 ± 25 μg/L, V = ~4 L, Q_{Ar} = 16–18 L/min, pH 5.3–8.0, U = −35 kV, time = 60 min	~75%	-	-	[8]
	discharge reactor/Ar	[P] = 5.9 ± 0.6 mg/L, V = ~750 mL, U = −30 kV, time = 120 min	96.7%	-	-	[9]
	discharge reactor/Ar	[P] = 1220 ng/L, [CTAB] = 0.2 Mm, V = 1.5 L, Q_{Ar} = 4.3 L/min, T = 10 °C, U = −30 kV, time = 120 min	~95.90%	-	-	[10]
PFPeS	discharge reactor/Ar	[P] = 7.4 ± 1.3 mg/L, V = ~750 mL, U = −30 kV, time = 120 min	100%	-	-	[9]
	discharge reactor/Ar	[P] = 200 ng/L, [CTAB] = 0.2 mM, V = 1.5 L, Q_{Ar} = 4.3 L/min, T = 10 °C, U = −30 kV, time = 120 min	~87.50%	-	-	[10]

3.2. Reaction Mechanisms

As mentioned above, the degradation of PFOA and PFOS by electron beam irradiation was mainly dominated by highly reactive species such as e_{aq}^{-}, $^{\bullet}OH$, and $^{\bullet}H$ [24,32,41,42]. Both PFOA and PFOS exist as their anion species ($C_7F_{15}COO^{-}$ and $C_8F_{17}SO_3^{-}$) in water, which can rapidly react with e_{aq}^{-} to form the corresponding radical anions (Figures 3 and 4). Afterward, defluorination occurs at a high reaction rate to produce $C_7F_{14}COO^{\bullet-}$ and $C_8F_{16}SO_3^{\bullet-}$, respectively. Two decomposition pathways were reported for the former one, i.e., reaction with $^{\bullet}OH$ to yield $C_6F_{13}COO^{-}$ with a loss of F^{-}, and reaction with $^{\bullet}H$ to form $C_7F_{14}HCOO^{-}$, which resulted in the reductive reaction mediated by e_{aq}^{-} and $^{\bullet}H$ to form $C_6F_{13}COO^{-}$ with losses of F^{-} and CH_2 group. The second reaction pattern was also applicable for $C_8F_{16}SO_3^{\bullet-}$ for the stepwise defluorination of PFOS without loss of the sulfonic acid group during electron beam irradiation. Subsequent reactions continued in the same manner to generate the final products of F^-, CO_2, and H_2O. In a recent study, Kim et al. [32] reported on the combination of an electron beam and persulfate for the prominent destruction of PFOS, in which e_{aq}^-, $^\bullet OH$, and $SO_4^{\bullet -}$ functioned together for effective desulfonization and stepwise defluorination. Additionally, defluorination and decarboxylation were proposed as two major reaction pathways of PFHpA after electron beam irradiation [40].

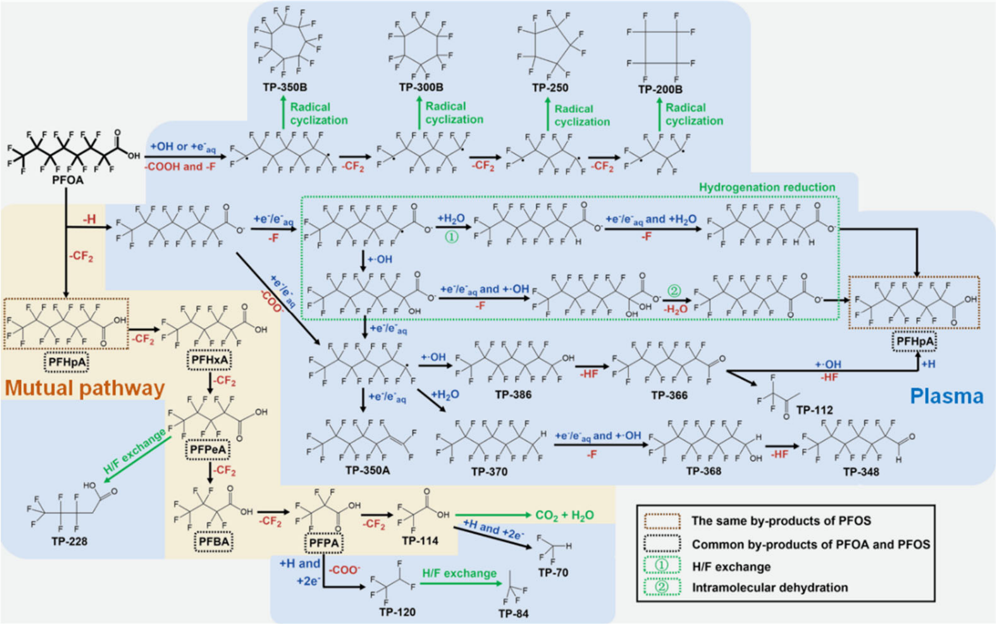

Figure 3. Transformation pathways and reaction mechanisms of PFOA during the treatments using electron beam and plasma irradiation. Note: Blue area: the pathway of PFOA during the plasma irradiation; orange area: the pathway of PFOA during both electron beam and plasma irradiation.

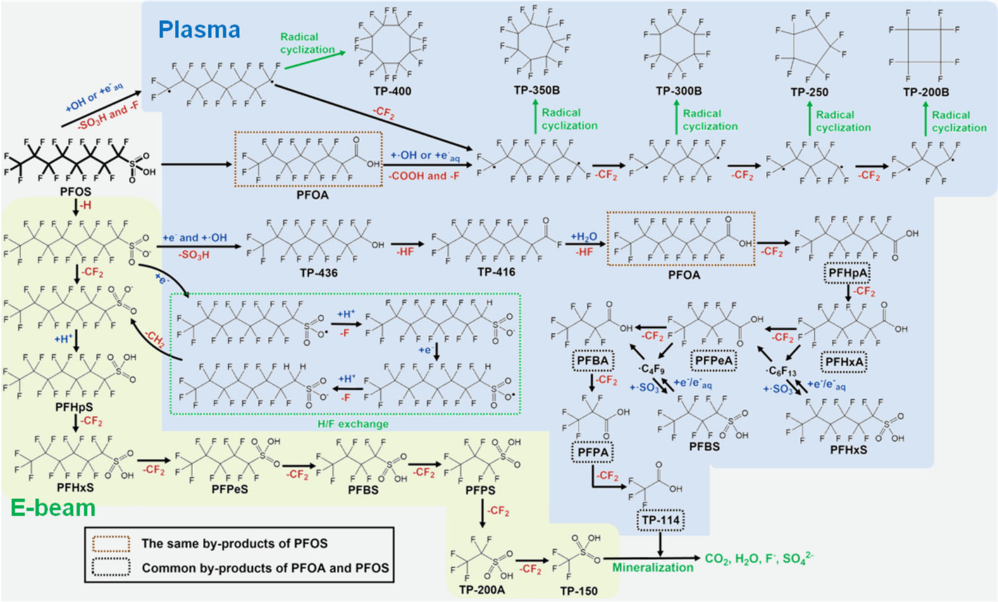

Figure 4. Transformation pathways and reaction mechanisms of PFOS during the treatments using electron beam and plasma irradiation.

In the plasma treatment systems, e_{aq}^- was considered the dominant species responsible for the significant degradation of PFASs [31,37]. It is generally reported that the reactive species could induce the cleavage of C-F, C-C, or C-S bonds of PFAS molecules during chain reactions, achieving successive defluorination with the final mineralization (Figures 3 and 4). In terms of PFOA, the most common reaction mechanism was the continuous realization of HF elimination during the chain initiation and growth. Briefly, e^-/e_{aq}^- attacked the -COOH group to form the unstable perfluoroalkyl radicals (i.e., electron-mediated chain initiation) and the subsequent reactions with e_{aq}^- or $^{\bullet}OH$ to accomplish the successive HF elimination (i.e., chain growth). This can lead to the formation of intermediates, including perfluorool (via $^{\bullet}OH$ recombination), perfluoroketone, and perfluoric acid [33,34,37]. It needs to noted that alcohols and acids with the same number of carbon atoms may be dehydrated and condensed between molecules to form aldehydes [37]. Subsequently, studies have also shown that alkyl radicals formed during chain initiation may be protonated to form ^{1}H-perfluoroalkaffins or undergo F elimination to form perfluoroolefins [34]. The former can be further defluorinated and gradually converted to perfluoroaldehyde, while the latter can proceed further to shorten the carbon chain by removing F or adding H. The second pathway can be ascribed to hydrogenation reduction, which could result in the direct loss of fluorine atoms. One possibility is that H addition occurs immediately, followed by the repetition of the H/F exchange process. The formed hydrofluoride carboxylic acids can be excited to produce perfluoroalkyl radicals and $^{\bullet}COOH$, thereby shortening the carbon chain. Another possibility is that the intermediates after C-F breaks can react with $^{\bullet}OH$ through intramolecular dehydration, eventually leading to the formation of perfluorocarbonyl radicals [33]. Furthermore, the third reaction pathway can be initiated via special epoxidation. The intramolecular recombination of carbon–carbon radicals in PFOA/PFOS molecules can lead to cyclization reactions, i.e., $^{\bullet}OH$ or e_{aq}^- caused the cleavage of C-F bonds and functional groups, resulting in the generation of cyclic radicals to yield perfluoroalkanes with different carbon numbers [37]. Regarding the decomposition of PFOS by plasma treatment, similar reaction pathways took place as mentioned for PFOA. The reactive species attacked the C-S bond of the PFOS molecule, leading to the loss of the SO_3^- group with the formation of C8-based perfluoroalkyl radicals. Subsequent chain growth occurred to form the perfluoroolsketo/acid intermediates. Notably, PFOA was also detected as one product of PFOS during plasma treatment [33,37]. Overall, the reaction products of PFOA have been mostly observed during the plasma treatment of PFOS, which could produce additional products such as the short-chain perfluoroalkyl compounds containing the sulfonic acid group.

4. Environmental Risks of TPs of PFASs

As mentioned above, treatment of PFASs using electron beam and plasma irradiation leads to the formation of multiple reaction intermediates, of which the possible risks remain largely unknown. Only Trojanowicz et al. [41,42] recently reported negligible or reduced cytotoxicity of PFOA and PFOS before and after electron beam irradiation. However, the information on the toxicity of the reaction mixtures to other organisms or endpoints is still very scarce. Increasing studies have demonstrated the QSAR-based prediction tools as excellent toxicity assessment alternatives for the reaction products of organic compounds, which mostly lack the chemical standards for bioassays [48–50]. For example, Guo et al. [37] reported a decrease in in silico acute toxicity along with the plasma treatment of PFOA and PFOS. In this study, the secondary environmental risks of PFOA and PFOS during these two AO/RP treatments were systematically evaluated using different kinds of prediction programs. Specifically, the genotoxic effects of these two PFASs and their TPs were estimated on different test species using QSAR Toolbox software, while the developmental toxicity and endocrine-disrupting effects were predicted using an online CompTox program. Additionally, the acute and chronic toxicity levels and biodegradability of PFOA, PFOS, and their TPs were assessed using the EPI SuiteTM software. As tabulated in Table 3, genotoxic alerts and developmental toxicity were partially observed for some TPs of PFOA and

PFOS. Meanwhile, most of the TPs manifested biodegradability recalcitrance and aquatic toxicity to fish, daphnids, and green algae (Figure 5). In this sense, it is noteworthy that the aqueous decomposition of PFASs by electron beam and plasma irradiation introduced multiple structurally stable TPs, which possessed comparatively higher and unexpected environmental risks than the parent compounds. Therefore, these treatment technologies should be further strategically optimized to improve the mineralization of PFASs and eliminate the toxic effects of the derived TPs in water.

Table 3. The predicted multi-endpoint toxicity levels of PFOA, PFOS, and their TPs generated from the treatments using the electron beam and plasma irradiation.

a	**SMILES Code**	**In Silico QSAR Predictions**						
		QSAR Toolbox				**CompTox**		
		A	**B**	**C**	**D**	**E**	**F**	**G**
PFOA	C(F)(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(=O)O	PFOA	NA	NA	NA	ND	ND	ND
PFOS	C(F)(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)S(=O)(=O)O	NA	NA	NA	NA	ND	ND	ND
PFHpS	C(F)(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)S(=O)(=O)O	NA	NA	NA	NA	ND	ND	ND
PFHpA	C(F)(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(=O)O	PFOA	NA	NA	NA	ND	ND	ND
PFHxS	C(F)(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)S(=O)(O)=O	NA	NA	NA	NA	ND	ND	ND
PFHxA	C(F)(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(=O)O	PFOA	NA	NA	NA	ND	ND	ND
PFPeS	C(F)(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)S(=O)(O)=O	NA	NA	NA	NA	ND	ND	ND
PFPeA	C(F)(F)(C(F)(F)C(F)(F)C(=O)O)C(F)(F)F	NA	NA	NA	NA	ND	ND	ND
PFBS	C(F)(F)(F)C(F)(F)C(F)(F)C(F)(F)S(=O)(=O)O	NA	NA	NA	NA	ND	ND	ND
PFBA	FC(F)(F)C(F)(F)C(F)(F)CC(O)=O	NA	NA	NA	NA	Yes	No	ND
PFPS	C(F)(F)(F)C(F)(F)C(F)(F)S(=O)(=O)O	NA	NA	NA	NA	ND	No	ND
PFPA	C(F)(F)(F)C(F)(F)C(=O)O	NA	NA	NA	NA	Yes	No	No
TP-482	C(F)(H)(C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F)S(=O)(=O)O	NA	NA	NA	NA	ND	ND	ND
TP-464	C(H)(H)(C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F)S(=O)(=O)O	NA	NA	NA	NA	ND	ND	ND
TP-436	C(F)(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)O	NA	NA	NA	NA	ND	ND	ND
TP-416	C(F)(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(=O)F	AH	NA	AH	AH	ND	ND	ND
TP-412	C(F)(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(O)C(O)=O	NA	NA	NA	H	ND	ND	ND
TP-410	C(F)(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(O)(O)C(O)=O	NA	NA	NA	H	ND	ND	ND
TP-400	C1(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C1(F)F	PHC	NA	NA	NA	ND	ND	ND
TP-396	C(F)(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(H)C(=O)O	NA	NA	NA	NA	ND	ND	ND
TP-392	C(F)(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(=O)C(O)=O	NA	NA	NA	H	ND	ND	ND
TP-386	C(F)(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)O	NA	NA	NA	NA	ND	ND	ND
TP-378	C(F)(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(H)(H)C(=O)O	NA	NA	NA	NA	ND	ND	ND
TP-370	C(F)(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)H	NA	NA	NA	NA	ND	ND	ND
TP-368	C(F)(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(O)H	NA	NA	NA	NA	ND	ND	ND
TP-366	C(F)(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)=O	AH	NA	AH	AH	ND	ND	ND
TP-350A	C(F)(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)=C(F)F	TE	NA	NA	NA	ND	ND	ND
TP-350B	C1(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C1(F)F	PHC	NA	NA	NA	ND	ND	ND
TP-348	C(F)(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(=O)H	SA	NA	SA	SA	ND	ND	ND
TP-300	C1(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C1(F)F	PHC	NA	NA	NA	ND	ND	ND
TP-250	C1(F)(F)C(F)(F)C(F)(F)C(F)(F)C1(F)F	PHC	NA	NA	NA	ND	ND	ND
TP-214	C(F)(F)(F)C(F)(F)C(F)(F)C(=O)O	NA	NA	NA	NA	Yes	No	ND
TP-200A	C(F)(F)(F)C(F)(F)S(=O)(O)=O	NA	NA	NA	NA	Yes	No	ND
TP-200B	C1(F)(F)C(F)(F)C(F)(F)C1(F)F	PHC	NA	NA	NA	ND	ND	ND
TP-150	C(F)(F)(F)S(=O)(O)=O	NA	NA	NA	NA	Yes	Yes	No
TP-120	C(F)(F)C(F)(F)F	NA	NA	NA	NA	Yes	No	No
TP-114	C(F)(F)(F)C(=O)O	NA	NA	NA	NA	Yes	No	No
TP-112	C(F)(F)(F)C(C)=O	NA	NA	NA	NA	Yes	No	No
TP-84	C(F)(F)(F)C	NA	NA	NA	NA	Yes	No	No
TP-70	C(F)(H)(F)F	NA	NA	NA	NA	ND	No	No

Type of alerts: PFOA: Perfluorooctanoic acid (Nongenotox); PHC: (Poly)halogenated cycloalkanes (nongenotoxic); SA: Simple aldehyde (genotoxic); AH: Acyl halides (Genotox); H: H-acceptor-path3-H-acceptor; TE: Trichloro (or fluoro) ethylene and tetrachloro (or fluoro) ethylene (nongenotoxic); NA: No alert found. QSAR Toolbox models: (A) Carcinogenicity (genotox and nongenotox) alerts by ISS; (B) DNA alerts for AMES, CA, and MNT by OASIS; (C) in vitro mutagenicity (Ames test) alerts by ISS; (D) in vivo mutagenicity (Micronucleus) alerts by ISS. CompTox: (E) Developmental toxicity; (F) Ames mutagenicity; (G) estrogen receptor binding.

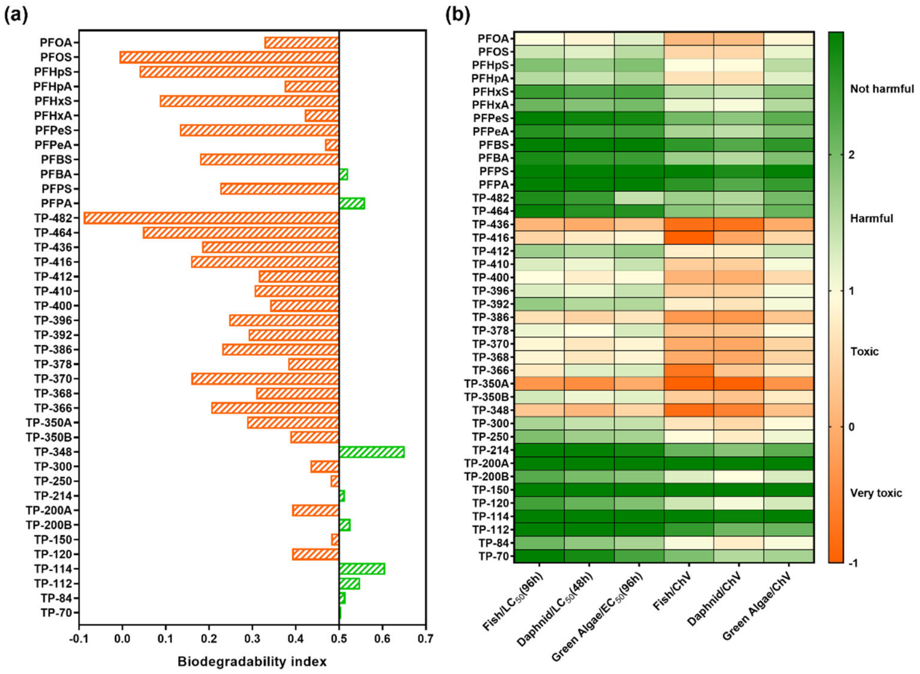

Figure 5. The estimated biodegradability (**a**) and acute and chronic toxicity (**b**) levels of PFOA, PFOS, and their TPs generated during the treatments using the electron beam and plasma irradiation.

5. Cost Analysis

The above studies have demonstrated the high efficiency of both electron beam and plasma irradiation technologies in removing PFASs from aqueous environments. In terms of the practical applications, the treatability cost is also a critical factor affecting their wide use in treating PFAS-contaminated water and wastewater. According to the current literature, a cost analysis for aqueous PFAS elimination via electron beam irradiation is still not available. Regarding the plasma treatment, the electric energy per order (EE/O) was calculated for the energy requirements for PFAS treatment in water. The available EE/O values of plasma technologies for PFOA and PFOS were in the range of 9.2–31.0 kWh/m^3 (enhanced contact plasma reactors) [44], 216.5–332.0 kWh/m^3 (needle-plate pulsed discharge plasma reactor with a water jet and microbubble generator) [34], and 1.7–56.0 kWh/m^3 (electrical discharge plasma) [45]. Higher EE/O values (380.0–830.0 kWh/m^3) for the plasma technology were recently reported for a high-level PFAS removal process from ion-exchange regenerant still-bottom samples [17]. Overall, these values were significantly lower than the EE/O data for some reported advanced oxidation techniques in remediating PFOA- and PFOS-contaminated water, such as sonochemical treatment (>20,000 kWh/m^3) [51], photocatalytic oxidation (2666.7 kWh/m^3) [52], and microwave treatment (3584.0 kWh/m^3) [53]. These results collectively demonstrate the cost feasibility and great promise of plasma treatment in removing PFASs from natural water systems.

6. Conclusions and Perspectives

This review article focused on the abatement efficiency, reaction mechanisms, and environmental risks of PFASs using electron beam and plasma irradiation in water. The current literature demonstrated the superior elimination performance of PFASs using these two emerging treatment technologies. The limited defluorination rate in conjugation with the product analysis indicated the production of multiple refractory TPs of PFASs. Subsequently, the transformation pathways and reaction mechanisms of PFOA and PFOS were summarized and elucidated, which mainly included desulfonization, decarboxylation, H/F exchange, radical cyclization, and stepwise losses of CF_2 groups. Notably, the treatment-derived toxicity evolution analysis suggested that the degradation of PFOA and PFOS introduced TPs with comparative or even higher environmental risks than the parent chemicals. These unexpected results require future studies involving more in-depth investigations into the strategic optimization of these two treatment technologies for the complete mineralization or defluorination of these highly worrying PBT pollutants. According to the current knowledge, additional research can be pursued in the following areas:

- PFAS treatment under realistic conditions: The current literature showed that the electron beams function efficiently for the aqueous removal of PFASs under extremely alkaline conditions (i.e., pH 13.0). This seems impractical for treating PFAS-contaminated natural water bodies, which generally have neutral pH values. Additionally, some other operating factors significantly affected the elimination performance of PFASs using electron beam irradiation, such as scavenger-based enhancement using t-butanol, Ar gas, the combination with other oxidants, and super-high doses (i.e., 2000 kGy). Furthermore, the test concentrations of PFASs (mg/L in most cases) during these two kinds of AO/RP treatments were relatively higher than their environmental levels (ng/L-μg/L). Considering the potential interference of background water constituents (humic acid and bicarbonate), the reported removal efficiency may not reflect their abatement in complicated natural water systems. Therefore, future studies are needed to optimize the operating conditions of electron beam and plasma irradiation to achieve high remediation efficiency for trace-level PFASs in real water matrices;
- Toxicity assessment of reaction mixtures of PFASs: This review unveiled the overlooked but serious secondary environmental risks of the TPs derived from the treatments of PFASs using electron beam and plasma irradiation. Considering the potentially jointed effects of the reaction mixtures, it is urgently required to perform comprehensive toxicity and risk assessments to decipher the ecological safety of the treated water and wastewater. Additionally, as potential emerging contaminants in natural waters, the key toxic TPs contributing to the high secondary risks should also be screened in both lab and field studies. The combination of non-targeted environmental monitoring techniques and high-throughput toxicity screening methods would facilitate a better understanding of the life cycle and environmental impacts of PFASs during practical applications of these two AO/RT treatments in water decontamination.

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