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Advanced oxidation and reduction processes for PFAS treatment: Transformation products, toxicity risks, and detoxification challenge

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Per- and polyfluoroalkyl substances (PFAS) are globally persistent and highly recalcitrant, necessitating destructive remediation approaches beyond conventional phase-transfer methods. Advanced oxidation/reduction processes (AOPs/ARPs) can achieve >90% degradation of terminal PFAAs and PFAS precursors, yet complete mineralization is uncommon. Treatment generates transformation products (TPs), including partially defluorinated organics, short-chain perfluoroalkyl acids (C4–C6 PFCAs/PFSAs), and inorganic fluoride. High-resolution mass spectrometry (HRMS)-based non-target screening shows that a single PFAS precursor may form 20–100 fluorinated species (polyfluoroethers, unsaturated acids, fluorotelomer olefinic acids). However, their toxicological significance remains poorly understood. Evidence indicates transient toxicity increases during AOP treatment, while QSAR studies suggest some short-chain TPs may exhibit toxicity comparable to or greater than the original PFAS compounds (e.g., PFOA, PFOS). Consequently, PFAS destruction does not necessarily correspond to toxicity reduction. Remediation outcomes depend on water matrix characteristics, defluorination extent, and operational conditions, highlighting the need to prioritize detoxification alongside degradation.

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Introduction

Per- and polyfluoroalkyl substances (PFAS) are man-made, diverse group of >12,000 fluorinated chemicals with distinctive properties such as hydrophobicity, thermal and chemical stability, wetting ability, and oleophobicity. The carbon–fluorine bond, with a dissociation energy of 485–582 kJ/mol and an F/F^- redox potential of 3.6 eV, is exceptionally stable, rendering PFASs recalcitrant to physico-chemical and natural degradation. These properties have led to their applications in various applications (e.g., surfactants, food packaging, non-stick coating, firefighting foams and textiles among others). Due to their extensive usage, PFASs cause ubiquitous environmental contamination and human health risks such as immunotoxicity, low fertility, dyslipidemia, liver disease, hormonal imbalance, and cancer. Stricter regulations, including U.S. EPA maximum contaminant levels (MCLs) of 4 ng/L for perfluorooctanoic acid (PFOA)/perfluorooctane sulfonate (PFOS) and EU-wide PFAS restrictions have been established. Germany has introduced the additional parameter Summe PFAS-4 with a limit value of 20 ng/L, to be implemented from January 12, 2028, for the sum of the concentrations of the four PFASs viz., perfluorononanoic acid (PFNA), perfluorohexane sulfonic acid (PFHxS), PFOA and PFOS. Non-destructive technologies viz. adsorption, membrane filtration/distillation, foam fractionation and electrocoagulation have the drawback of generating waste streams with high concentrations of PFAS [1–4].

Destructive technologies, such as advanced oxidation processes (AOPs) and advanced reduction processes (ARPs) exhibit varying PFAS removal efficiencies in model/real waters [5]. These processes enable partial longer-chain PFAS breakdown to shorter-chain intermediates or complete mineralization to CO_2 and F^-. Commercially viable AOPs, generating powerful oxidants, achieve defluorination of recalcitrant C–F bonds, with >80% PFOA/PFOS removal [6–8]. Particularly in ARP systems generating hydrated electrons, the PFAS degradation follows a stepwise decarboxylation-hydroxylation-elimination-hydrolysis (DHEH) cycle,

yielding transformation products (TPs) including shorter-chain PFCAs (e.g. perfluorobutanoic acid (PFBA), perfluoropropionic acid (PFPeA)), polyfluorocarboxylates, and unsaturated fluorides from perfluoroalkyl radical intermediates. Shorter-chain TPs exhibit increased aqueous mobility and solubility, potentially elevating environmental exposure risks despite reduced bioaccumulation potential [2,6,9]. The current assessment of treatment performance disproportionately emphasizes pseudo-first-order kinetics, often overlooking metrics like fluorine mass balance and the toxicity of TPs. This inattention creates treatment-induced hazard that may be multiplied by the shortage of direct toxicity assessment of the transformation products. The toxicity may reduce, increase, or persist during the AOP treatment of PFAS, as evidenced by in vivo, in vitro, and in silico studies [1,2,7]. Therefore, demonstrable toxicity reduction must be established before asserting that AOPs can effectively degrade PFAS. Relying solely on the removal of the target terminal PFAA (e.g. PFOA, PFOS) can be misleading to the decision makers and regulators. This current review critically assesses the PFAS degradation through AOPs/ARPs with specific focus on (i) TP speciation, (ii) toxicity assessment through in-vivo and in-vitro analysis, QSAR studies and bioassay, (iii) associated risk implications.

PFAS destruction by AOPs/ARPs

PFAS degradation via (i) advanced reduction processes (ARPs) such as UV/sulfite, UV/iodide and non thermal plasma systems, which generate reductive hydrated electrons essential for the defluorination of terminal perfluorinated compounds and (ii) purely oxidative AOPs, including UV/hydrogen peroxide (H_2O_2), UV/persulfate (PS), UV/peroxymonosulfate (PMS), electrochemical oxidation (EO) and ozonation, which generate sulfate radicals ($SO_4^{\cdot-}$) and hydroxyl radicals ($\cdot OH$), facilitates the cleavage of the C−F bond along with stepwise decarboxylation or desulfonation, depending on the specific PFAS compound treated (polyfluorinated precursor or therminal PFAA). The degradation rates of different PFASs differ markedly. For instance, PFOA degrades ∼10 times faster than PFOS, signifying the influence of functional group accessibility and molecular structure. Under commonly reported operating conditions, including UV/PS (acidic to near-neutral pH and PS in excess of PFAS, and related radical systems, the removal of 80−95% of thet target PFAS compound within 1−3 h has been achieved. Although defluorination is usually limited to a few tens of percent (approximately 30−60%), indicating incomplete mineralization and the persistence of short-chain transformation products [10−13]. The EO systems with boron-doped diamond (BDD) or mixed metal oxide (MMO) anodes are highly effective for the treatment of concentrated streams, achieving over 95 % removal of target terminal PFAAs (PFOA/PFOS) and a recovery of 70−90 % fluoride, even under hypersaline solutions. Non-thermal plasma systems (e.g., corona, glow discharge) degrade PFAS and precursors (e.g., 6:2 FTS, GenX) via reactive oxygen/nitrogen species and hydrated electrons (making it a hybrid AOP/ARP system), resulting in 40−70 % mineralization. However, the energy requirements for these systems are very high (10−100 kWh/m^3) [6−8]. Photocatalytic systems based on TiO_2, g-C_3N_4, and modified catalysts (e.g., MoS_2) degrade ∼ 88−100% PFAS through photogenerated holes. However, the defluorination remains limited to 20−74 %. Some studies have reported enhanced performance where AOPs are coupled with other techniques. Nanofiltration coupled with UV/PS achieved about 90% degradation of PFAS, whereas reactive electrochemical membranes (Ti_4O_7) achieved >99.9% removal with about 70% defluorination at moderate energy demand. It has been observed that photo-assited hybrid systems show a varied range of defluorination (32−82%) due to the formation of short chain perfluorocarboxylates PFCAs. In organic-rich matrices, the AOPs do not perform effectively due to the radical scavenging, leading to incomplete mineralization and accumulation of persistent short-chain TPs [14,15]. Among the various AOPs used in PFAS degradation Ti_4O_7 reactive electrochemical membranes showed the lowest electrical energy per order (EEO) of 5.1−6.7 kWh/m^3 for PFOA/PFOS removal, surpassing BDD anodes (EEO: 20−240 kWh/m^3 at lab-to-pilot scale). The UV-based photocatalytic systems showed the EEO values in the range of 18.9−426 kWh/m^3 [16,17].

Intermediates and byproducts: analytical Frontiers

Transformation patterns

PFAS is degraded by AOPs through three interconnected mechanisms: (i) progressive backbone shortening through the loss of CF_2 unit ($\Delta m/z \approx -50$ Da), (ii) headgroup transformation to carboxylate from sulfonate, and (iii) stepwise defluorination with fluorine substituted with H/OH and release of F^-. In case of perfluorosulfonates (PFSAs), PFOS undergoes side-chain cleavage during AOP treatment, producing perfluorohexane sulfonic acid (PFHxS) and perfluorobutane sulfonic acid (PFBS), alongside perfluorocarboxylates such as $C_6F_{11}COOH$. However, in the case of PFCAs, PFOA can temporarily undergo chain length redistribution before progressing to over-oxidation. This leads to the formation of short-chain acids such as PFBA, the release of CO_2, and fluoride ions, which indicates the partial mineralization. A distinct degradation pathway is followed by ether-based PFAS replacements. For instance, GenX initially hydrolyzes to HFPO-DA; thereafter, ether bond cleavage and reductive transformations lead to the formation of

shorter perfluoroacids (e.g., CF_3CF_2COOH, CF_3COOH) and inorganic fluoride. The high-resolution non-target HRMS analysis reveals that a single precursor can produce approximately 20–100 fluorinated species (C1–C10 and 1–17 F) consisting of polyfluoroethers, unsaturated acids, and fluorotelomer olefinic acids (FOAs) [6,10,18].

Identification methods and limitations

Standard LC–MS/MS methods (e.g., EPA 533/537) quantify primarily about 20–30 short-chain PFCAs/PFSAs at low ng/L levels. This ensures reliable concentrations but cover only a limited portion of PFASs and their TPs [Figure-1]. Suspect screening typically adds 10–20 additional features per sample, against large PFAS inventories. However, non-target analysis using mass-defect and van-Krevelen-type plots decipher numerous additional fluorinated groups (e.g. $C_4F_9O_2$ series) without reference standards. Complementary techniques like ^{19}F NMR and EOF/AOF improve the fluorine mass balance; however, oxidative TOP assays may overestimate poly-PFAS by converting diverse precursors into a narrow set of PFCAs [10,19–23]. Even with the most sophisticated techniques, the key analytical challenges still remain, namely: many intermediates are extremely short-lived (lifetimes <5 min), about 80% of the environmentally relevant TPs lack standards, and matrix-induced ion suppression often reaches 10–50%. For example, UV/PS treatment of 6:2 FTS produces several HRMS-resolved TPs, including branched species (e.g. $C_5F_{11}O_3H$) which can be tentatively identified via MS^2 spectra. Similarly, BDD oxidation of GenX, degrades the parent chemical but retains fluorine in stable ether-containing products. The integration of $^{13}C/^{19}F$-based fluorine analysis with high resolution non-target HRMS analysis will enable reliable structural confirmation [19,24].

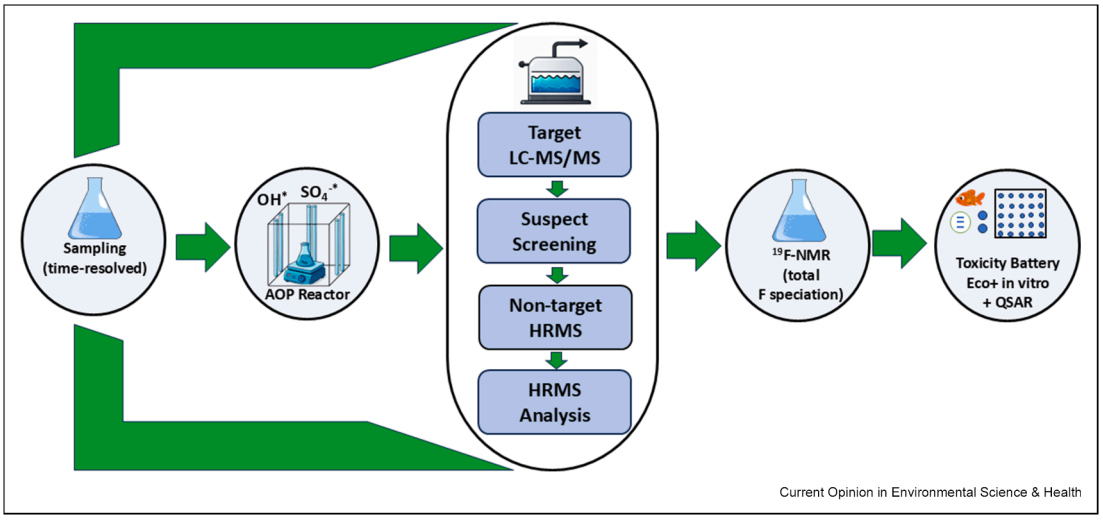
Toxicity of PFAS AOP or ARP by-products: evidence and gaps

This section examines emerging evidence that AOPs/ARPs alter the toxicity of PFAS during the treatment, highlighting the temporal changes in toxicity rather than focusing merely on terminal PFAS removal [25,26] [Figure 2].

Toxicity dynamics of PFAS and their transformation products

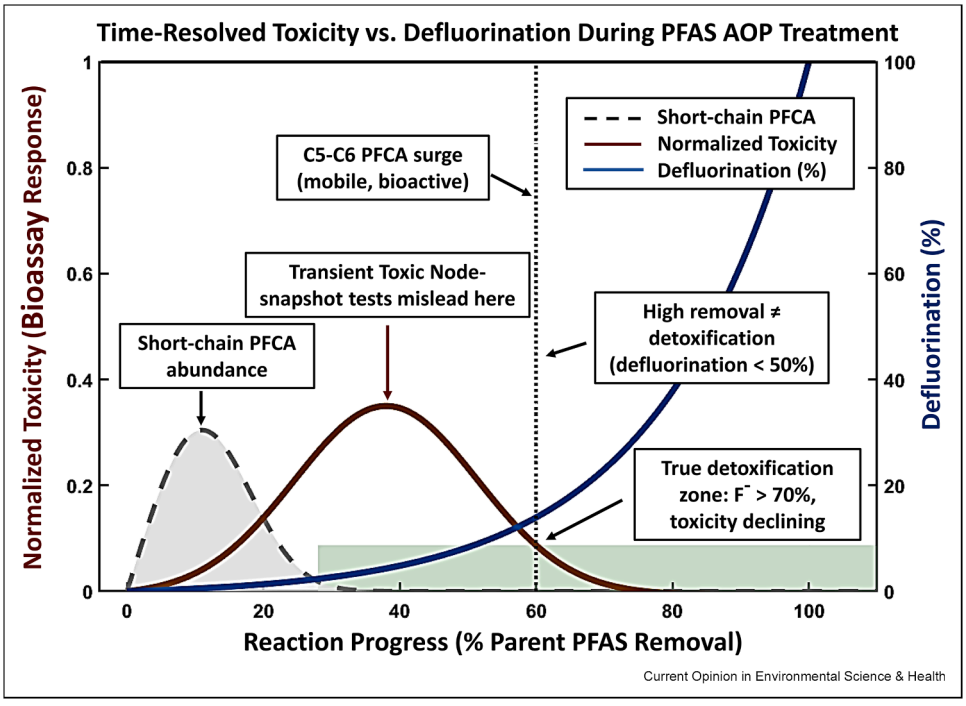
Few studies investigating the application of AOPs/ARPs for PFAS degradation incorporate toxicity evaluation. These studies primarily assessed the acute aquatic endpoints, viz., Daphnia immobilization, algal inhibition, or fish lethality, with no attention to chronic or mechanistic markers. This limited evidence base is further weakened by two factors: one is inconsistent experimental designs, the second is the implicit assumption that target PFAS removal equates to risk reduction [26,27]. Emerging in-vitro models and in-vivo zebrafish studies show that short-chain PFASs cannot be regarded as harmless substitutes for their long-chain counterparts, as they can disrupt the endocrine systems, trigger oxidative stress, and induce genotoxicity even in micromolar concentrations [28,29]. Consistent with this, mixture and grouping assessments report at least additive toxicity when short and long-chain PFASs are combined. QSAR and in vivo data also indicate that certain short-chain PFAAs may approach the developmental and liver-toxicity of PFOA, even though their bioconcentration is much lower [30,31]. The shorter-chain PFCAs (C4–C6) exhibit higher aqueous

Figure 1



Analytical workflow for PFAS AOP transformation products characterization.

Figure 2



Time-resolved toxicity and defluorination during PFAS-AOP treatment.

mobility and membrane permeability, which enable nuclear receptor interactions (PPARα, PPARγ) and the activation of other adverse outcome pathways, viz., oxidative stress and neurodevelopmental signaling, distinct from those of their long-chain precursors, as shown by transcriptomic studies [32].

Integrating defluorination and toxicity

Dependence on the toxicity assay of the parent substance alone masks the latent toxicity arising from the evolving mixture of TPs. The reduction in toxicity requires two coupled conditions. First is the significant (>70%) defluorination, and second is the progressive decrease in both the signal intensity and the structural diversity of TPs. Accumulation of short-chain PFCAs during the AOP represents a critical failure mode, since the C5 and C6 species are highly mobile, persistent, and bioactive. Therefore, pose chronic toxicity greater than or comparable to that of the parent PFAS substance, as shown in Table 1. The toxic response is also temporally dynamic. The specific TPs and distinct degradation stages can temporarily elevate the toxicological biomarkers. Therefore, single-time-point measurements or parent-only assays are not sufficient. A scientifically robust evaluation of AOP performance should use time-resolved sampling at defined degradation stages of the parent substance, such as 0%, 25%, 50%, 75%, and >95% removal. At these different stages, a tiered bioassay battery encompassing acute lethality, mechanistic endpoints, and genotoxicity can be used.

Outlook and recommendations

Since pollutant removal and toxicity reduction are rarely evaluated together, PFAS "removal" is often mistakenly equated with complete destruction and detoxification. To address this issue, following recommendations have been proposed for researchers, practitioners, and policymakers.

For research

There have been target PFASs studied for destruction through AOPs, fragmenting the research field. To improve comparability and consistency, it is necessary to establish a standardized reference panel covering chain lengths, headgroups, and precursors, along with defined test matrices viz., synthetic water, wastewater, surface and groundwater. A transition towards time-resolved analytical–toxicological workflows is essential to simultaneously monitor parent PFAS removal, intermediates, and toxicity. Toxicity peaks and true risk reduction can be identified by integrating HRMS-based

Table 1

PFAS treatment by AOPs: Removal, TPs, and Toxicity Outcomes.

S.No.	PFAS types and matrix	AOP process	PFAS removal/ defluorination/ TOC trend	Main identified intermediates	Toxicity endpoints assessed	Observed toxicity patterns	Key implication for risk and technology design	Reference
1.	PFOA, landfill leachate	Microwave plasma torch in argon flow at atmospheric pressure	Not reported	Not reported	Battery of bioassays, including acute immobility of Daphnia magna and algal growth inhibition	Toxicity towards aquatic organisms decreased progressively with plasma treatment time. Shorter treatment durations showed only partial toxicity reduction.	Design and operation for plasma treatment must ensure sufficient exposure time.	[33]
2.	PFOS	Hyperbolic vortex plasma reactor	Almost complete removal after 75 min. TOC decrease is only partial and atmosphere-dependent	PFOA, PFHpA, PFHxA, PFPeA, and PFBA, alongside fluoride ions, smaller organic acids, and ROS/RNS-related products.	In vitro cytotoxicity (MTS assay, HepG2) and in vitro genotoxicity (Ames MPF, Salmonella TA98/TA100)	Cytotoxicity and genotoxicity showed atmosphere-dependent changes, with both decrease and clear genotoxic peaks (argon plasma) rather than a uniform decrease.	Plasma PFAS treatments must be optimized and controlled with in vitro cyto/ genotoxicity assays,	[34]
3.	PFOS	Neutron irradiation as a radiolytic destructive treatment	PFOS in water shows clear structural transformation and partial defluorination	Oxygenated PFOS-derived structures inferred from new carboxylate and carbonyl bands plus enhanced O−H stretching	In vitro cytotoxicity of irradiated vs non-irradiated PFOS solutions using MTT assay in human umbilical vein endothelial cells	Marked cytotoxicity of non-irradiated PFOS at 50−100 μg/mL decreased to control-like viability after neutron irradiation	Future reactor designs must optimize neutron flux/irradiation time and add quantitative PFAS/defluorination monitoring before considering specialized ex-situ treatment applications.	[35]
4.	Raw PFAS-contaminated groundwater	UV only, UV/H_2O_2, UV/TiO_2, UV/BN, UV/TiO_2+BN, O_3/H_2O_2	100% removal of parent PFAS	AOP converted long chain PFAS to short chain ones leading to an increase in ΣPFAS concentration ranging from 95% to 340%.	Risk metric used: Hazard Index (HI) as per USEPA proposed drinking-water regulation	Some AOPs worsen the HI (UV/H_2O_2, O_3/H_2O_2, UV/TiO_2), some marginally improve (UV only), and photocatalytic systems with BN drastically improve HI despite increased ∑PFAS via shorter-chain products.	Operating at very high AOP doses may lead to precursor oxidation without full mineralization, so design should balance oxidation strength, contact time, and follow-up polishing to capture generated short-chain PFAS	[2]

(*continued on next page*)

Table 1. (*continued*)

S.No.	PFAS types and matrix	AOP process	PFAS removal/ defluorination/ TOC trend	Main identified intermediates	Toxicity endpoints assessed	Observed toxicity patterns	Key implication for risk and technology design	Reference
5.	Mixtures of 13 PFAS (C4–C14 PFCAs, PFBS, PFHxS, PFOS, N-MeFOSAA, N-EtFOSAA)	CTAB-enhanced plasma-based process	86 to >99% removal in lab-prepared water and 29 to >99% in reverse osmosis (RO) reject water	PFHpA (C7), PFPeA (C5), and PFBS (C4),PFPA, TFA, and triflate	Not reported	Not reported	Surfactant type/dose must be carefully optimized to avoid hindering long-chain PFAS removal in real waters	[36]
6.	PFOA in distilled water and river water	UV-driven BiOCl@PMoV-X with PS	PFOA removal reached 95.0%, defluorination 44.4%, and TOC removal 42.1% after 6 h	Stepwise shorter-chain PFCAs ($C_6F_{13}COOH$, $C_5F_{11}COOH$, C_4F_9COOH, C_3F_7COOH, C_2F_5COOH, CF_3COOH)	In silico aquatic toxicity was evaluated with ECOSAR	Predicted acute and chronic toxicity decreased progressively as PFOA was transformed to shorter-chain PFCAs and finally to non-harmful products	Real-water design must optimize operating conditions and account for matrix effects and residual short-chain PFCA formation.	[37]
7.	PFOA in ultrapure water	N-CQDs/TiO_2 photocatalysis	PFOA removal reaches 97.28% and defluorination 77.34% after 18 h	Short-chain PFCAs (C3–C7, plus residual C8) and fluoride ions	In vivo acute toxicity, bioaccumulation and trophic transfer, plus zebrafish concentration-dependent transcriptomics, targeted biomarkers, and neurotransmitter metabolomics.	Degradation products are more acutely toxic than parent PFOA to algae, daphnids, and especially zebrafish, with increasing toxicity at higher degradation extent and multiple pathways activated at lower effect thresholds	PFOA degradation that stops at short-chain PFCAs and fluoride can enhance ecological risk—especially via acidification-driven bioaccumulation and multiorgan toxicity—so PFAS technologies and regulations must target complete mineralization and explicitly evaluate mixture toxicity of degradation products	[38]
8.	28 polyfluoroalkyl substances	UV/H_2O_2	Many PoFAS were fully or largely transformed, but insignificant overall defluorination (e.g., ~9% for 6:2 FTSA)	Hydroxylated and ketone intermediates and terminal perfluoro- and perfluoro-dicarboxylates of varying chain length, plus FOSA	Toxicity was evaluated in silico with ECOSAR v2.2 for aquatic toxicity of parents and selected intermediates/ products	ECOSAR predictions showed that some intermediates can be more toxic than their PoFAS precursors, and overall mixture toxicity can increase	Process design and regulation must consider structure-dependent kinetics, intermediate/product toxicity, and the need for follow-on steps that achieve true defluorination/ mineralization.	[39]
9.	PFOA in laB water and tap, rain,	Biomass-derived lignin-doped TiO_2	~60% PFOA degradation, Near	Short-chain PFCAs PFHpA, PFHxA, PFPeA, and PFBA	In vivo duckweed (*Lemna minor*) ecotoxicity for	Toxicity to L. minor decreases with PFAS chain length and	Long-term ecotoxicity monitoring is	[40]

	groundwater, wastewater		complete removal of some intermediates		individual PFOA/ PFHpA/PFHxA and for time-resolved degradation mixtures	declines markedly after even short photocatalytic treatment, then continues to drop over 16 days despite plateaued PFAS concentrations	essential, as detoxification dynamics and matrix effects differ from simple kinetic decay	
10.	PFOA in distilled water and real PFAS-contaminated groundwater	Non-thermal plasma dielectric barrier discharge falling-film reactor	63.75% reduction in initial PFOA concentration	Short-chain PFCAs PFHpA, PFHxA, PFPeA, and PFBA	Not reported	Not reported	Treatment optimization and comprehensive PFAS-profile (and future toxicity) monitoring are essential before implementation	[41]

PFOA – Perfluorooctanoic acid; PFOS - perfluorooctane sulfonic acid; PFHpA – Perfluoroheptanoic acid; PFHxA – Perfluorohexanoic acid; PFPeA – Perfluoropentanoic acid; PFBA – Perfluorobutanoic acid; PFBS – Perfluorobutanesulfonic acid; PFPrA – Perfluoropropanoic acid; TFA – Trifluoroacetic acid; PFHpA - Perfluoroheptanoic acid; PFPeA - Perfluoropentanoic acid; PFBS - Perfluorobutanesulfonic acid; PFCA - Perfluoroalkyl Carboxylic Acid.

screening with rapid toxicity assays or QSAR. Prioritizing toxicologically relevant intermediates via QSAR and reported literature enables focused quantification, improved efficiency, and stronger risk-based evaluation of PFAS treatment.

For field practice

PFAS treatment should prioritize risk reduction rather than energy efficiency, guided by metrics, viz., ≥90% target PFAS (PFAA) removal, ≥50% PFAS mineralization, and ≥70% defluorination and minimal intermediates (<10% mass) with equal or lower toxicity, alongside optimized energy use [7,14,15,42–46]. It is acknowledged that no single, globally standardized benchmarking framework currently exists for PFAS treatment performance metrics. In real water matrices, bromide and other halides naturally present may be oxidized by AOPs to bromate or brominated DBPs, thereby introducing additional treatment-induced hazards beyond PFAS transformation products. Pretreatment halide assessment and AOP parameter optimisation should therefore be considered during field application to minimise co-formation of halogenated byproducts [47]. Residual PFAS and the amount of intermediates can be minimized through hybrid or staged AOPs, thereby enhancing safety. Regulatory approval should require evidence of toxicity evaluation, intermediate identification, time-resolved toxicity, and pilot-scale validation across diverse water matrices, distinguishing actual destructive technologies from merely transformative ones.

For implementation through policy

A critical gap has been left in the domain of PFAS treatment technologies as regulatory bodies in the US and EU focus on parent PFAS removal but neglect the toxicity assessment of treated water. The policies should require a directive for acceptable toxicity data (e.g. in vitro, in vivo, or QSAR with confidence limits) and establish thresholds (e.g., toxicity below background or ≥50% reduction vs. untreated water). Large-scale systems may need in vivo validation methods, while smaller systems can rely on in vitro or QSAR validation approaches. The treatment claims should be clearly classified as “destruction” (complete mineralization), “probable destruction” (≥80% mineralization with lower toxicity), “partial destruction,” or “transformation,” ensuring transparent reporting and safer technology deployment.

Closing opinion

Although AOPs represent a promising approach for the PFAS degradation, they cannot be categorised as a truly destructive technique until the effective/comprehensive target PFAS (including terminal PFAAs via ARPs) transformation is observed and TPs are also characterized and, shown to be less toxic. Until such validation is

attained, the AOPs should be selectively applied, viz., in dilute systems, followed by a post-treatment polishing step. The long-term toxicity monitoring should also be part of the AOP application. Responsible implementation requires prioritization of risk reduction over the parent PFAS removal, which should also be supported by a strong regulatory framework.

Credit authorship contribution statement

Shilpi Verma: Writing – review & editing, Writing – original draft, Visualization, Methodology, Formal analysis, Conceptualization. Stephan Zimmermann: Writing – review & editing. Harald Horn: Writing – review & editing, Supervision, Conceptualization.

Use of AI

During the preparation of this work the authors used ChatGPT in order to reduce the number of words from around 2050 to below 2000. After using this tool/service, the authors reviewed and edited the content as needed and take full responsibility for the content of the published article.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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* of special interest
** of outstanding interest

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