Complete defluorination of per- and polyfluoroalkyl substances — dream or reality?

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The consensus of removing per- and polyfluoroalkyl substances (PFAS) from the environment is widely recognized and enlightened by the near-zero standards released from the U.S. Environmental Protection Agency in 2023. The only way to achieve the goal of zero fluoro-pollution is to fully defluorinate or mineralize PFAS, but current technologies only partially defluorinate a limited number of PFAS, which can lead to the creation of potentially more toxic short-chain intermediates. Therefore, we discuss herein the need to broaden the scope of tested PFAS, summarize the state-of-the-art degradation technologies, and provide perspectives to achieve complete defluorination. Besides fundamental knowledge gaps in defluorination reactions, technological gaps in the aspects of water matrix effects, pilot tests, and cost analysis also limit the application and comparison of different treatment technologies. This work would shed light on further research to find solutions in the complete defluorination of PFAS.

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Introduction

Per- and polyfluoroalkyl substances (PFAS), manufactured and utilized for decades, are widespread in both natural and engineered water systems [1••, 2]. The PFAS classification is still under discussion, but novel inclusive investigations propose the molecular structure and fluoride content as the determining parameters [3•]. PFAS degradation in different environmental media is extremely challenging due to the persistency of their C—F bond (485 kJ/mol [4••]), a large variety of analogs (~15,000) [3•], and low concentration in water, yielding increasing interest in defluorination (DeF) research (Figure 1).

In 2023, the U.S. Environmental Protection Agency announced new standards for perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) in drinking water to be 4.0 ppt. To meet this near-zero standard, technological innovations enabling complete DeF, not only degradation, of parent PFAS compounds, are desired. Specifically, the term DeF refers to the percentage of F^- ions released from the PFAS molecules. Complete DeF is critical since partial DeF can lead to potentially more harmful and persistent short-chain byproducts with a higher degree of bioaccumulation in animal or human bodies [5]. While the global occurrence of PFAS highlights the challenge to transition the aims from degradation to DeF, the development of zero fluoro-pollution technologies becomes imperative to ensure human and environmental safety (e.g., clean water supply) [2]. Therefore, the comparison and improvement of the state-of-the-art destruction technologies should be pursued for PFAS complete DeF.

In the context of 'Zero Pollution' reinforced by the European Commission, current technologies need to be updated or innovated to address challenges associated with operational conditions, energy consumption, and chemical addition in PFAS remediation. Particularly, the low PFAS concentrations at the ppt level will lead to increased energy and chemical usage for high DeF, which is not sustainable. Furthermore, the concern on PFOA and PFOS (Figure 1**, subgraph)** should not exclude the presence of a broad spectrum of PFAS in testing environments [6], demonstrated through a variety of PFAS identification assays (e.g., total oxidizable precursor, target and non-target analysis). The novel compounds reported [7•] and upcoming regulations justify the need to expand the degradation spectrum. A broadened PFAS spectrum can shed light on the

Figure 1
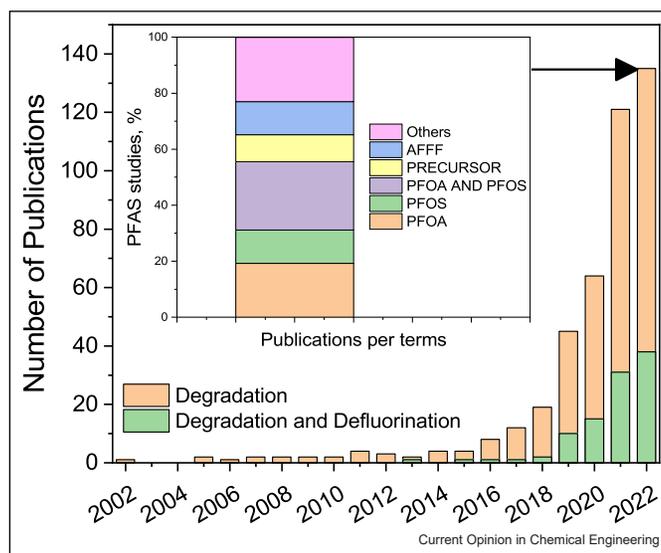
Number of publications involving the term "PFAS" and "Degradation" (orange bar) and "Defluorination" (green bar). Subgraph: composition of the PFAS publications in 2022 (searching the terms "PFAS" and "Degradation" and each term in the legend excluding the others. Data obtained in Web of Science (26/01/2023).

PFAS structural influence [8••], provide insights into the degradation mechanisms, and design effective and structure-independent degradation strategies. In this article, we specifically discuss the state-of-the-art PFAS degrading technologies and identify their feasibility to achieve complete DeF and thus the zero fluoro-pollution goal (Figure 2). This zero fluoro-pollution ambition protects not only human health but also biodiversity, consistent with the climate, energy, and circular economy goals. It should be noted that the current review mainly focuses on PFOA and PFOS degradation studies, which allows holistic comparisons of different treatment technologies.

Current PFAS defluorination technologies
This section summarizes and compares the DeF performance of state-of-the-art technologies (Table 1) by highlighting the feasibility of reaching complete DeF for each technology.

Direct irradiation
Direct irradiation can be a chemical-free technology in water purification. Compared with ultraviolet A (UVA), ultraviolet C (UVC) and visible light, vacuum ultraviolet (VUV) irradiation is the best-performing technology for PFAS degradation, reaching 17% DeF of PFOA in 2 hours [9]. Due to the high energy intensity of light irradiation, water molecules are ionized to form reactive species (RS) such as hydrated electrons (e_{aq}^-), hydroxyl radical ($^\bullet OH$), and hydrogen atom ($^\bullet H$) [10]. The addition of oxidative and reductive chemicals further promotes reactive species (RS) production and thus PFAS

degradation. In UV/persulfate system, oxidative RS like sulfate radical ($SO_4^{\bullet-}$), $^\bullet OH$, and superoxide radical ($O_2^{\bullet-}$) result in effective PFOA degradation, despite the long treatment time (8 hours) to achieve satisfactory DeF rates (59%) [11]. Likewise, reductive UV/Sulfite [12,13] and UV/Iodide [14] systems form e_{aq}^- (NHE = −2.9 V) [15] that effectively defluorinate perfluoroalkyl carboxylic acids (PFCAs), and perfluoroalkyl sulfonic acids (PFSAs). Specifically, the e_{aq}^--induced reduction reaction in the indole-derivates system achieved 74.8% PFOA DeF in 8 hours [16]. The formed e_{aq}^- enhances the DeF compared to other advanced oxidation processes (AOPs), which produce less effective species (e.g., $^\bullet OH$) to start the degradation [17,18]. Furthermore, the addition of surfactants (e.g., cetyl-trimethylammonium bromide [CTAB]) can create micelles that accumulate PFOA/PFOS and thus enhance the transfer of photogenerated electrons from a photosensitive substance (e.g., indole acetic acid [IAA]) to the PFAS [19]. This process can reach 90% DeF in 2.5 hours for PFOA, under an ambient atmosphere and neutral pH conditions. The positively charged micelle is also prone to interact with the produced e_{aq}^- to promote internal reactions with PFAS [19]. Although the chemical addition promotes RS production and DeF in the irradiation systems, chemical-free processes are preferred in terms of green chemistry.

Complete DeF in a simple, chemical-free process is still a far-fetched goal for PFAS treatment, even though the use of low-energetic photolytic systems is an attractive approach that deals with concentrated streams. Scaling

Figure 2
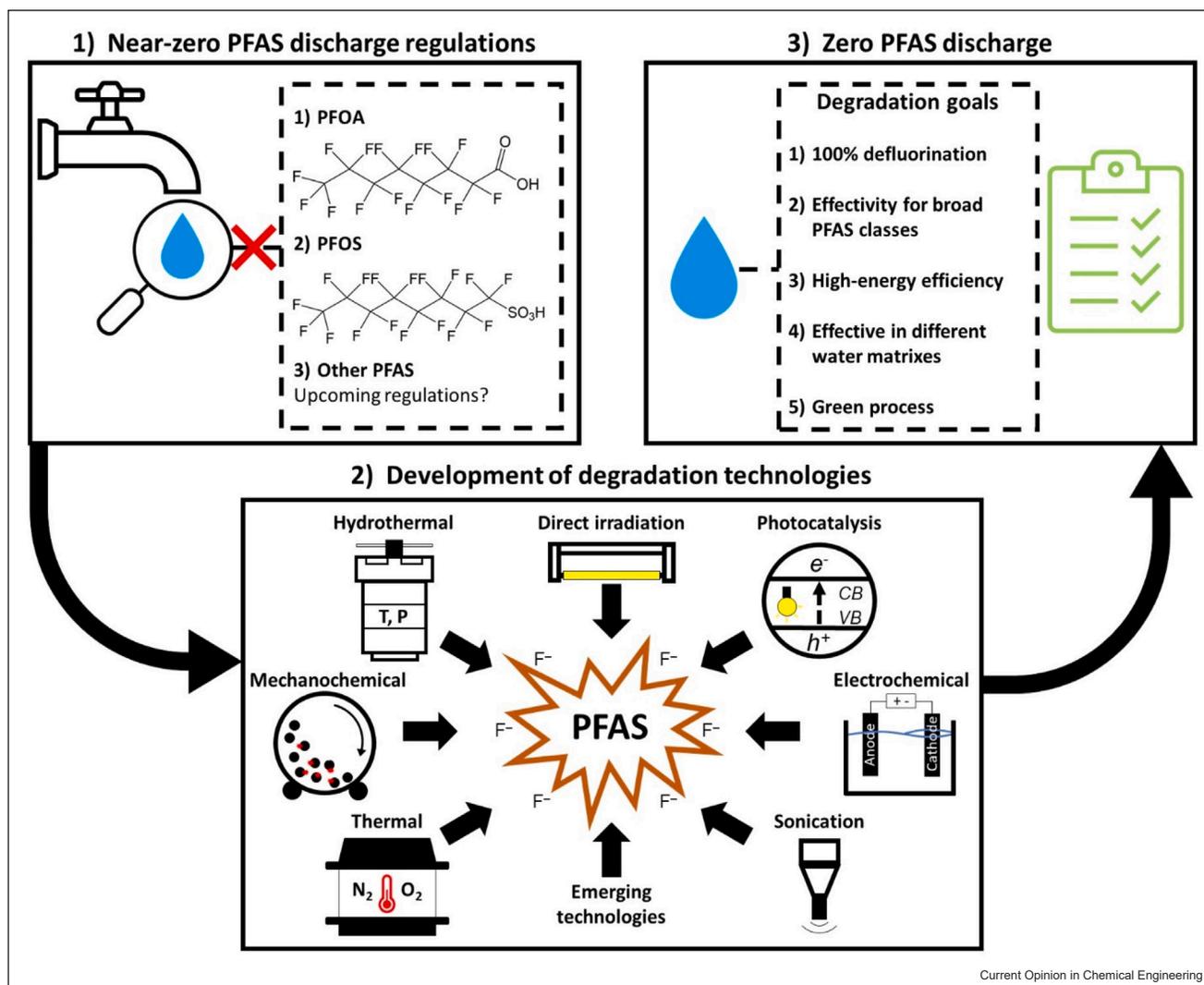
Summary of the zero-PFAS discharge goal technological context and main general considerations.

up the technology to completely defluorinate PFAS in threshold concentration must consider the presence of complex water matrixes, pH limitations, light intensity decrease, chemical overuse, and techno-economic analysis (TEA) on the energy and supplies consumed.

Photocatalysis

Semiconductor photocatalysts excite electrons (e^-) to the conduction band, generating holes (h^+) in its valence band when an irradiation wavelength meets its bandgap requirements [4••]. The e^- and h^+ can directly react with PFAS or react with H_2O and O_2 to generate RS such as H_2O_2, $^\bullet OH$, $O_2^{\bullet-}$ [4••]. Metallic ions, typically Fe^{3+}, are not semiconductors but they can complex PFAS leading to a ligand-to-metal charge transfer degradation process. It is reported that Fe^{3+}/VUV [20] systems completely defluorinated PFOA after 72 hours, despite the strict

acidic conditions (pH = 3–4). Likewise, the Fe^{3+} catalyst is later regenerated from Fe^{2+} with system oxidant species (e.g., $^\bullet OH$ and O_2) [20,21].

Similar to direct photolysis, the performance of semiconductor photocatalysis is also influenced by the irradiation wavelength. The boron nitride (BN) coupled with titanium dioxide (BN/TiO_2) can defluorinate PFOA in different extends under UVC (55% in 1 hour), UVA (37% in 4 hours), and solar light (68% in 7 hours) irradiation [4••]. Apparently, further studies are considered necessary to demonstrate the feasibility of photocatalysis to complete DeF. Catalyst design is critical to enhancing the DeF, with heterojunctions and optimized adsorption sites (e.g., monodentate and bidentate complexation) [22]. By harnessing the advantages of cutting-edge photocatalysts and strong adsorbent materials, an

Table 1

Summary of the defluorination performance for different technologies. Abbreviations: titanate nanotubes (TNT); activated carbon (AC); perfluoroalkyl carboxylic acids (PFCAs); perfluoroalkyl sulfonic acids (PFSAs).

Method	Source	Dose PFAS (ppm)	Chemical/Catalyst Dose (mM)	pH	N_2	Time (h)	DeF %	Pollutants	Ref
Irradiation	UVC - Persulfate	62.11	15	2.81	No	8	59	PFOA	[11]
Irradiation	UVC - Sulfite	25 μM	10	12	No	1	> 39	PFCAs/PFSAs	[12]
Irradiation	UVC - KI	10	0.3	9	Yes	14	> 99	PFOA	[14]
Irradiation	UVC - Indole	~10	1	6	Yes	8	74.8	PFOA	[16]
Irradiation	UVC - IAA/CTAB	10	1/0.14	6	Yes	2.5	> 90	PFOA/PFOS	[19]
Irradiation	VUV	14.9	-	3.9	No	144	> 99	PFOA	[20]
Photocatalysis	Solar - TiO_2@BN	50	0.5 g/L	3.2	No	7	68	PFOA	[4]
Photocatalysis	VUV - Fe^{3+}	14.9	0.02	3.9	No	72	> 99	PFOA	[20]
Photocatalysis	UVC - Fe/TNT@AC	0.1	1 g/L	7	No	4	62	PFOA	[25]
Sonication	900 W / 20 kHz	0.5	-	-	No	4	> 99	PFOA	[28]
Thermal	AC/700°C	-	-	-	Yes	0.5	> 80	PFOA/PFOS	[35]
HT Subcritical	350°C 16.5 MPa - NaOH	50	1000	> 13	No	1.5	> 80	PFOS	[37]
HT Supercritical	650°C 25 MPa	43.32	-	-	No	0.0078	> 99	PFOS	[38]
Electrochemical	50 mA cm^{-2} - NaCl / Na_2SO_4	0.2	10 / 500 ppm	-	No	74	> 87.3	PFOS	[46]
Electrochemical	4 mA cm^{-2} - Na_2SO_4	8.28	100	-	No	2.5	72	PFOS	[47]
Mechanical	BN / 580 rpm / Steel or Zr ball	0.23 mmol	19-21 mmol BN	-	No	4	~100	PFOA, PFOS	[52]
H_2 Reduction	H_2/Pd	41.4	~0.9 g/m^2	4	Yes	35	46	PFOA	[48]
Plasma	40 Hz, 30 kV	8.3	0.1M NaCl	4.6	No	2	> 58	PFOA, PFOS	[41]
DMSO/NaOH	120°C - NaOH	36 800	30eq	-	No	24	> 78	PFCA	[51]

innovative "concentrate-and-degrade" strategy was practiced [23]. However, only a few adsorbents (e.g. activated carbon [24,25] or zeolites [21]) have been tested as adsorptive photocatalysts for PFOA/PFOS degradation. PFOA/PFOS adsorption mainly relies on hydrophobic interactions, which is not a dominant process for hydrophilic short-chain analogs. By shifting the material charge, for example, through amination processes [26], electrostatic interactions with negatively charged short-chain PFAS would be promoted. Besides, the fast-settling properties of these composite materials allow simple catalyst separation resulting in the reuse of the materials following the complete degradation of surface-bound PFAS.

The novel designs of different composite formations, solar-driven materials, and adsorptive photocatalysts promoted PFAS destruction, yet their applications are limited by the harsh pH requirements, long treatment time, lack of tests on the full PFAS spectrum, light utilization efficiency, and catalyst leaching and recovery. It is of both fundamental and practical importance to innovate catalyst design that can overcome these drawbacks to realize complete PFAS DeF through photocatalysis.

Sonolysis

Sonication of the water medium creates cavitation bubbles, the collapse of which yields hot spots with extreme temperatures (4000–10000°C) and pressure conditions (1000 bar) [27]. The high performance of sonication in PFAS DeF is due to the adsorption of the surfactant pollutants onto cavitation bubbles. Although sonication-induced RS was ascribed to the PFAS decomposition in some studies [27], thermolysis of PFAS in the bubble core, and at the bubble-water interface is the main DeF mechanism [28•, 29]. The power input and oscillation frequency are the main energy-dependent and degradation-controlling parameters [27]. The power input determines the system's energy density, collapse pressure, and maximum temperature. Generally, the degradation increases with the power input [30]. Similarly, the oscillation frequency affects the critical bubble size, the lifetime of cavitation bubbles, and the RS formed [27,30]. High frequencies rapidly induce bubble collapse increasing the number of cavitation bubble events and thus the PFAS degradation. An optimal frequency exists because the mass transfer to the bubble-water interface eventually becomes the rate-limiting step [31].

Since it is not energy-economic to treat low-concentration PFAS because of the high energy consumption and localized effects, sonication is a candidate to deal with preconcentrated PFAS streams from membrane filtration or ion exchange processes. Besides the complete DeF capacity for PFOA in 4 hours, sonication is also a chemical-free treatment [28•]. However, further enhancements of the technology involve its coupling with other technologies, such as radical oxidation [27] and UV irradiation [29]. Synergies created from hybrid processes can reduce energy consumption. For example, the VUV/sonication system requires less energy (0.348 kWh) than sonication (0.400 kWh) to achieve the same PFOS DeF [29]. The synergy, originating from the thermal

degradation by sonication and the C–S bond cleavage by VUV, led to a cooperative DeF mechanism. Specifically, at pH 7, the DeF constant of the combined process (k = 7650 min^{-1}) outperformed VUV (k = 220 min^{-1}) and sonication (k = 5790 min^{-1}) systems for 10 ppm PFOS. In addition, leveraging localized effects that limit its application can increase the final DeF performance for possible zero PFAS discharge.

Thermolysis

Thermal processes in the temperature range of 300–1000°C can degrade PFAS through combustion (O_2 presence) and pyrolysis (O_2 absence) [32]. Combustion processes tend to outperform pyrolysis in PFAS decomposition, but release carbonyl fluoride (COF_2), CO_2, CO, and HF [32]. Noted, the emission of colorless, odorless, and toxic gases (e.g., COF_2) is an apparent limitation of the process. Similarly, pyrolysis also emits fluorinated greenhouse gases (e.g., CF_4, C_2F_4) [33]. It is therefore critical to limit the emissions of these fluorinated gases [34]. When combined with catalysts (e.g., CaO, SiO_2, and Al_2O_3), further decomposition of these fluorinated gases was observed [32,34]. Since it is not practical to directly thermolyze PFAS in wastewater, an attractive approach is to adsorb PFAS on activated carbon [35,36•] and undergo thermolysis afterwards. In this context, the development of novel adsorbents may promote the treatment of a broader PFAS spectrum, particularly short-chain analogs, and reduce energy consumption for material regeneration [36•].

Hydrothermal processes are alternative thermal methods employing subcritical (100–350°C) [37] or supercritical (> 375°C; > 22.5 MPa) waters [38•]. Subcritical water systems generally require less energy but need additives, typically NaOH [37] that promote the nucleophilic substitution of OH^- for F^-. The high temperature and pressure of the supercritical system, sometimes facilitated by the presence of oxidizable hydrocarbons, form oxidative RS ($^\bullet$OH and H_2O_2) for PFAS degradation [38•]. Li et al. recently scaled up the process to demonstrate its superior effectiveness (99.9% DeF at 650°C and 25 MPa) in an ethanol-water mixture under continuous conditions and a reduced residence time of 28 s [38•]. Microwave is often considered to assist the hydrothermal processes (60–130°C and 15–40 psi). In the presence of persulfate, microwave treatment can reach 87.4% PFOA DeF in 12 hours [39].

Thermal degradation technologies can achieve complete DeF rates. However, thermal treatments often suffer from high energy demand, especially when dealing with bulk waters. Therefore, a preconcentration step might be critical to reducing energy utilization and closing the PFAS cycle [36•]. In addition, regenerable materials and green additives are preferred to avoid secondary contamination [40].

Plasma irradiation

Plasma technologies produce a complex mixture of oxidative and reductive RS (e.g., $O_2^{\bullet-}$, O_3, and e_{aq}^-) in the aqueous and gas phases under ambient conditions. This emerging method can achieve high DeF in short treatment times (77% and 58% for PFOA and PFOS, respectively, in 2 hours) [41], although energy efficiency remains a drawback [42]. Extending the reaction times might lead to complete DeF, which encourages testing of different PFAS compounds and further analysis of the degradation byproducts [43]. The plasma treatment can be enhanced by creating bubbles or foams to attract hydrophobic pollutants like long-chain PFAS [44]. Heterogeneous catalysts (e.g., TiO_2 and WO_3) were used to harvest plasma-generated light for additional RS production [43]. However, further mechanistic studies and TEA analysis on energy consumption might shed light on the large-scale application of the technology.

Electrochemical methods

Electrochemical oxidation is an energy-efficient, scalable, and modular process, where an electrolyte affects the transport of PFAS to the reactive anode allowing different operability to defluorinate PFAS [45]. The electrode materials are critical in terms of performance since it limits electron transfer which drives the DeF process. The oxidation reactions occur at the anode made of Ti-based or boron-doped diamond materials [45,46], while the cathode is typically stainless steel [46,47]. As a common anode material, Magnéli-phase (Ti_nO_{2n-1}) demonstrates extremely high electrical energy per order (EEO) of 4,000 kWh m^{-3} with around 90% DeF for PFOS [46]. Therefore, research on new materials and strategies is strongly encouraged. For example, porous anode membranes with enhanced mass transfer were synthesized from Ti-based materials serving as wastewater filters and anodes simultaneously, achieving over 80% DeF for PFOS [47].

Electrochemical methods present high DeF efficiencies, yet limitations such as high cost, short electrode lifetime, toxic metal leaching, and energy efficiency; all these limitations challenge their application in water treatments. In addition, studies related to water matrixes are still lacking to fully understand the effect of real water analytes on PFAS transport and electrode performance.

Other emerging technologies

a) Reductive H_2 hydrodefluorination

Reductive hydrodefluorination is a novel approach that uses the H_2 co-adsorbed onto a Pd^0 catalyst to reductively defluorinate PFOA [48]. The degradation mechanism is based on H_2-dissociation and activation at the Pd^0 surface and the subsequent DeF of the F-chain adsorbed onto the hydrogenated catalyst surface. It can achieve 66% degradation and 46% DeF of PFOA in 35h, leading to partially fluorinated octanoic acids, i.e., a direct

Figure 3

Current Opinion in Chemical Engineering
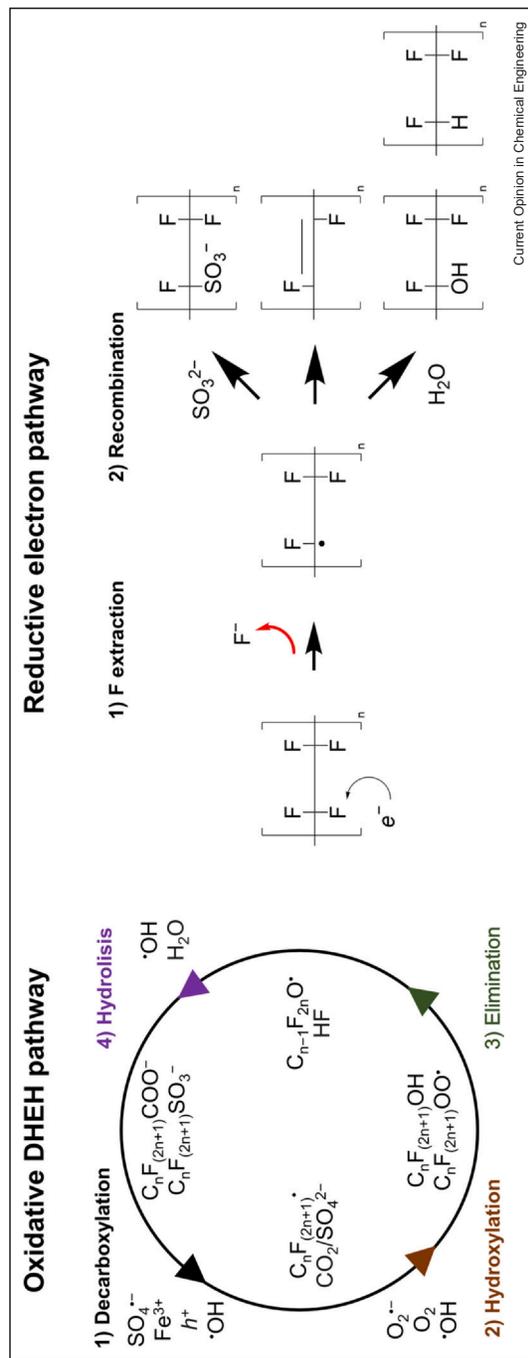
Model PFOA/PFOS degrading mechanisms: **(a)** DHEH oxidative mechanism (e.g., persulfate [39], electrochemical [47], or photocatalysis [21,24]) and **(b)** Electron reduction pathway (e.g., iodide [14] or sulfite [12,13]).

fluoride extraction mechanism. The technology is featured by the upswing of H_2 as green gas and the simplicity in operation, but its DeF performance to different PFAS needs to be further verified. In addition to insights into the hydrodefluorination mechanism, catalyst selection and the control of H_2 use can decrease the degradation time and operational cost, which are the main drawbacks of the technology.

b) Organic solvents

Interestingly, it is found that perfluoroalkyl ether carboxylic acids can degrade in common polar aprotic solvents, such as acetone, acetonitrile, and dimethylsulfoxide, without any external energy inputs [49]. The H-bond accepting nature of these polar solvents promotes a proton transfer mechanism from the PFAS molecules to the solvent [49], which destabilizes PFAS functional groups and promotes decomposition (e.g., decarboxylation) [50]. Further studies on the degradation pathways are needed to design effective processes and reduce the treatment time. In addition, PFAS degradation in organic solvents may be enhanced in combination with other processes, such as mild temperatures. For example, the combination of an organic solvent with NaOH at relatively low temperatures (80–120°C) has achieved 78 to ~100% DeF for PFCAs within 24 hours [51••]. This process can reduce energy consumption compared to thermal treatments and achieve complete mineralization of PFCAs. However, the use of organic solvents is undesirable in terms of green chemistry and strategies to treat PFAS-containing wastewater. Hence, recovery and reuse of the solvents and extending the performance beyond PFCAs are needed to achieve the zero PFAS discharge goal.

c) Mechanochemical methods

Mechanochemical methods based on ball milling are high-performing solid-state PFAS degradation technologies. The process involves the base addition for nucleophilic OH^- substitution reaching 40% and 50% DeF for PFOA and PFOS, respectively [52••]. Effective PFAS destruction with co-milling materials (e.g., BN [52••] and SiO_2 [53]) was also observed. For example, BN can reach complete DeF of PFOA and PFOS in 4 hours due to the atomic displacement produced by mechanical impact, which generates a piezoelectric redox potential ($> 4\,V_{RHE}$) that can oxidize PFAS through electron transfer from the micropollutant to BN [52••]. However, their application is still limited in solid-phase PFAS treatments, and the stability of the co-milling materials needs to be further evaluated.

PFAS degradation mechnisms

Up to date, mechanistic elucidation involves indirect evidence such as byproduct analysis based on mass spectrometry or theoretical calculations of reactive species reacting with PFAS molecules. It is revealed that oxidative methods degrade PFOA/PFOS through initial head group removal, such as decarboxylation, and then stepwise degradation through a hydroxylation-elimination-hydrolysis (DHEH) process (Figure 3). In comparison, reductive methods can also involve hydrated electrons (e_{aq}^-) to directly extract F from the C–F bond (Figure 3), where anoxic conditions become critical to avoid the scavenging of e_{aq}^- by oxygen [54] to form less reactive $O_2^{\bullet}$ (1.9×10^{10} $M\,s^{-1}$) [17]. For the thermal degradation of PFAS, little research has focused on determining the byproduct composition due to the challenging quantification of gaseous streams and ashes. The generation of many alternative byproducts suggests that thermal degradation processes did not follow a certain mechanistic pathway compared to classic oxidation/reduction processes. Therefore, the mechanistic elucidation in thermal treatment is process-dependent.

Meanwhile, operational parameters are essential for mechanistic determination and technology application. For example, the reactivity of radical species is different for protonated and deprotonated forms (e.g., $HO_2^{\bullet}$ and $O_2^{\bullet-}$) at different pH. Although PFAS are mostly anions in the tested pH range, the performance of added catalysts varied at different pH since the catalyst surface charge, along with solution chemistry (e.g., conductivity or interfering species), are pH-dependent. Therefore, the PFAS degradation mechanisms should be elucidated carefully under different conditions.

Outlook

Although current technologies can defluorinate PFAS to some extent (Table 1), the goal of complete DeF is still far-fetched. The achievement of complete DeF includes several stages: 1) demonstration of a complete degradation profile of different PFAS classes; 2) tailored design of green chemicals and materials for effective DeF reactions, and 3) engineering of applicable systems is critical to finally achieve the near-zero PFAS discharge regulation. Specifically, we identified the following key research directions to complete PFAS DeF:

• The low PFAS concentration is one of the limiting factors to applying degradation technologies. We forecast that application of PFAS treatments, such as sonication, pyrolysis, and photocatalysis, would benefit from an initial concentration step. In this context, the development of reusable concentration technologies (e.g., ion exchange, adsorption, or membrane filtration) coupled with high-performing degradation strategies should be encouraged to reach near-zero PFAS regulations.

• The scope of PFAS selection can focus on the regulated substances to meet the regulations, or different classes of PFAS to determine the limitations of the technology since PFAS degradation varies upon the chain length and headgroups.

- The zero fluoro-pollution goal involves complete PFAS DeF to avoid byproduct formation. Meanwhile, the development of chemical-free and green catalytic technologies with reusability is encouraged to prevent any secondary contamination. Employing renewable solar or wind energy is also critical to driving the water treatment technology one step forward to carbon neutrality in the water sector.
- The lack of effort in studying, comparing, and discussing the process optimization should be recouped, including water matrices effect (pH, salt effects, coexistence of pollutants), reactor design, and synergies with different treatment technologies. It is essential to drive the research one step forward to the real application by focusing on practical considerations (e.g., realistic PFAS concentrations, removal efficiency, and energy input).
- UV treatment technologies present relatively low EEO ($< 1\,\mathrm{kWh/m^3}$), compared to plasma or electrochemical methods (1–$100\,\mathrm{kWh/m^3}$) and photocatalysis or ultrasound ($> 100\,\mathrm{kWh/m^3}$) [42]. However, current technical comparisons lack homogenous parameters to compare energy spending and costs during PFAS remediation. We hence suggest the development of more relevant TEA methods to find economically practical threshold values. Since DeF is the most critical parameter to ensure zero pollution ambitions, the cost comparison versus DeF constants in different concentrations and systems should be emphasized. For example, the extended use of EEO normalized by DeF rates can be an adequate indicator to compare and elucidate different destruction technologies.

Data Availability

Data will be made available on request.

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.

Acknowledgements

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