

Review

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Disrupting the forever chemicals: cutting-edge physicochemical techniques for PFAS purification

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Abstract

Per- and poly-fluoroalkyl substances (PFAS) have emerged as persistent organic pollutants (POPs) of global environmental concern due to their remarkable chemical stability, hydrophobic and oleophobic properties, and widespread use in the industrial sector. Their persistence and ubiquity in aquatic ecosystems pose significant threats to ecological health and human well-being, highlighting the urgent need for effective removal and advanced purification strategies. In response, water treatment research has increasingly focused on developing efficient remediation technologies. Among these, physicochemical methods have garnered substantial interest due to their high degradation efficiency, broad applicability, and potential for technological innovation. This study presents a comprehensive review of research advancements over the past three years in cutting-edge physicochemical approaches for PFAS removal from water. It examines the removal mechanisms, treatment performance, and operational characteristics of key technologies, including adsorption, membrane separation, electrochemical treatment, UV-based advanced oxidation and reduction, photocatalysis, thermal decomposition, ultrasonic oxidation, and plasma processes. Additionally, the study analyzes major challenges in practical applications, such as high energy demands, low mineralization rates, the formation of potentially hazardous by-products, and limitations in engineering scalability. Emerging directions—including synergistic multi-technology approaches, the design of novel composite materials, and deeper mechanistic insights—are also discussed. Finally, the study offers forward-looking perspectives on the development of high-efficiency, low-carbon, and sustainable PFAS treatment technologies. These findings aim to support effective PFAS remediation, inform risk management strategies, and guide the implementation of large-scale engineering solutions in aquatic environments.

Keywords: PFAS, New contaminants, Emerging pollutants, Wastewater treatment, Physicochemical technologies, Per- and poly-fluoroalkyl substances

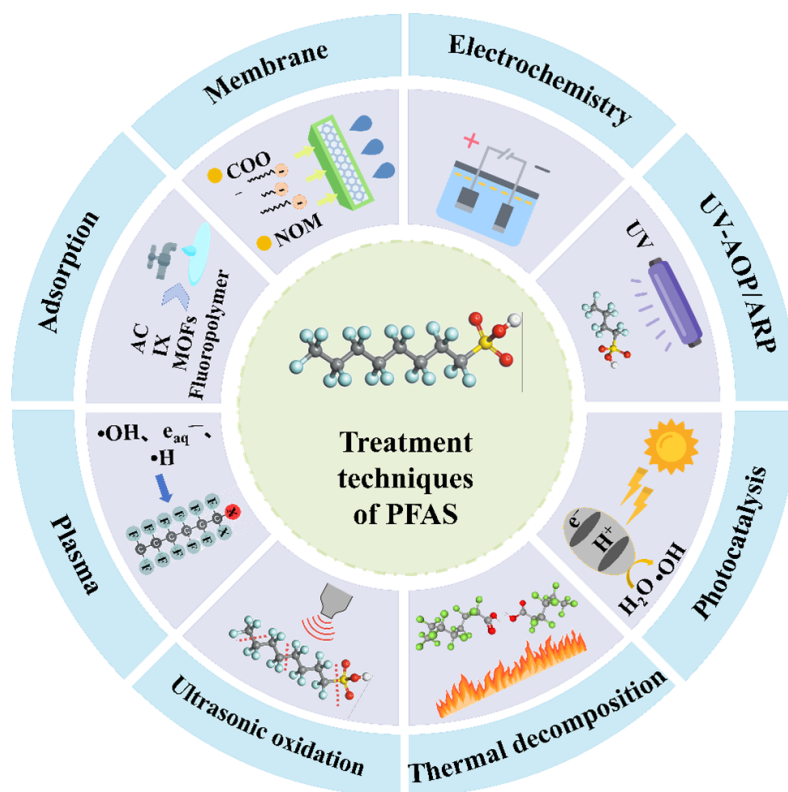
Highlights

- Recent advances in eight physicochemical technologies for PFAS water treatment.
- Comparative analysis reveals trade-offs in PFAS removal efficiency and scalability.
- Synergistic multi-technology systems proposed for high-efficiency PFAS degradation.
- Future strategies focus on sustainable, low-carbon PFAS remediation in real waters.

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Graphical abstract



Introduction

Per- and poly-fluoroalkyl substances (PFAS) are a class of emerging persistent organic pollutants (POPs). Their exceptional chemical stability—driven by a high carbon–fluorine bond dissociation energy (531.5 kJ/mol)—along with their hydrophobic and oleophobic properties^[1], has led to widespread industrial applications. PFAS are commonly used in products such as surfactants, non-stick cookware, food packaging, aqueous film-forming foams, and semiconductor manufacturing^[2,3]. Since their initial synthesis in the 1940s, PFAS have been detected globally across diverse environmental media^[4], particularly in aquatic systems, including surface water, groundwater, drinking water, tap water, and industrial wastewater^[5–9]. They have also been found in air, sediments, and biological tissues^[10–14]. PFAS enter the environment through both point and non-point sources. Point sources include fluorochemical production facilities, industrial operations, firefighting training sites, wastewater treatment plants, and landfills. Non-point sources involve atmospheric deposition, degradation of precursor compounds (both biotic and abiotic), surface runoff, precipitation, and the breakdown of consumer products^[15–17]. Long-term exposure to PFAS-contaminated environments has been linked to a range of adverse health outcomes. Research has demonstrated associations between PFAS exposure and liver dysfunction, immune system suppression, reproductive and developmental disorders, among other health effects^[5,14,18–20]. In response to the environmental persistence and health risks posed by PFAS, regulatory agencies worldwide have implemented increasingly stringent control measures. For instance, in 2024, the United States Environmental Protection Agency (EPA) established new maximum contaminant levels (MCLs) for PFAS in drinking water: 4 parts per trillion (ppt) for both perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS),

and 10 ppt for perfluorononanoic acid (PFNA), perfluorohexane sulfonate (PFHxS), and hexafluoropropylene oxide dimer acid (HFPO-DA)^[21]. According to the latest policy adjustments by the US EPA, the MCLs for PFOA and PFOS remain unchanged at 4 ppt; however, the compliance deadline has been extended from the originally scheduled 2029 to 2031. Meanwhile, the EPA has decided to withdraw or reconsider the individual MCLs of 10 ppt previously established for PFHxS, PFNA, GenX (HFPO-DA), and perfluorobutane sulfonic acid (PFBS). In China, the national standard GB 5749–2022 limits PFOA and PFOS concentrations in drinking water to 80 ng/L and 40 ng/L, respectively. These regulations underscore the urgent need for advanced purification technologies to protect both ecological and human health.

Given the poor biodegradability of PFAS, physicochemical technologies remain the most viable approach for their removal from aquatic environments. In recent years, notable progress has been made in the development and optimization of these methods. Physical treatments, such as adsorption^[22], and membrane separation^[23], have gained widespread attention due to their process maturity and operational flexibility. These methods play a key role in controlling PFAS migration, particularly in preliminary treatment stages. However, they are largely 'transfer-based', meaning they do not degrade PFAS but rather concentrate and relocate them, posing subsequent disposal challenges^[24]. In contrast, chemical treatment technologies, including electrochemical processes^[4,25], UV-based advanced oxidation and reduction^[26], photocatalysis^[27], thermal decomposition^[28], ultrasonic oxidation^[29], and plasma treatment^[30], offer greater potential for mineralization (Fig. 1). These approaches can cleave the stable molecular structure of PFAS, leading to detoxification. Nonetheless, chemical methods often face practical limitations, such as high energy consumption, incomplete mineralization,

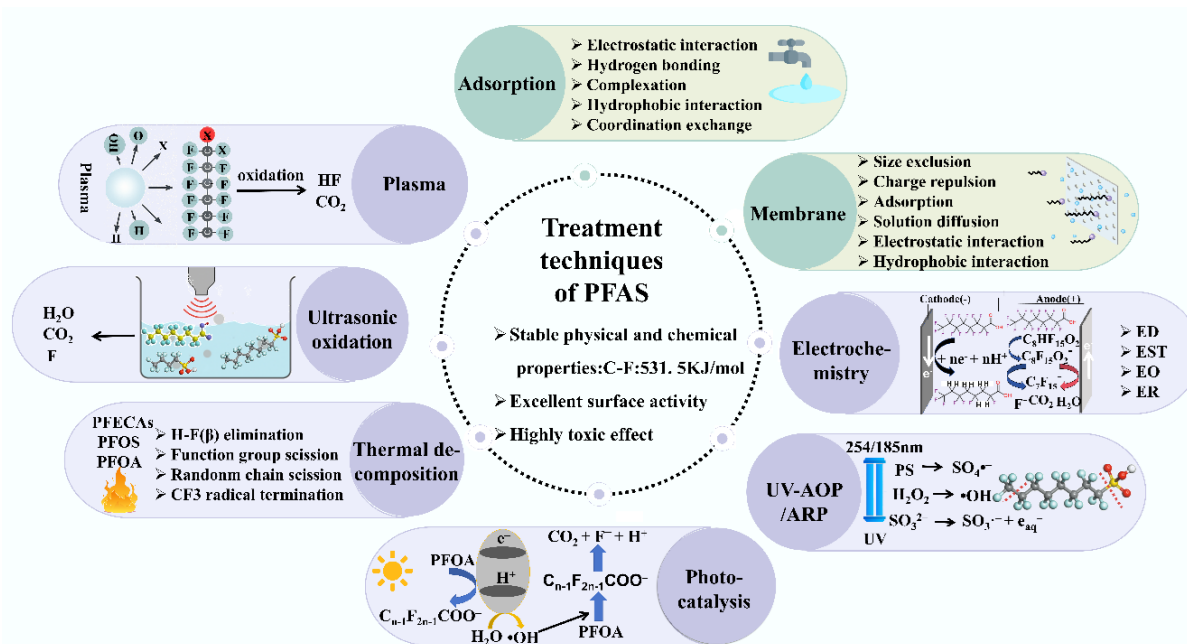


Fig. 1 Physical (green), and chemical (purple) technology principles for treating PFAS wastewater.

formation of potentially harmful by-products, and cost barriers to large-scale implementation^[31]. Therefore, the development of high-efficiency, low-carbon, and sustainable PFAS treatment technologies is urgently needed to meet growing environmental and regulatory demands.

This paper seeks to address the following core research question: How can recent advances in physicochemical technologies be critically assessed and strategically integrated to overcome the key challenges associated with PFAS removal in aquatic environments? To answer this, we establish a comparative evaluation framework focusing on mechanistic robustness, energy efficiency, scalability, and environmental trade-offs. This integrated approach enables cross-technology analysis, identifies existing knowledge gaps, and provides guidance for future research and engineering-scale implementation.

Physicochemical remediation technologies

Adsorption technology

Adsorption is a key technology for the removal of per- and polyfluoroalkyl substances (PFAS), particularly effective for long-chain compounds. Its widespread use stems from its operational simplicity, relative low cost, broad applicability, and high treatment efficiency. PFAS adsorption involves multiple interaction mechanisms, including electrostatic attraction, hydrogen bonding, hydrophobic interactions, complexation, and coordination exchange (Fig. 2a)^[32]. Long-chain PFAS primarily interact through hydrophobic forces and van der Waals interactions, while short-chain PFAS rely more on electrostatic attraction and hydrogen bonding. Common adsorbents include activated carbon (AC), ion exchange resins (IX), metal-organic frameworks (MOFs), and fluorinated polymers.

AC is widely employed in water treatment due to its high specific surface area and strong adsorption performance. Both granular activated carbon (GAC) and powdered activated carbon (PAC) have been shown to effectively remove PFAS, with long-chain compounds exhibiting significantly higher removal efficiencies than

short-chain PFAS^[37]. The adsorption performance of AC is strongly influenced by its physical characteristics—greater surface area and a higher number of functional groups enhance PFAS adsorption, explaining the superior performance of PAC compared to GAC^[38]. To improve AC performance, researchers have developed modification techniques such as acid washing combined with high-temperature thermal treatment (1,050 °C). This process reduces surface oxygen content, enhances hydrophobicity, accelerates adsorption kinetics, and increases capacity^[39]. However, the presence of dissolved organic matter (DOM) in water can inhibit AC performance. To address this, Huang et al. modified AC using organosilicon (C-OS) and inorganic silicon (C-IS) compounds (Fig. 2b). The C-IS-modified AC demonstrated significantly enhanced adsorption, with capacities for PFOA and PFOS increasing by 15.08-fold and 3.65-fold, respectively, compared to unmodified AC^[33]. Wu et al. evaluated the adsorption of 6:2 chlorinated polyfluoroalkyl ether sulfonate (6:2 Cl-PFAES or F-53B) using coconut shell-activated carbon (CSAC). The study identified a synergistic mechanism involving electrostatic attraction, hydrogen bonding, hydrophobic interactions, and cation bridging. CSAC achieved a maximum adsorption capacity of 261.64 mg/g and > 99.9% removal of 1 mg/L F-53B within 8 h, reaching equilibrium at 24 h^[40].

Ion exchange resins (IX) remove PFAS primarily through electrostatic interactions between their positively charged functional groups and the negatively charged PFAS head groups, supplemented by hydrophobic and van der Waals forces^[41]. Short-chain PFAS removal is dominated by electrostatic attraction, while long-chain PFAS benefit from additional non-electrostatic interactions^[42]. While IX resins perform well for perfluorosulfonic acids (PFSAs), their selectivity toward perfluorocarboxylic acids (PFCAs) and 6:2 fluorotelomer sulfonate (6:2 FTS) in industrial wastewater remains limited. To address this, 16 anion exchange resins (AERs) with varying quaternary ammonium groups and pore structures were synthesized. AERs featuring long-chain asymmetric amine groups, such as (12-1-1), demonstrated enhanced hydrophobic and synergistic electrostatic–non-electrostatic interactions, improving selectivity for

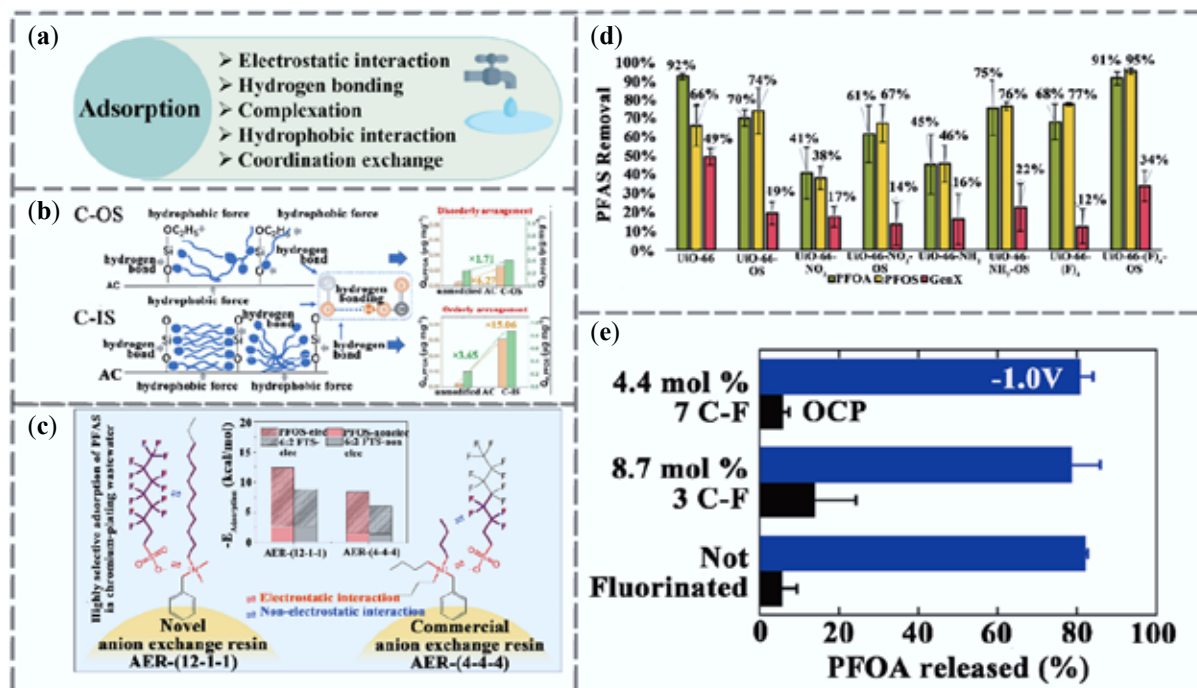


Fig. 2 Research progress on adsorption technologies for PFAS removal. (a) Adsorption removal mechanism. (b) Removal of PFAS using organosilicon (C-OS) and inorganic silicon (C-IS) modified activated carbon^[33]. (c) Adsorption of PFAS by AERs with different quaternary ammonium functional groups and pore structures^[34]. (d) Adsorption performance of UiO-66 MOFs for PFOA, PFOS, and GenX^[35]. (e) Open circuit potential (OCP) of PFOA after 1-h adsorption at -1 V vs Ag/AgCl or at 1 V. Error bars represent standard deviations ($n = 3$)^[36].

PFAS like 6:2 FTS. These materials achieved adsorption capacities up to $380 \mu\text{g/g}$ —2.1 times higher than that of the commercial resin PFA694E (Fig. 2c)^[34].

Metal-organic frameworks (MOFs), known for their ultra-high surface areas, tunable pore structures, and excellent water stability, have emerged as promising materials for PFAS adsorption. Traditional adsorbents like GAC and IX often suffer from low capacity, poor regeneration, and limited efficiency for short-chain PFASs. In contrast, zirconium-based MOFs, particularly UiO-66 variants (e.g., UiO-66-NH₂, UiO-66-NO₂, UiO-66-(F)₄), and their composites (e.g., UiO-66-X-PDMS, UiO-66-X-OS), exhibit strong performance due to synergistic electrostatic attraction between Zr(IV) centers and PFAS head groups, and fluorophilic F-F interactions. Notably, UiO-66-(F)₄-OS achieved over 90% removal efficiency for PFOA, demonstrating its potential for trace-level PFAS remediation (Fig. 2d)^[35].

Fluorinated polymers leverage F-F interactions to maintain high PFAS selectivity, even in complex water matrices. These materials can remove both long- and short-chain PFAS through high fluorine density or tailored pore and electric field structures^[43]. For instance, Yang et al. developed PFPE-IE-X, a fluorinated ion-exchange material combining fluorosulfonate and electrostatic interactions. It removed 11 types of C₄–C₁₀ PFAS (1–10 ppb) with > 98% efficiency, achieving a maximum GenX adsorption capacity of 518.9 mg/g ^[44]. Román Santiago et al. synthesized a trifunctional copolymer with fluorinated, amine, and redox-active TEMPO groups, enabling electro-controlled PFAS adsorption and desorption. Application of $+0.9$ V promotes PFAS capture, while -0.5 V facilitates release, eliminating the need for chemical regeneration. The copolymer achieved adsorption capacities of 205.8 mg/g for PFBA and 860.8 mg/g for PFHxA. Short-chain PFAS easily penetrated polymer pores, whereas long-chain PFAS accumulated on the surface, enhancing desorption rates. Over 80% of the electrodes were regenerable via this process

(Fig. 2e)^[36,45]. Recent studies also demonstrate chain-length-dependent adsorption by fluorinated porous polymer PPN-6-FNDMB. Long-chain PFAS are adsorbed via fluorophilic and hydrophobic interactions, while short-chain PFAS interact primarily through electrostatic and hydrogen bonding mechanisms. PPN-6-FNDMB exhibited a capacity of 4.0 mmol/g and reached adsorption equilibrium within 30 s. In real water treatment tests, it removed over 99% of 21 PFAS compounds, although further assessment of its environmental safety is necessary^[46].

While adsorption offers significant advantages—such as cost-effectiveness, ease of use, and broad PFAS applicability—most studies are limited to controlled laboratory conditions. In real-world scenarios, natural organic matter, inorganic ions, and co-existing pollutants can compete for active sites, reducing adsorption performance. Additionally, challenges related to adsorbent regeneration and safe PFAS disposal after adsorption persist. Future research should focus on integrating adsorption with degradation technologies or developing multifunctional composite materials that enable both PFAS enrichment and mineralization. These strategies could significantly enhance treatment efficiency and environmental sustainability.

Membrane separation technology

Membrane separation is a physical water treatment technology that achieves selective retention based on differences in particle size and physicochemical properties. It is widely applied in the removal of micropollutants such as PFAS, utilizing semipermeable membranes that permit water molecules to pass while retaining larger solutes and contaminants^[47]. Based on pore size, membrane processes are categorized into microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). Of these, NF and RO are the most effective for PFAS removal, as MF and UF generally lack the resolution

needed to retain small molecular contaminants. The mechanisms underlying PFAS rejection in NF and RO membranes include size exclusion, charge repulsion, solution diffusion, adsorption, hydrophobic interactions, and electrostatic effects (Fig. 3a)^[48].

Nanofiltration

NF membranes possess pore sizes intermediate between UF and RO membranes. PFAS removal by NF membranes primarily depends on size exclusion and electrostatic repulsion. While NF exhibits strong retention for long-chain PFAS, its performance is typically lower for short-chain PFAS due to the inherent trade-off between membrane permeability and selectivity. To address this limitation, Lu et al. introduced ethanol (ETOH) as a co-solvent during interfacial polymerization (Fig. 3b)^[49]. This approach enhanced monomer enrichment, intensified exothermic reactions, and promoted nanobubble formation, resulting in an ETOH-4 NF membrane with a highly wrinkled, ultrathin, and dense selective layer. The membrane achieved high water permeability (17.54 LMH/bar) while removing 93.42%–99.99% of 22 PFAS compounds, including short-chain species. Mahofa et al. developed a graphene oxide- β -cyclodextrin (GO- β CD) composite NF membrane featuring asymmetric nanochannels^[50]. This design utilized host-guest affinity between PFAS fluorocarbon chains and β CD cavities, combined with high transport energy barriers, to enhance PFAS retention. The membrane achieved > 90% removal efficiency for short-chain PFAS, with binding energies approximately 20% higher than those of comparable α -cyclodextrin systems (Fig. 3c).

Reverse osmosis

RO membranes operate by applying high pressure to overcome osmotic gradients, allowing selective transport of water molecules

while rejecting solutes. RO is highly effective at removing a wide range of contaminants—including inorganic salts, colloids, and organic compounds—and is widely used in seawater desalination and potable water treatment. PFAS removal by RO membranes typically exceeds 99% due to the combined effects of size exclusion, solution diffusion, and electrostatic repulsion. However, RO systems incur high energy and operational costs and generate concentrated PFAS brines, which require further management. Consequently, targeted PFAS-focused research has often favored NF systems over RO. Nevertheless, RO remains critical in high-performance water treatment scenarios. For instance, Choe et al. compared ozone oxidation, GAC adsorption, and RO for PFAS removal, demonstrating that an integrated RO-GAC system achieved > 99.5% PFAS removal, even when ozone treatment was ineffective^[52]. Lee et al. implemented a treatment train combining UF and two-stage RO for semiconductor wastewater reuse (Fig. 3d), achieving PFAS removal rates of 96%–99% and wastewater recovery exceeding 75% (Fig. 3e)^[51]. Studies also indicate that surfactants such as sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB) do not significantly affect PFOA or PFBA rejection by RO membranes. In contrast, NF membrane performance was slightly enhanced (by ~2%–3%) in the presence of cationic surfactants or divalent cations. Temperature increases had minimal impact on PFAS rejection by RO membranes but slightly decreased short-chain PFAS retention in NF systems^[53].

Despite their effectiveness, NF and RO membranes face challenges related to membrane fouling, especially in high-salinity or organic-rich waters. PFAS and other organic compounds can accumulate on membrane surfaces or within pores, leading to decreased flux, pore blockage, and long-term performance decline. To

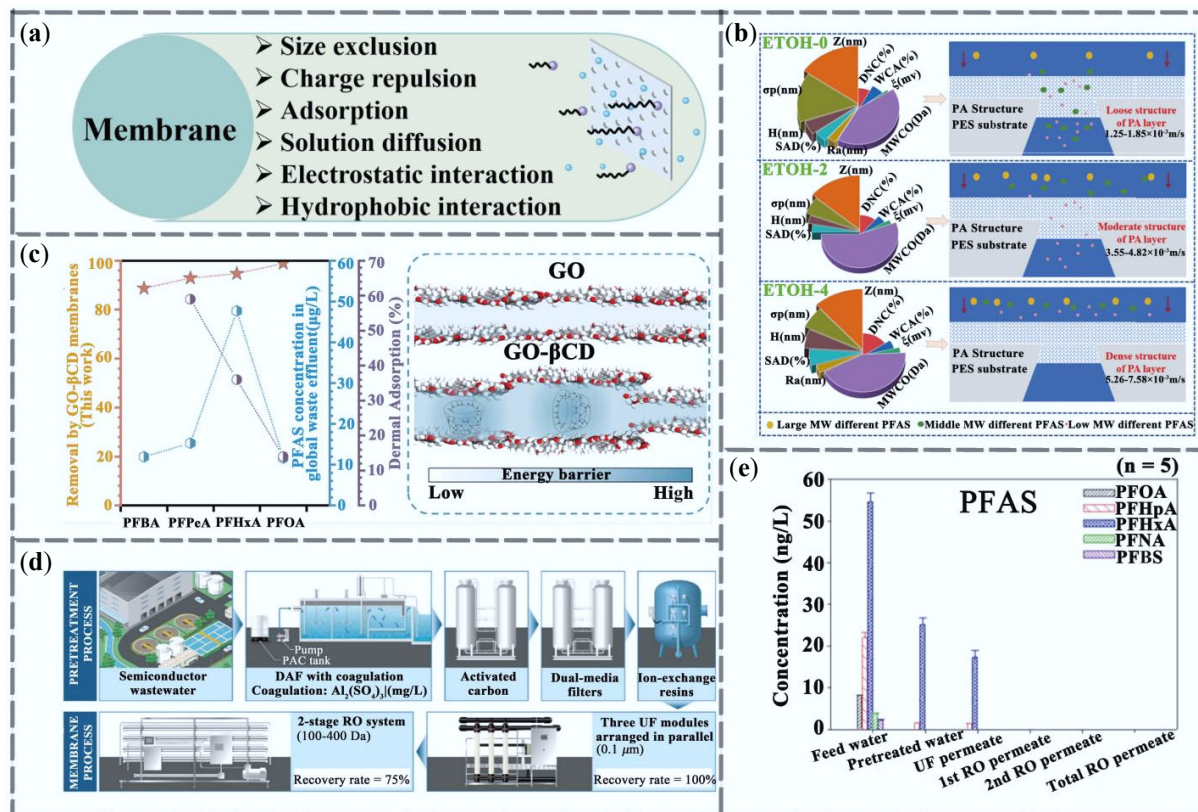


Fig. 3 Research progress on membrane separation technology for PFAS removal. (a) Membrane separation removal mechanism. (b) PFAS removal mechanism of ETOH-regulated NF membranes^[49]. (c) Retention of PFAS by GO- β CD composite membranes^[50]. (d) Trends in the removal of PFAS from semiconductor wastewater reuse systems on a pilot scale ($n = 3$)^[51]. (e) Schematic diagram of pilot-scale semiconductor wastewater reuse system composed of DAF, activated carbon, ion exchange resin, dual-media filter, UF and two-stage reverse osmosis membrane^[51].

mitigate fouling, Zhang et al. combined dielectric barrier discharge (DBD) and nitrite pretreatment with UF membranes for treating Yangtze River water^[54]. Reactive species, including $\cdot\text{OH}$ (33.25%), $\text{SO}_4^{\cdot-}$ (28.49%), e_{aq}^- (20.56%), and $\cdot\text{O}_2^-$ (11.32%), collectively contributed to fouling mitigation. PFOA degradation occurred via two primary pathways: (1) $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ -initiated Kolbe decarboxylation and hydrolysis of the carboxyl group; and (2) e_{aq}^- attacked CF_2 moieties, promoting fluorine-hydrogen exchange and progressive carbon chain cleavage. The DBD/nitrite pretreatment improved flux recovery (> 84.10%) and achieved > 85.13% PFOA degradation. However, elevated pH inhibited radical formation, reducing both fouling control and degradation efficiency. Ying Shi et al. explored direct contact membrane distillation (DCMD) for PFAS separation from groundwater using polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF) membranes under 120-h continuous operation (PFOA concentration: 10 mg/L)^[55]. PTFE membranes exhibited rapid PFAS adsorption due to strong F–F interactions, but surface hydrophilization and pore wetting led to structural degradation. PVDF membranes, with weaker F–F interactions and tail-oriented adsorption, maintained hydrophobicity and structural integrity. PVDF membranes showed only a 15% flux decline (vs 43% for PTFE), maintained 80% PFOA rejection (vs 51% for PTFE), and demonstrated superior resistance to fouling under high-salinity and high-TOC conditions.

Future research on membrane separation technologies for PFAS remediation should focus on developing novel membranes with high selectivity and anti-fouling properties, elucidating membrane fouling mechanisms, and optimizing regeneration strategies. Moreover, exploration of membrane surface modifications (e.g., imparting oleophobicity and resistance to inorganic/organic fouling), application of fluorine-free alternative materials, operational condition optimization, permeate post-treatment methods, and fouling behaviors under various water qualities and PFAS chain lengths are necessary. Furthermore, integrating membrane separation with destruction technologies (such as advanced oxidation and electrochemical oxidation) will contribute to enhancing environmental sustainability and engineering feasibility.

Electrochemical technologies

Electrochemical methods have garnered significant attention for their capacity to achieve deep degradation and complete mineralization of PFOS, PFOA, and other PFAS compounds^[56]. A typical electrochemical treatment system comprises an anode, a cathode, and an external power source, and includes processes such as electrodialysis (ED), electroadsorption (EST), electrochemical oxidation (EO), and electrochemical reduction (ER).

ER technology is considered a promising approach for PFAS remediation due to its mild operating conditions and relative simplicity^[57]. The degradation of PFAS via ER typically follows two pathways: (1) stepwise two-electron transfer; and (2) concerted two-electron transfer. In the former, the initial electron transfer produces a halogenated radical anion ($\text{R-X}^{\cdot-}$), which undergoes R–X bond cleavage to generate a radical ($\text{R}\cdot$) and a halide ion (X^-). The latter pathway involves simultaneous electron transfer and bond cleavage, directly forming $\text{R}\cdot$, which rapidly accepts a second electron to yield the carbanion (R^-), thereby accelerating degradation^[58]. On gold electrodes, PFOA degradation predominantly follows the concerted mechanism, which facilitates C–F bond cleavage but often results in limited defluorination efficiency^[59]. To improve ER performance, Wang et al. developed a cathode modified with quaternary ammonium surfactants. This design enriched anionic PFAS at the electrode surface through electrostatic–hydrophobic

interactions, enabling direct electron transfer and C–F bond cleavage at -1.6 V (vs Ag/AgCl), achieving PFMeUPA removal and defluorination efficiencies of 99.81% and 78.67%, respectively (Fig. 4b)^[60].

EO is more widely used in water treatment applications, often achieving PFAS removal efficiencies exceeding 99%. EO operates via two main mechanisms: (1) direct electron transfer (DET) from PFAS molecules to the electrode, which is equivalent to oxidation by surface-generated holes (h^+); and (2) indirect oxidation by hydroxyl radicals ($\cdot\text{OH}$), formed at the anode surface^[64].

Anode material plays a crucial role in EO efficiency. Current research focuses on 'non-active' anodes such as boron-doped diamond (BDD), lead dioxide (PbO_2), and antimony- or fluorine-doped tin dioxide (SnO_2), which exhibit high oxygen evolution overpotentials. These materials generate large amounts of $\cdot\text{OH}$ radicals and facilitate efficient electron transfer while remaining chemically inert, thus avoiding unwanted side reactions^[65,66]. BDD electrodes are widely used due to their chemical stability, corrosion resistance, long operational lifespan, and broad electrochemical potential window^[65]. Their weak adsorption of $\cdot\text{OH}$ radicals and low electrochemical energy requirements promote effective degradation of PFAS through mechanisms such as DET, Kolbe decarboxylation, defluorination, and C–C bond cleavage^[67]. BDD electrodes can be synthesized via chemical vapor deposition (CVD) on substrates such as Si, Ti, W, Mo, Nb, and Pt^[56,66]. PbO_2 - and SnO_2 -based electrodes, especially Sb– SnO_2 , also efficiently generate $\cdot\text{OH}$ radicals. These radicals attack PFAS molecules through sequential decarboxylation, desulfonation, hydrolysis, oxidation, HF elimination, and hydration steps, leading to progressive carbon chain shortening and eventual mineralization into CO_2 , H_2O , and F^- ^[65,68].

Duinslaeger & Radjenovic achieved synergistic removal of C4–C8 PFAS using boron-doped graphene sponge anodes, combining electroadsorption (7.4%–35%) with EO (9.3%–32%) to reach defluorination efficiencies of 74%–87%^[69]. Fang et al. developed a hybrid process integrating anion exchange resin (AER) adsorption with BDD-based EO, attaining adsorption rates up to 96.2% for long-chain perfluoroalkyl ether carboxylic acids (PFECAs) (e.g., PFDOHPA) and > 99.999% degradation and > 85% defluorination in the EO stage, with intermediates such as trifluoroacetic acid identified for the first time (Fig. 4c)^[61]. In chloride-containing water, Song et al. found that Pt anodes preferentially generate $\text{Cl}\cdot$ radicals, enhancing PFOA degradation (89.4%–94.9%). The additional presence of $\cdot\text{OH}$ facilitated stepwise carbon chain cleavage and mineralization, underscoring the importance of balancing $\text{Cl}\cdot$ and $\cdot\text{OH}$ contributions for optimal degradation (Fig. 4d)^[62]. For comprehensive PFAS removal across various chain lengths, integrated electrochemical systems have been developed. Guan et al. proposed a sequential UV/sulfite (UV/S) reduction followed by EO. The UV/S stage effectively defluorinated long-chain PFAS, while EO mineralized short-chain intermediates, achieving nearly 100% total defluorination and mineralization of PFAS in aqueous film-forming foams (AFFF)^[70]. Kim et al. designed a coupled electrodialysis–electroadsorption system using water-soluble redox polymers and nanofiltration membranes to remove PFAS ranging from ultra-short-chain (C2) to long-chain (\geq C6). The system achieved 82%–94% removal and 76%–100% defluorination, with electroadsorption contributing up to 90% of long-chain PFAS removal, while also addressing membrane fouling and enabling simultaneous desalination (Fig. 4f)^[63].

Despite their potential, electrochemical technologies face several barriers to practical application, including the high cost, limited activity, and insufficient durability of current electrode materials. Most studies have been conducted under controlled laboratory conditions using simplified water matrices, raising concerns about

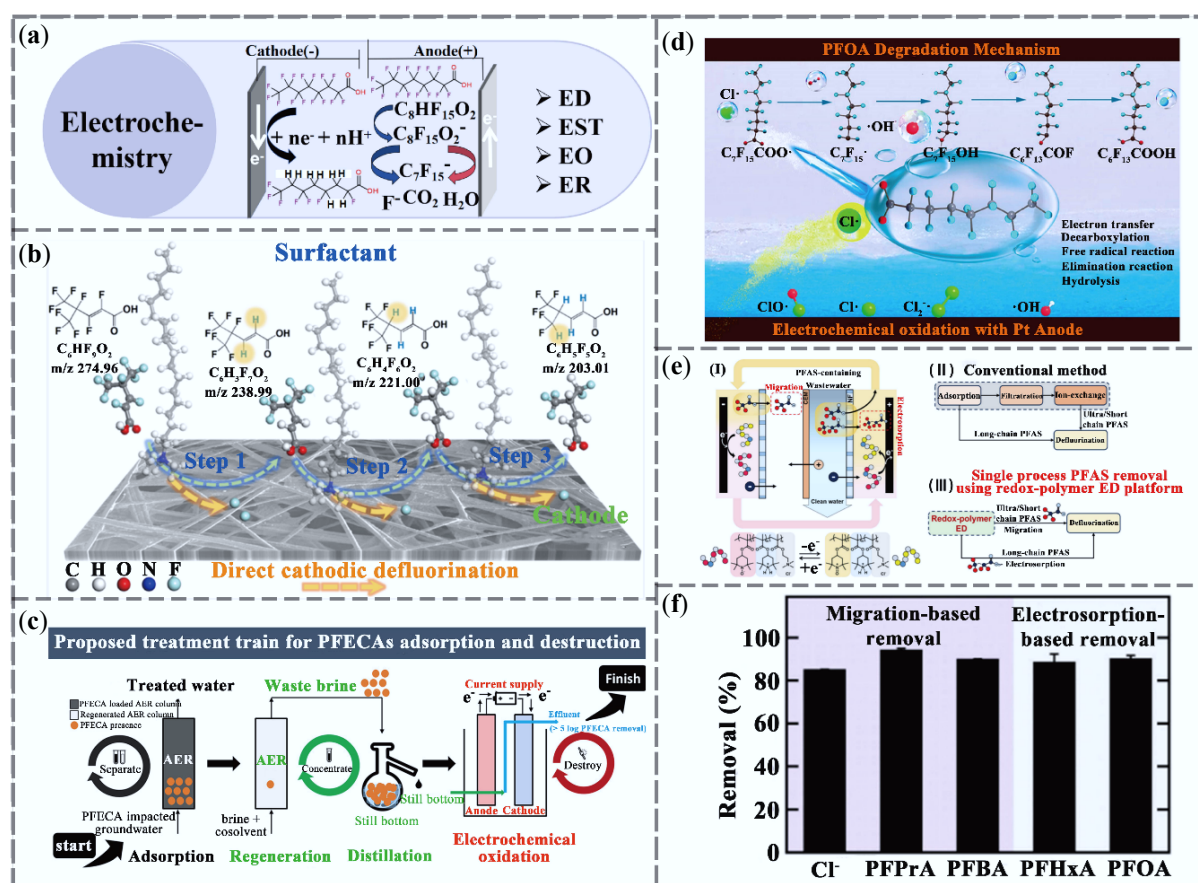


Fig. 4 Research progress in electrochemical technologies for PFAS removal. (a) Electrochemical removal mechanism. (b) Electroreduction system with quaternary ammonium surfactant-modified cathode for the degradation of unsaturated PFAS^[60]. (c) Combined AER and EO process for removal and degradation of four structurally different perfluoroalkyl ether carboxylic acid (PFECA) compounds^[61]. (d) Study on PFOA degradation in an EO system triggered by Cl[•] radicals^[62]. (e) Electrodialysis system for removal of PFAS from oxidized polymers and mechanism diagram^[63]. (f) Removal efficiencies of PFAS with different carbon chain lengths by the redox polymer electrodialysis system^[63].

real-world scalability and empirical validity. Furthermore, few comprehensive techno-economic or life-cycle assessments have been conducted, limiting insights into their environmental and financial viability. Future research should prioritize the development of cost-effective, high-performance, and durable electrode materials, deepen mechanistic understanding under complex water conditions, and validate treatment efficacy in pilot-scale or real-world systems. Integration with complementary technologies and improved system design will also be essential to enhance environmental sustainability and engineering feasibility.

UV-advanced oxidation and reduction technologies

Ultraviolet advanced oxidation–reduction processes (UV-AOPs/ARPs) employ UV light to activate oxidants (e.g., H₂O₂, persulfate [PS/PMS]) or reductants (e.g., sulfite, iodide, Fe²⁺), generating highly reactive species such as hydroxyl radicals (•OH), sulfate radicals (SO₄^{•-}), and hydrated electrons (e_{aq}⁻). These reactive species attack PFAS molecules directly or indirectly, promoting effective defluorination and mineralization (Fig. 5a)^[71]. Owing to their efficiency in cleaving C–F bonds, UV-AOPs/ARPs have emerged as a prominent research focus for advanced PFAS treatment.

To address the varied degradation behaviors of different PFAS (e.g., PFHpA, PFHxS, and 6:2 FTS), a VUV/UV (vacuum ultraviolet/ultraviolet)-driven dynamic reduction–oxidation switching strategy

was developed^[76]. In the reduction phase (UV/sulfite), e_{aq}⁻ generated by 185 nm light cleaves the C–F bonds of PFHpA and PFHxS through a hydrogen/fluorine exchange mechanism, achieving 60%–65% defluorination. In the subsequent oxidation phase (UV/H₂O₂), •OH targets C–H bonds in 6:2 FTS and mineralizes intermediates. This oxidation–reduction–oxidation (ORO) sequence yields 83.9% defluorination of 6:2 FTS while reducing energy consumption by 50%. The study also revealed that sulfonate-induced steric hindrance inhibits •OH attack, contributing to persistent short-chain PFCA byproducts. Under real water conditions, degradation efficiency declined by 43%–49%, with ~27.7% of fluorine retained in refractory intermediates, underscoring the challenge of achieving complete mineralization.

For emerging perfluorononene oxybenzene sulfonate (OBS) using UV/PS and UV/sulfite (UV/SF) systems^[72]. In the UV/PS system, OBS was mainly degraded via oxidation by SO₄^{•-} and •OH, exhibiting a rapid degradation rate (k_{obs} = 1.05/min), but a low defluorination rate of 27.6%. Conversely, in the UV/SF system, e_{aq}⁻ predominantly cleaved the C–F bonds through H/F exchange and HF elimination mechanisms, achieving a defluorination rate of 87.7%. In diluted OBS-based fluorescent protein foam, UV/SF achieved over 90% defluorination within 10 h (Fig. 5b), demonstrating promising engineering application potential. Qi et al. designed a UV/S + α-Fe₂O₃ system using α-Fe₂O₃ nanoparticles (Fe(800)) with hydrophobic

confinement and oxygen vacancies^[77]. Under anaerobic conditions, e_{aq}^- enabled GenX degradation via ether bond and C–H bond cleavage, achieving nearly 100% removal and 88.8% defluorination. Even under aerobic conditions, defluorination reached 57.4%, outperforming the UV/S system alone and addressing a key limitation of e_{aq}^- -based methods. Gu et al. studied the degradation of C7 HFPO-TA under UV/PS and identified a novel decarboxylation–hydroxylation–defluorination–hydrolysis (DHEH) pathway, with $C_6F_{12}O_3$ ester detected as a key intermediate^[73]. Molecular branching was found to influence reactivity: longer branches reduced steric hindrance, enhancing interaction with reactive species. Despite > 99.9% degradation of C7 HFPO-TA and co-contaminant PFHxA, defluorination rates remained below 55%, indicating a bottleneck in short-chain mineralization (Fig. 5c). Tan et al. demonstrated that electron transfer (ET) from e_{aq}^- , not C–F cleavage, is the rate-limiting step in UV/S systems^[74]. Applying Marcus' theory, they predicted PFAS degradability ($R^2 = 0.744$) across 41 species. Long chains (CF_2)_n ≥ 6 and CF_2COO^- groups facilitated ET, while C–H and SO_3^- groups hindered it (Fig. 5d). Carboxylate PFAS (e.g., PFOA) were degraded via α - CF_2 attack, leading to intermediate buildup. In contrast, PFOS and other sulfonates underwent direct mid-chain attack, allowing simultaneous defluorination. These findings offer mechanistic insight into PFAS degradation and guidance for molecular design.

Traditionally viewed as inhibitory, nitrate was shown by Feng et al. to enhance PFOA defluorination by 54% at 100 μ M concentration^[75]. Reactive nitrogen species (RNS) derived from nitrate stretched the H–O bond in water, lowered its dissociation energy, and activated the DHEH pathway (Fig. 5e). This overturned previous assumptions about the role of nitrate and highlighted the potential of microenvironment engineering. In bromide-rich waters, a UV/S-driven reductive–oxidative cycle (ROC) was proposed^[26]: wherein e_{aq}^- -driven defluorination was coupled with reactive bromine species (RBS)-mediated C–H bond cleavage. This synergistic process achieved 96% PFOA defluorination and 100% BrO_3^- removal within 240 min, presenting a viable route for simultaneous treatment of PFASs and co-contaminants.

UV-AOPs/ARPs enable efficient defluorination (often > 96% for long-chain PFASs) by leveraging the synergistic actions of radicals and hydrated electrons, while significantly reducing energy consumption. The elucidation of ET as the rate-limiting step and the discovery of nitrate-enhanced degradation provide valuable theoretical foundations for future advancements. However, several challenges persist, including incomplete mineralization of short-chain PFAS, matrix interferences, and functional group-dependent reactivity. Future research should focus on developing strategies for short-chain mineralization, microenvironment regulation to resist

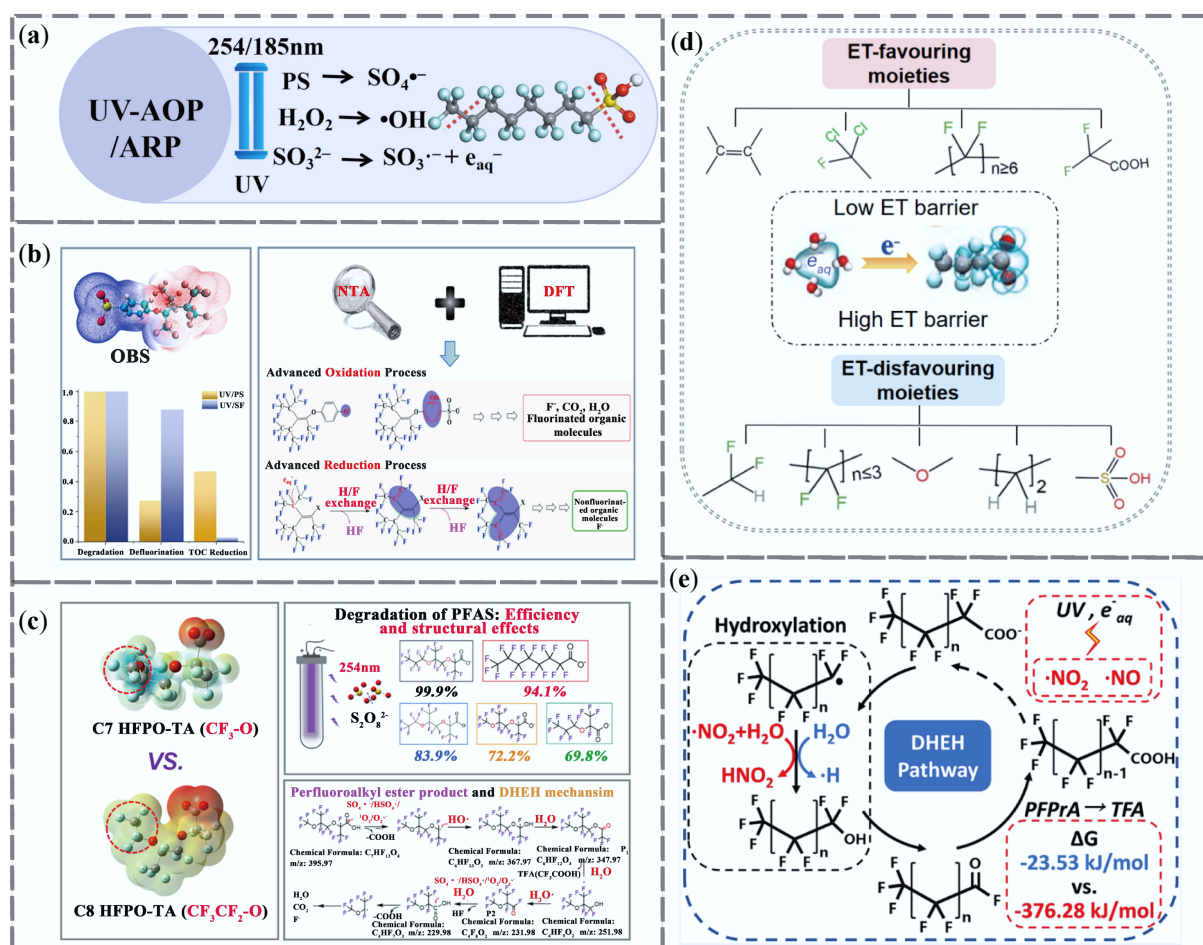


Fig. 5 Research progress of ultraviolet advanced oxidation and reduction technologies for PFAS removal. (a) UV-AOP/ARP removal mechanism. (b) Mechanisms of OBS degradation by UV/PS and UV/SF processes, along with degradation, defluorination, and TOC reduction after 10 h treatment of OBS-based fluorescent protein foam^[72]. (c) Mechanism of C7 HFPO-TA degradation in the UV/PS system and the effect of carbon chain length on degradation efficiency^[73]. (d) Functional groups promoting ET shown in pink regions, and those inhibiting ET shown in blue regions^[74]. (e) DHEH pathway of nitrate-assisted PFAS degradation in the UV/S system^[75].

interference, molecular design based on electron transfer theory, and the engineering integration of green processes such as reductive-oxidative cycling (ROC), to advance this technology from laboratory research toward practical application.

Photocatalytic technology

Photocatalysis is a light-driven process in which a catalyst absorbs photons, promoting electrons (e^-) from the valence band to the conduction band and generating electron-hole pairs (e^-/h^+). These pairs subsequently produce reactive species such as hydrated electrons (e_{aq}^-), hydroxyl radicals ($\cdot OH$), and superoxide radicals ($\cdot O_2^-$), which attack the strong C-F bonds in PFAS molecules, facilitating defluorination and mineralization (Fig. 6a)^[78]. Owing to its sustainability, mild operating conditions, and controllability, photocatalysis has gained significant attention. However, the strong C-F bond energy in PFAS often limits photocatalytic degradation efficiency, resulting in prolonged reaction times, low mineralization rates, and incomplete defluorination.

Pure TiO_2 , with its wide bandgap (3.2 eV) and high electron-hole recombination rate, exhibits limited photocatalytic efficiency for PFAS degradation^[81]. To overcome these limitations, Chowdhury & Choi developed a composite photocatalyst—Pb-doped TiO_2 modified with reduced graphene oxide (TiO_2 -Pb/rGO)—which improved PFOA degradation efficiency to 98% and achieved a defluorination rate of 34%. Pb doping introduced oxygen vacancies, reducing the bandgap, while rGO enhanced electron mobility and adsorption capacity, enabling broadband performance under UVA, UVB, and UVC light sources. The system primarily relied on reactive species, including holes, superoxide radicals, and singlet oxygen to degrade PFAS while maintaining high energy efficiency (4.05 kWh/m³)^[82]. In semiconductor photocatalysis, hole scavengers such as methanol, formic acid, acetic acid, triethanolamine, and EDTA are frequently

used to inhibit electron-hole recombination and enhance degradation efficiency^[83]. Wang & Zhang found that using TiO_2 under 254 nm UV light, PFOA degradation rates were 10.5% (oxygen atmosphere), and 12.4% (nitrogen atmosphere). With 3 mM oxalic acid (pH 2.47) in oxygenated conditions, the degradation rate decreased to 6.6%. However, nitrogen purging (to remove oxygen) increased degradation efficiency to 86.7%, indicating that oxalic acid, as a hole scavenger, promotes reductive defluorination of PFOA. Potassium iodide was found to inhibit PFOA degradation, while electron scavengers such as $K_2S_2O_8$ suppressed the reaction entirely^[84]. In related research, Shah & Patel demonstrated that TiO_2 photocatalysts, combined with EDTA or oxalic acid, could effectively degrade lindane under acidic conditions (pH = 2.8). EDTA notably enhanced electron-hole separation, driving reductive dechlorination and achieving complete lindane removal within 90 min. Oxalic acid at concentrations below 25 mM showed minimal inhibitory effects on oxidative degradation. These findings suggest that further optimization under neutral pH conditions and mitigation of dissolved oxygen interference are critical for real-world applications^[85].

Titanium-based composite materials also exhibit enhanced performance. Wen et al. developed a titanium-based MOF photocatalyst (MIL-125-NH₂), employing a synergistic mechanism in which e_{aq}^- drove reductive defluorination and $\cdot OH$ promoted carbon-chain cleavage and mineralization (Fig. 6b)^[79]. Using glucose as a sacrificial reductant at near-neutral pH (4.6–5.8), MIL-125-NH₂ achieved 98.9% PFOA degradation and 66.7% defluorination within 24 h (Fig. 6c), with good recyclability over three cycles. Bismuth-based photocatalysts also show promise. Zhu et al. synthesized a Bi/TNTs@AC composite, comprising bismuth-loaded titanate nanotubes supported on activated carbon^[86]. Under 254 nm UV irradiation, $\cdot OH$ and H^+ generated by Bi/TNTs@AC facilitated GenX degradation. With 1 g/L of catalyst, 100 $\mu g/L$ of GenX was adsorbed within

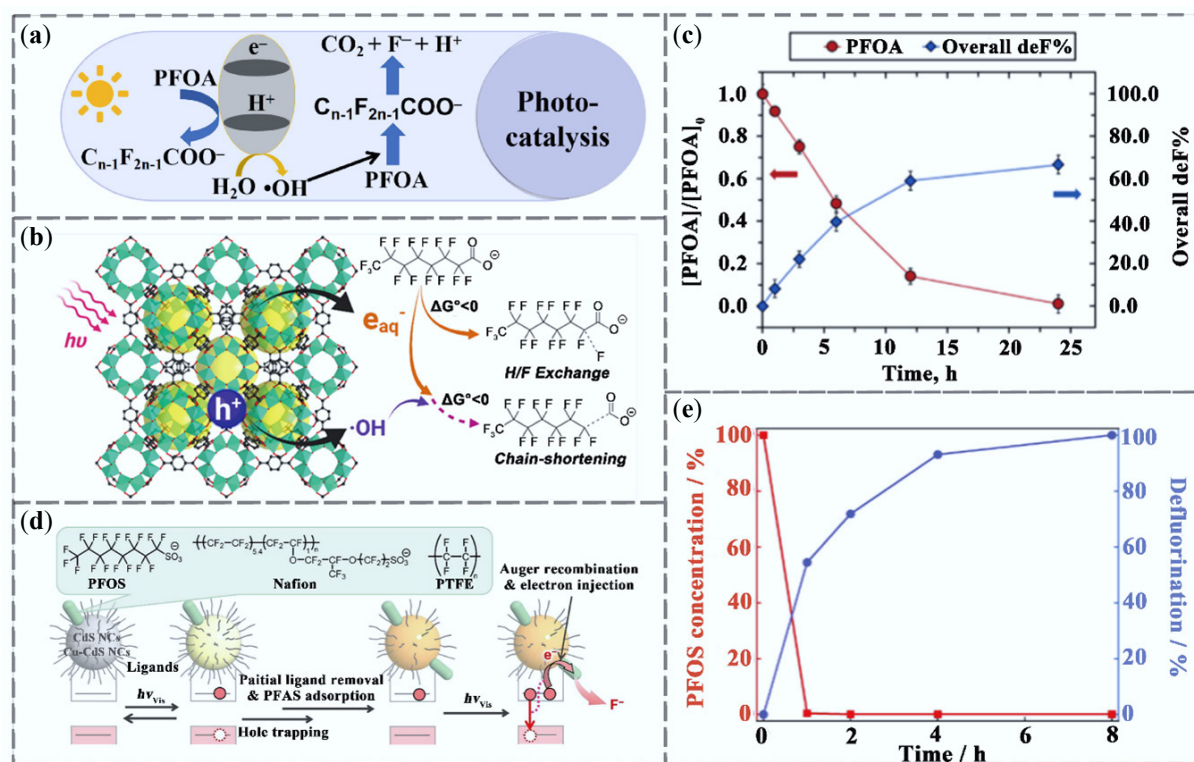


Fig. 6 Research progress on PFAS removal by photocatalytic technology. (a) Photocatalytic removal mechanism. (b) e_{aq}^- -dominated reductive defluorination of PFOA using Ti-based MOF materials^[79]. (c) degradation of PFOA under irradiation and corresponding defluorination rate^[79]. (d) reaction mechanism of PFAS defluorination by CdS under visible light^[80]. (e) Concentration of PFOS in the reaction solution and its defluorination rate^[80].

this by reducing bond dissociation energies—for instance, lowering the C–O bond energy in HFPO-DA to 75.4 kcal/mol^[89]. While thermal degradation is often conducted under inert or controlled atmospheres, the reaction mechanism strongly influences byproduct profiles. β -elimination pathways tend to yield perfluoroacyl fluorides, whereas radical-mediated mechanisms favor the formation of short-chain PFAS or cyclic perfluorocarbons^[88]. Therefore, regulating the reaction environment—particularly oxygen concentration—is vital for maximizing mineralization and minimizing the generation of secondary pollutants.

Despite their proven effectiveness, thermal and catalytic thermal degradation technologies face several practical limitations. The requirement for high temperatures and pressures complicates integration into conventional water treatment systems. Moreover, these processes often generate a variety of fluorinated byproducts, and the absence of standardized reference materials and robust analytical methods hinders comprehensive quantification and risk assessment. Future research should focus on the development of low-temperature, high-efficiency catalysts and the elucidation of their synergistic degradation mechanisms. Additionally, efforts are needed to determine key physicochemical properties of organofluorine compounds—such as Henry's law constants—to better understand their environmental behavior. Integrating thermal degradation with resource recovery and low-carbon emission technologies represents a promising pathway toward sustainable PFAS remediation.

Ultrasonic oxidation technology

Ultrasonic oxidation technology utilizes the cavitation effect induced by ultrasound to achieve efficient degradation of PFAS under extreme localized conditions. The application of ultrasound to liquids causes the formation, growth, and violent collapse of microbubbles, generating transient hotspots with temperatures reaching up to 5,000 K and pressures around 1,000 atm^[93]. These extreme conditions lead to the dissociation of water molecules, producing reactive radicals such as $\cdot\text{OH}$ and $\text{H}\cdot$, while also facilitating high-temperature thermal decomposition of PFAS through direct cleavage of C–F bonds^[94].

Key operational parameters, including ultrasonic frequency and power density, significantly influence degradation efficiency. Ilić et al. employed an adjustable-frequency reactor (375–1,140 kHz, 200–400 W/L) and found that at 580 kHz and 400 W/L, GenX degradation was below detection limits within 90 min, while PFOA and PFOS achieved degradation rates of 99% and 90%, respectively^[95]. The study also revealed an inverse relationship between PFAS degradation rates and thermal stability (GenX > PFOA > PFOS).

The presence of coexisting ions and organic pollutants in water can influence sonochemical degradation. Anions affect bubble–liquid interface dynamics by altering reactive site availability and heat transfer, impacting degradation rates. The degradation trend in the presence of various anions follows: $\text{ClO}_4^- > \text{NO}_3^- \approx \text{Cl}^- > 0 > \text{HCO}_3^- > \text{SO}_4^{2-}$. ClO_4^- , NO_3^- , and Cl^- enhances degradation, whereas HCO_3^- and SO_4^{2-} inhibit it; cations have negligible influence^[96,97]. Additionally, organic compounds may reduce PFAS degradation through competitive adsorption at bubble interfaces or by lowering interfacial temperatures. Volatile organic compounds such as methanol, acetone, and methyl isobutyl ketone can significantly inhibit PFOA and PFOS decomposition, whereas dissolved organic matter has minimal impact^[98].

While ultrasonic oxidation offers promising PFAS degradation performance, complete defluorination at low frequencies remains challenging. To enhance mineralization, ultrasound is often combined with persulfate ($\text{SO}_4^{\cdot-}$). However, the US/PS system shows

limited defluorination efficiency (~12.1%), and direct surfactant addition to reactors can cause secondary pollution. Addressing this, Lei et al. proposed introducing surfactants (e.g., Triton X-100, CTAB, SDS) into the surrounding ultrasonic water bath instead of the PFAS-containing solution^[99]. This approach lowers the surface tension of the bath and alters cavitation bubble dynamics—reducing the volume-to-shape (R1), and shape-to-transient (R2) transition sizes while increasing the transient-to-shape (R3) threshold. These changes promote transient cavitation, enhancing acoustic streaming, shock wave generation, and free radical production. Optimizing ultrasound power to 900 W, the system achieved 100% defluorination within 4 h without any chemical additives, yielding only CO_2 , H_2O , and F^- as final products^[100]. Interestingly, the addition of persulfate reduced defluorination efficiency by up to 17%, likely due to competition for adsorption sites and energy consumption at the bubble interface. Molecular dynamics simulations and bond energy analyses confirmed that defluorination reactions predominantly occur within the high-temperature bubble core (> 4,000 K), rather than at the cooler interface ($\leq 1,500$ K). Yao et al. introduced a piezo-catalytic approach using polytetrafluoroethylene (PTFE), which generates an internal electric field under ultrasonic stimulation. This field drives charge separation and the generation of H^+ , $\cdot\text{O}_2^-$, and $\cdot\text{OH}$, promoting PFAS degradation^[101]. Without external oxidants, this system achieved PFOA degradation and defluorination rates of 93.4% and 91.5%, respectively, within 1 h, and complete GenX removal within 2.5 h. The catalyst also demonstrated strong stability over 10 cycles, with low operational costs: USD \$0.168,86/L for PFOA, and USD \$0.39192/L for GenX degradation. This study highlights a promising strategy for utilizing natural mechanical energy sources (e.g., tidal energy) for PFAS remediation.

Despite its potential, ultrasonic oxidation faces practical limitations, including high energy consumption, low utilization efficiency of reactive species, challenges in scale-up, and uncertainties regarding intermediate byproduct toxicity. Future research should focus on optimizing process parameters, identifying and assessing toxicological risks of intermediates, and developing energy-efficient, low-carbon reactors suitable for pilot-scale and full-scale implementation.

Plasma technology

Plasma technology degrades PFAS through the synergistic action of oxidative (e.g., $\cdot\text{OH}$, O , $\text{O}_2^{\cdot-}$) and reductive species (e.g., hydrated electrons e_{aq}^- , $\text{H}\cdot$). In the case of PFOA, oxidative species primarily target the $-\text{COOH}$ group, generating a reactive perfluoroheptyl radical ($\text{C}_7\text{F}_{15}\cdot$), which subsequently reacts with $\cdot\text{OH}$ to form perfluoroheptanol ($\text{C}_7\text{F}_{15}\text{OH}$). This intermediate undergoes β -scission, releasing HF and shortening the carbon chain. Similarly, PFOS degradation is initiated by the cleavage of the C–S bond, resulting in the loss of the sulfonic acid group ($-\text{SO}_3$) and formation of the perfluorooctyl radical ($\text{C}_8\text{F}_{17}\cdot$), which undergoes a series of redox chain reactions to achieve stepwise defluorination and generate short-chain PFAS byproducts^[102]. However, plasma degradation efficiency is significantly influenced by PFAS chain length. Chen et al. demonstrated that long-chain compounds such as PFOA and PFDA exhibited 80%–90% degradation in a dielectric barrier discharge (DBD)–ozone cascade reactor due to their preferential enrichment at the gas–liquid interface. In contrast, short-chain PFAS like PFBA and PFHxA, which have lower interfacial affinity and more stable C–F bonds, achieved less than 32% degradation within 60 min—highlighting the limitations of conventional plasma systems for short-chain PFAS removal^[103].

To address this challenge, Isowamwen et al. developed an interfacial engineering strategy using the cationic surfactant CTAB, which

electrostatically binds to perfluorobutane sulfonate (PFBS), thereby constructing a gas–liquid interfacial migration channel^[104]. Under argon gas bubbling, this method enhanced PFBS interfacial concentration by 99%, achieving 67% degradation, and 43% defluorination within 1 h. Despite the success in enhancing short-chain PFAS removal, the mechanistic role of free electrons remains unclear.

Further insights were provided by Song et al., who investigated the 'electron memory effect' in DBD plasma systems. Their study revealed that an ultra-strong electric field (1.816×10^6 V/m) can drive electrons to penetrate interfacial water films ≥ 2.5 nm thick and directly attack the carboxyl group of PFOA, contributing over 80% to its degradation^[105]. This finding not only elucidates the degradation advantage of long-chain PFAS under plasma treatment but also supports the mechanistic rationale for interfacial enrichment strategies (Fig. 8b).

Argon bubbling discharge plasma reactors have proven particularly effective in treating long-chain PFAS in complex water matrices. CTAB addition facilitates short-chain PFAS removal by inducing differential micelle formation: long-chain PFAS (e.g., PFOA, PFOS) form hydrophilic mixed micelles that inhibit their migration, while short- and ultrashort-chain PFAS form hydrophobic complexes that are efficiently transported to the gas–liquid interface via argon bubbles (Fig. 8c). In high-salinity reverse osmosis (RO) concentrate (conductivity = 47 mS/cm), this plasma–surfactant system achieved complete degradation of long-chain PFAS within 10 min and > 99% removal of short-chain PFAS within 6 h with CTAB enhancement (Fig. 8d). However, ultrashort-chain PFAS removal efficiency was

reduced to 29%–64% under these conditions due to competitive adsorption by background anions^[106].

Despite its effectiveness, plasma-based PFAS degradation technologies face several challenges. Most studies do not comprehensively quantify degradation byproducts or assess the toxicity of intermediate species, limiting the ability to evaluate potential environmental risks. In addition, high energy requirements and sensitivity to water conductivity hinder their scalability and long-term sustainability. Future research should focus on optimizing plasma system design for energy efficiency and complete mineralization, performing in-depth characterization of degradation pathways and byproducts, and integrating plasma treatment into hybrid or modular water treatment systems for broader practical application.

Comparative analysis of technologies

To provide a comprehensive comparative analysis of PFAS treatment technologies, Tables 1 and 2 summarize and compare the degradation performance, defluorination rates, scalability potential, energy consumption, and inherent advantages and limitations of eight major physicochemical methods. These consolidated data serve as valuable references to guide technology selection and future system integration.

Table 1 demonstrates that physical methods, such as adsorption and membrane separation, achieve high removal efficiencies primarily through phase-transfer mechanisms, but generally do not accomplish defluorination. In contrast, thermal decomposition,

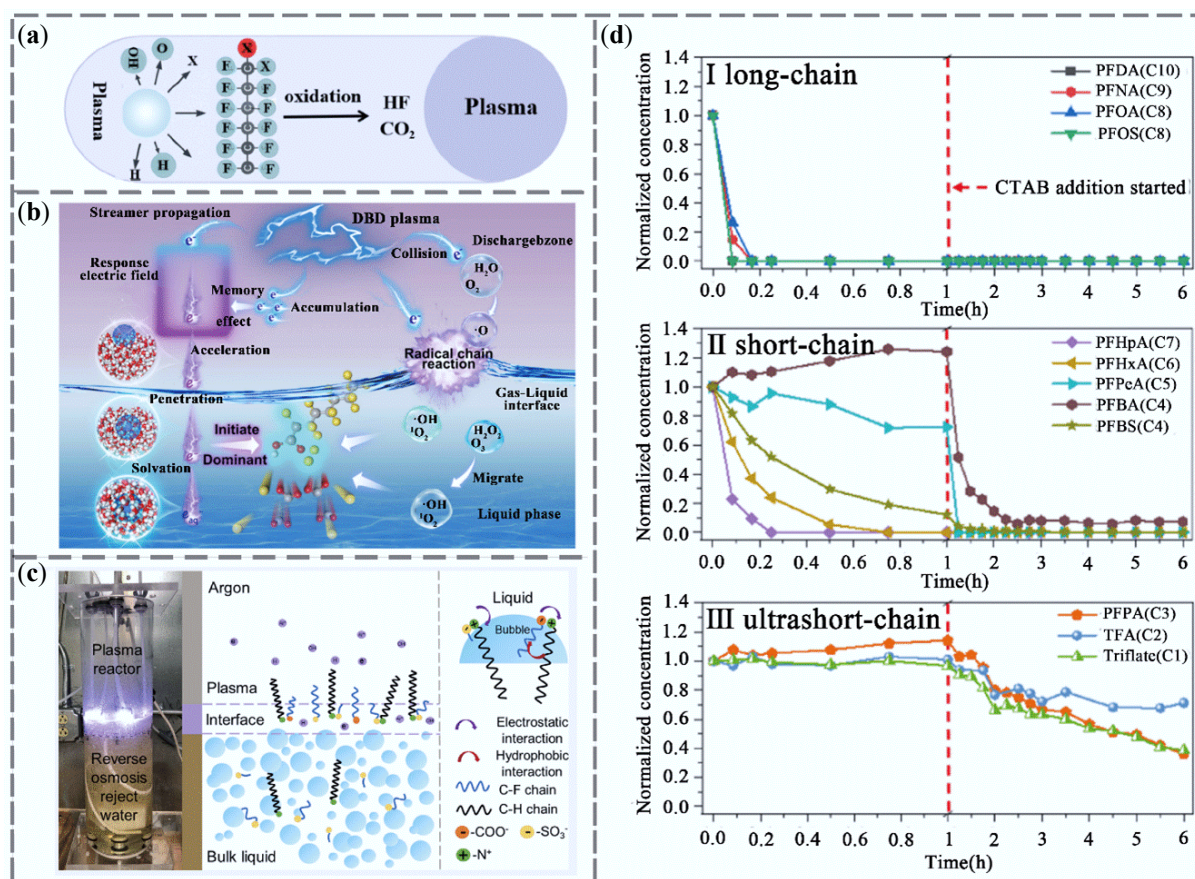


Fig. 8 Research progress of plasma technology for PFAS removal. (a) Plasma removal mechanism. (b) Schematic diagram of PFOA degradation initiated by electrons in DBD plasma^[105]. (c) Degradation mechanism of PFAS in RO wastewater by plasma^[106]. (d) Degradation rates of (I) long-chain, (II) short-chain, and (III) ultra-short-chain PFAS in RO wastewater by plasma^[106].

Table 1 Performance comparison of PFAS removal technologies

Technology	Target PFAS	Degradation efficiency	Defluorination rate	Scalability potential	Energy consumption
Adsorption	Medium- to long-chain, emerging PFAS	72%–100%	< 10%	High	Low
Membrane separation	Most PFAS species	80%–99.99%	< 10%	Moderate	Medium
Electrochemical treatment	All PFAS chain lengths	> 67%	16.7%–~100%	High	High
UV-AOP/ARP	PFOA, PFOS, emerging PFAS	> 85.3%	40%–~100%	Moderate	High
Photocatalysis	PFOA, PFOS, emerging PFAS	70%–~100%	16.5%–100%	High	Medium–high
Thermal decomposition	Almost all PFAS, including short-chain	90%–100%	30%–100%	Low	Extremely high
Ultrasonic oxidation	PFOS, PFOA, some short-chain PFAS	28.0%–93.4%	33.84%–95%	Low	High
Plasma treatment	Broad-spectrum PFAS	32%–99%	10%–80%	Medium–high	High

Table 2 Advantages and disadvantages of PFAS treatment technologies

Technology	Advantage	Disadvantage
Adsorption	Low cost, simple operation, high selectivity	Does not degrade PFAS; only transfers contaminants
Membrane separation	Highly efficient retention, applicable to a wide range of PFAS	Prone to membrane fouling; requires regular replacement
Electrochemical treatment	Enables complete mineralization, effective for full degradation	Expensive anode materials, high energy demand
UV-AOP/ARP	Can be enhanced with oxidants/reductants to increase reactivity	May generate toxic intermediate products
Photocatalysis	Suitable for solar-driven systems, environmentally friendly	Catalyst instability and limited lifespan
Thermal decomposition	Completely destroys PFAS structures	Requires high-temperature and high-pressure equipment
Ultrasonic oxidation	No need for chemical reagents, relatively safe operation	Efficiency highly dependent on solution composition
Plasma treatment	Strong mineralization potential, effective across diverse PFAS types	Complex equipment, requires precise operational control

Table 3 Comparative analysis of traditional and emerging PFAS

Comparison dimension	Traditional PFAS (e.g., PFOA, PFOS)	Emerging alternative (e.g. F-53B, HFPO-DA)
Treatment difficulty	Treatment technologies are relatively mature with extensive literature support; several processes (e.g., activated carbon, RO, electrochemical) are industrialized	More structurally complex; conventional technologies show lower removal efficiency; higher water solubility complicates adsorption
Degradation pathway	Typically begins at carboxylic or sulfonic acid groups; involves α -C cleavage, decarboxylation, and sequential C–F bond breakage	More diverse, involving ether linkages and branched structures; may include oxidative/reductive mechanisms and persistent intermediates
Environmental persistence	Long half-life, high mobility, and bioaccumulative in aquatic/biological environments	Often more persistent; short-chain products are highly mobile and difficult to detect
Defluorination efficiency	16%–100% possible with chemical methods	Generally < 50%, but Genx can sometimes achieve a 90% rate, intermediate products may pose unknown risks
Adsorption behavior	Strong affinity for activated carbon and ion-exchange resins	Weak interaction with conventional adsorbents; lower adsorption capacity
Analytical challenges	Well-established detection standards and databases	No unified detection protocol; often requires high-resolution, non-targeted analysis

electrochemical oxidation, and plasma technologies exhibit strong mineralization potential but face challenges related to high energy consumption and limited scalability. Hybrid or multifunctional systems may provide balanced performance by leveraging the complementary strengths of individual techniques.

Table 2 outlines the inherent trade-offs of each approach. For example, electrochemical methods can achieve near-complete mineralization but require advanced materials and significant power input. Photocatalysis offers potential for solar-driven, decentralized applications; however, it currently suffers from limitations in catalyst stability and selectivity.

Table 3 systematically compares traditional PFAS (e.g., PFOA, PFOS) with emerging alternatives (e.g., F-53B, HFPO-DA) across key dimensions, including treatment difficulty, degradation mechanisms, environmental persistence, defluorination efficiency, adsorption behavior, and analytical detection. Established technologies effectively treat traditional PFAS, achieving high removal and defluorination rates through well-characterized degradation pathways and strong adsorption affinity. Emerging alternatives, characterized by increased structural complexity (e.g., ether linkages, branched chains) and enhanced water solubility, markedly reduce the efficacy of conventional treatments. Their degradation products are often more complex and persistent, with short-chain, highly mobile

species posing increased environmental risks. Additionally, these alternatives exhibit weaker adsorption capacities, generally lower defluorination efficiencies, and lack standardized detection protocols, often requiring high-resolution, non-targeted analytical techniques.

Conclusions and prospects

Physicochemical advanced treatment technologies have demonstrated substantial potential for degrading PFAS in aquatic environments. However, several unresolved challenges continue to hinder their widespread practical implementation. To enhance comprehensive PFAS remediation efficiency, future research should focus on the following key directions.

Synergistic mechanisms of materials and reaction systems: Catalytic–adsorptive bifunctional materials have garnered increasing attention due to their ability to simultaneously capture and transform PFAS. However, a trade-off often exists between adsorption capacity and catalytic activity, which limits overall removal efficiency. To overcome this limitation, future studies should aim to optimize interfacial design by rationally arranging adsorption sites and catalytic centers. Enhancing electron transfer efficiency and aligning the catalytic pathways with PFAS degradation reactions will

enable synergistic enhancement of both functionalities. Furthermore, multi-technology integration—such as photoelectrochemical, redox-assisted, and adsorption–catalysis coupled systems—has shown promise in improving PFAS degradation. A critical research priority is to clarify the spatial and temporal sequence of these reaction units, understand mass transfer and interfacial phenomena, and identify key control steps and synergistic mechanisms within such integrated systems.

Degradation pathways and toxic intermediate tracking: To comprehensively understand PFAS degradation mechanisms, it is essential to employ advanced *in situ* analytical tools such as high-resolution mass spectrometry (HRMS) and ultrafast spectroscopy, in conjunction with molecular dynamics (MD) simulations and quantum chemical calculations. These approaches can enable the construction of complete reaction pathway maps, covering intermediate formation, transformation, and final product evolution. Special attention should be given to the cleavage of C–F bonds and associated electron transfer processes. Additionally, the potential generation of unknown or toxic fluorinated intermediates necessitates the development of non-targeted screening algorithms based on machine learning. These tools can enhance the sensitivity and accuracy of trace byproduct detection and structural prediction, thereby improving the safety, reliability, and environmental controllability of PFAS treatment systems.

Adaptation optimization for multi-component/complex water matrices: The presence of coexisting ions, organic matter, and other pollutants in real-world water matrices can significantly interfere with PFAS removal. To address these challenges, molecularly imprinted intelligent materials—mimicking antibody–antigen recognition mechanisms—offer a promising strategy for improving selectivity, anti-interference capability, and trace PFAS detection. Additionally, given the frequent co-occurrence of short- and long-chain PFAS in contaminated waters, future research should focus on designing broad-spectrum, high-throughput treatment platforms. These could include composite material systems and synergistic multi-mechanism processes capable of effectively degrading complex PFAS mixtures. Such approaches will enhance the universality, robustness, and field applicability of treatment technologies.

Challenges and pathways from laboratory to engineering applications: To facilitate the transition from laboratory-scale studies to real-world deployment, efforts must be directed toward developing intelligent, integrated treatment systems. Incorporating digital twin frameworks and machine learning algorithms can enable dynamic process control, adaptive optimization, and reduction of energy consumption. Furthermore, comprehensive life-cycle techno-economic assessments—considering material inputs, energy demands, maintenance, and waste disposal—are essential to evaluate system viability. Tailored process configurations should be developed based on the PFAS contamination profiles of specific water bodies to improve engineering adaptability and deployment feasibility.

Author contributions

The authors confirm their contributions to the paper as follows: study conception and design: Bai M, Zhang Y, Zhang X, Song C, Cheng Y, Niu J; literature collection and summarization: Zhang X, Song C, Cheng Y; writing – draft manuscript preparation: Bai M; study guidance, writing – review & editing: Zhang Y, Niu J. All authors reviewed the results and approved the final version of the manuscript.

Data availability

Data sharing not applicable to this article as no datasets were generated or analyzed during the current study.

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Declarations

Competing interests

The authors declare that they have no conflict of interest.

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