CRITICAL REVIEW

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A review on technologies for the removal of per- and polyfluoroalkyl substances (PFASs) in aquatic environments

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Per- and polyfluoroalkyl substances (PFASs), emerging contaminants with significant biotoxicity, are widely present in aquatic environments. This review analyzes PFAS removal technologies (including adsorption, oxidation techniques—electrochemical, photocatalytic, and sonolytic—biodegradation, and membrane separation), examining their mechanisms, effectiveness, advantages, disadvantages, and applicability. Adsorption remains the most prevalent method, effectively removing PFASs across various concentration levels. However, limitations include long adsorption cycle, difficulty in removing short-chain PFASs, and less-than-ideal regeneration capabilities, which drives ongoing exploration of novel adsorbent materials. Electrochemical, photocatalytic, and sonolytic degradation technologies offer high removal efficiency, short reaction times, the ability to degrade short-chain PFASs, and mineralization potential. Achieving complete mineralization, however, requires stringent reaction conditions, and high energy demands lead to significant operational costs. For biodegradation technology, the search for microorganisms with high PFAS mineralization capabilities and plant species with high PFAS accumulation capacity remains crucial. Consequently, developing low-cost, highly efficient, and widely applicable PFAS removal technologies is an urgent priority. Combining these technologies with other removal methods may be an important direction for future development.

Environmental significance

Perfluoroalkyl and polyfluoroalkyl substances (PFASs) represent an emerging class of contaminants that are ubiquitously present in aquatic environments and exhibit significant biotoxicity. This review analyzes various PFAS removal technologies, including adsorption, oxidation, biodegradation, and membrane separation, examining their treatment mechanisms, effectiveness, advantages, disadvantages, and applicability. The urgent need for cost-effective, efficient, and broadly applicable removal technologies is underscored, with potential future directions for development proposed.

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1. Introduction

Per- and polyfluoroalkyl substances (PFASs) represent a novel category of synthetic, persistent organic compounds characterized by the partial or complete substitution of hydrogen atoms with fluorine atoms along the carbon chains.[1,2] Perfluorooctane sulfonic acid (PFOS) and its salts, as well as perfluorooctanoic acid (PFOA), are the most notorious representative substances.[3] Owing to their superior thermal and chemical resistance, pronounced surface activity, and notable hydrophobic and oleophobic characteristics, PFASs are extensively employed across various industrial procedures and an array of consumer goods, encompassing chemical manufacturing, metal electroplating, textile production, fire suppression, culinary utensils, and pharmaceutical preparations.[4,5] The robust bond energy of carbon–fluorine (C–F) linkages, coupled with the pronounced negative electronegativity of fluorine, confers PFASs with resistance to environmental degradation and biological decomposition. Toxicological research indicates that PFASs possess the capability to bind with proteins and accumulate within organisms upon entry, thereby eliciting substantial detrimental effects across various biological systems.[6] These impacts encompass adverse outcomes such as renal and hepatic impairment,[7] thyroid disorders,[8] immunotoxicity,[9] cardiotoxicity, neurological effects,[10] reproductive toxicity, and carcinogenicity.[11] The potential risks posed to human health by PFASs are not to be underestimated.[12]

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In the years 2009 and 2019, PFOS along with its salts and PFOA were incorporated into the Stockholm Convention's supplementary list of priority persistent organic pollutants. By 2018, the European Union had established a comprehensive limit of 0.5 µg L^{-1} for PFASs, with a more stringent threshold of 0.1 µg L^{-1} for individual compounds in potable water supplies. Echoing this, in 2023, the United States Environmental Protection Agency introduced the "National Primary Drinking Water Regulations," establishing legally enforceable standards for six PFAS compounds, including a maximum allowable concentration of 4.0 ng L^{-1} for both PFOA and PFOS.[13] Following the implementation of global prohibitions and restrictions on PFASs, the center of gravity for the production and utilization of PFASs has shifted from developed to developing nations. The rapid economic growth in these developing countries has fueled a significant increase in demand for high-performance materials containing perfluorinated compounds.[14] China, commencing in the early 2000s, embarked on large-scale production and application of PFASs, emerging as a major producer and consumer of fluoride compounds, and a predominant supplier of short-chain PFASs including PFBS and PFBA.[15] PFOS and its associated compounds were also added to China's "List of Key Regulated New Pollutants" in 2023.[12] The heightened water solubility and enhanced mobility in aquatic environments of short-chain PFASs have necessitated the advancement of sophisticated and effective treatment methodologies for the elimination of PFAS contaminants.[16–19]

Despite the hydrophobic nature of the carbon-fluorine chains in conventional PFASs, the presence of functional groups like sulfonates and carboxylates can impart significant water solubility and mobility to these compounds within aquatic systems.[20] This enables their entry into water bodies *via* processes like surface runoff and atmospheric deposition, subsequently leading to their conveyance into marine environments *via* riverine transport, thereby contributing to global contamination.[21,22] Consequently, PFASs are prevalent not only in areas of intense human activity but also in various remote environments, including the world's major oceans,[23] polar regions,[24–26] glaciers,[27] the Qinghai-Tibet Plateau,[28] and within the organisms inhabiting these areas.[26,29] Pala *et al.*[30] initially identified PFASs in Adélie penguins and their unincubated eggs in the Ross Sea, Antarctica. MacInnis *et al.*[31] observed an exponential increase in PFAS concentrations within Canadian Arctic lakes, a pattern that aligns with historical fluctuations in the market for PFAS production and inventory. Ahrens *et al.*[32] conducted a study on the spatial dissemination and migratory patterns of PFASs from Northern Europe to the South Atlantic. Their findings indicated that the concentration of individual PFAS compounds typically ranged within tens of picograms per liter, with PFOS and PFOA exhibiting the highest concentrations. Muir *et al.*[33] reported that in the Great Lakes of North America, the median concentrations of PFHxA, PFHpA and PFOA increased by factors of 3.0, 16, and 1.4, respectively, between the periods of 2000–2009 and 2015–2019. Additionally, Joerss *et al.*[34] examined the Baltic Sea, discovering that the cyclic compound PFECHS, a substitute for conventional PFAS, constituted the highest proportion of the detected PFAS,

underscoring the necessity of monitoring fluorinated alternatives. Yamashita *et al.*[35] discovered that the Tokyo Bay demonstrated substantially augmented concentrations of PFOS, PFHxS, and PFOA, which were approximately three degrees of magnitude greater than the concentrations detected in the marine regions of the Pacific Ocean. This finding suggests a strong association between the high levels of PFASs in Tokyo Bay and the urban and industrial activities in Tokyo. Wang *et al.*[36] reported that in the South China Sea, the concentrations of PFASs in surface seawater and bottom seawater ranged from 125 to 1015 pg L^{-1}, with PFBA and PFOA being the predominant compounds. This study also marked the first detection of PFAS substitutes, such as 6 : 2/8 : 2 Cl-PFESA and HFPO-DA in the South China Sea. The spatial distribution of PFASs in this region is influenced by river outflow and oceanic currents, with concentrations decreasing from the estuaries to the coastal areas due to dilution effects. Areas characterized by high population density and advanced industrial development generally exhibit higher PFAS concentrations. Moreover, there is an increasing detection of short-chain and novel PFASs (Table 1), some of which have gradually emerged as substitutes for long-chain PFASs, with their production rates on the rise.

A comprehensive topic search was conducted within the Web of Science Core Collection database for publications from 2005 to 2024, focusing on "PFAS" in conjunction with "removal", "adsorption", "oxidation", "bioremediation", and "membrane separation". This analysis generated Fig. 1(a), which illustrates the escalating research interest in PFAS removal, particularly post-2016. Keyword co-occurrence analysis (Fig. 1(b)) revealed that prominent research foci within PFAS removal encompass diverse PFAS classes, aqueous environments, adsorption processes, various oxidation technologies, and membrane techniques. Based on the data presented in Fig. 1(a), adsorption is the most extensively investigated removal method. Meanwhile, the proportion of publications concerning mineralization techniques capable of achieving PFAS mineralization in aqueous environments—such as electrochemical oxidation, photocatalysis, and sonolysis—has demonstrated a consistent annual increase. In contrast, the proportion of publications dedicated to other advanced oxidation processes (AOPs) (including ozonation, activated persulfate oxidation, Fenton-like reactions, supercritical water oxidation, electron beam irradiation, and plasma irradiation) as well as other treatment techniques (including hydrothermal processing, advanced reduction processes, and coagulation) remains comparatively low. Subsequently, publications specifically addressing PFAS removal from 2016 to 2024 – a period marked by rapid growth in publication output – were subjected to keyword clustering analysis (Fig. 1(c)). This yielded highly significant and robust clusters, as indicated by a modularity value (Q) of 0.7743 and a weighted mean silhouette score (S) of 0.9154 (where $Q > 0.3$ signifies a significant cluster structure, and $S > 0.7$ denotes highly efficient and convincing clustering). The identified significant and robust large clusters (*e.g.*, Cluster #0, #1, and #6) represent mature and persistently active core research directions within this field, commonly addressing PFAS removal from drinking water and removal methods utilizing activated

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Table 1 Typical chemical formulae of PFASs

PFAS	Acronym	Chemical formula	Classification	The number of publications	Predominant removal technologies studied
Perfluorooctanoic acid	PFOA	$C_8HF_{15}O_2$	Long-chain PFAS	1350	Adsorption (48%)/AOPs (27%)
Perfluorooctanesulfonic acid	PFOS	$C_8HF_{17}O_3S$	Long-chain PFAS	1103	Adsorption (53%)/AOPs (18%)
Perfluorobutyric acid	PFBA	$C_4HF_7O_2$	Short-chain PFAS	161	Adsorption (58%)/AOPs (20%)
Perfluorobutanesulfonate	PFBS	$C_4HF_9O_3S$	Short-chain PFAS	155	Adsorption (55%)/AOPs (12%)
Perfluorohexanoic acid	PFHxA	$C_6HF_{11}O_2$	Short-chain PFAS	113	Adsorption (37%)/AOPs (27%)
Perfluorohexanesulfonic acid	PFHxS	$C_6HF_{13}O_3S$	Long-chain PFAS	111	Adsorption (43%)/AOPs (14%)
Hexafluoropropylene oxide dimer acid (GenX)	HFPO-DA	$C_6HF_{11}O_3$	Short-chain PFAS	89	Adsorption (65%)/membrane (12%)
Perfluoropentanoic acid	PFPeA	$C_5HF_9O_2$	Short-chain PFAS	66	Adsorption (30%)/AOPs (24%)
6 : 2-Fluorotelomer sulfonic acid	6 : 2 FTS	$C_8H_5F_{13}O_3S$	Long-chain PFAS	59	Adsorption (29%)/AOPs (27%)
Perfluoroheptanoic acid	PFHpA	$C_7HF_{13}O_2$	Long-chain PFAS	57	AOPs (35%)/adsorption (26%)
Perfluorononanoic acid	PFNA	$C_9HF_{17}O$	Long-chain PFAS	36	Adsorption (39%)/AOPs (28%)
6 : 2 chlorinated polyfluorinated ether sulfonate (F-53B)	6 : 2 Cl-PFESA	$C_8ClF_{16}O_4S$	Long-chain PFAS	23	Adsorption (52%)/AOPs (26%)
Perfluorodecanoic acid	PFDeA	$C_{10}HF_{19}O_2$	Long-chain PFAS	2	AOPs(photocatalytic)(50%)/biodegradation (50%)
Perfluoroethylcyclohexane sulfonic acid	PFECHS	$C_8H_2F_{15}O_3S$	Long-chain PFAS	1	Adsorption
8 : 2 chlorinated polyfluorinated ether sulfonate	8 : 2 Cl-PFESA	$C_{10}ClF_{20}O_4S$	Long-chain PFAS	1	Flocculation, anaerobic digestion and aerobic digestion

carbon. In contrast, emerging smaller clusters exhibiting high intensity (*e.g.*, Cluster #11) may indicate novel technologies or breakthrough research avenues, such as mineralization techniques. Analysis of the top 17 keywords with the strongest citation bursts further underscores that removal technologies capable of achieving mineralization in aqueous environments represent a current critical research frontier. This finding corroborates the results of the aforementioned keyword burst analysis, which highlighted the recent emergence of sono-chemical and photochemical removal techniques. These cluster structures delineate the current knowledge landscape and research priorities within the PFAS removal field. In summary, the bibliometric analysis reveals that (1) research related to adsorption constitutes a substantial and steadily maintained volume. Its focus has evolved from an initial emphasis on activated carbon to include ion-exchange resins and biochar, and more recently, towards metal–organic frameworks (MOFs), covalent organic frameworks (COFs), and molecularly imprinted polymers (MIPs). (2) Research concerning electrochemical oxidation, photocatalysis, and sonolysis within the realm of AOPs exhibits exponential growth, particularly regarding investigations into their mineralization capabilities and mechanisms, representing the most cutting-edge exploratory directions. (3) For the relatively mature membrane separation technology, current research predominantly focuses on its integration with mineralization techniques such as electro-chemical and photolytic degradation, signifying a crucial development pathway for practical applications. (4) Publications related to biodegradation show relatively modest growth. Cluster analysis indicates that its research is more concentrated on mechanistic exploration and specific precursors, consistent with the challenges associated with its removal efficiency in actual water treatment. Collectively, these overarching trends establish an essential macroscopic context for the subsequent sections of this review to delve deeply into the principles, efficacy, challenges, and prospects of these four technologies.

This review critically appraises current and emerging technologies for removing persistent PFASs from aquatic environments. It systematically analyzes the mechanisms, efficacy, advantages, limitations, and applicability of adsorption, electrochemical oxidation, photocatalysis, sonolysis, biodegradation, and membrane separation. While adsorption remains widely used, significant gaps persist—including inefficient short-chain PFAS removal, slow kinetics, and poor regeneration—driving the need for novel materials. Advanced oxidation processes offer promising degradation and mineralization potential but face barriers like high energy costs and stringent operational requirements. Biodegradation, though environmentally attractive, is constrained by the limited availability of efficient mineralizing microbes or hyperaccumulating plants. By synthesizing these critical insights and limitations, this review underscores the urgent priority for developing cost-effective, scalable, and universally applicable PFAS treatment solutions. It further highlights the integration of complementary technologies as a pivotal strategy for future advancements in sustainable PFAS remediation.

Fig. 1 Analysis of literature research on PFAS removal from 2005 to 2024: (a) the number of publications and citations, (b) keyword co-occurrence analysis, and (c) keyword clustering visualization and top 17 keywords with the strongest citation bursts (2016–2024).

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2. Advanced treatment technologies for PFAS contamination in aquatic environments

2.1 Adsorption

Adsorption technology has emerged as a promising strategy for the efficient removal of PFASs from aquatic environments, characterized by its low operational costs and high efficiency.[37] This method employs porous solid materials as adsorbents, and extensive research has been dedicated to investigating the efficacy of various adsorbents in PFAS removal. The materials under scrutiny predominantly comprise activated carbon, biochar, anion exchange resins, as well as advanced materials such as metal–organic frameworks (MOFs), covalent organic frameworks (COFs), and molecularly imprinted polymers (MIPs) (Table 2).[38]

While numerous treatment methodologies, particularly oxidation degradation techniques, are under active investigation in laboratory settings,[39] the most prevalent technology in practical applications remains adsorption, with a focus on activated carbon and anion exchange resin adsorption processes.[40] Furthermore, when compared to other removal techniques, these adsorption technologies exhibit superior economic viability. However, the complex adsorption behavior and mechanisms of PFAS molecules, which possess hydrophilic groups alongside hydrophobic and oleophobic C–F chains, present challenges.[41] Despite this, the current adsorption technology, which involves the capture of PFASs without their degradation, necessitates the continuous disposal and regeneration of the adsorbent materials. Future research directions in this field will likely focus on developing adsorbents with high selectivity for PFASs that can be easily desorbed and reused in industrial applications, thereby enhancing the sustainability and efficiency of PFAS removal through adsorption technology.[42]

2.1.1 Carbon-based materials

2.1.1.1 Activated carbon. Activated carbon (AC), renowned for its affordability and robust adsorption capabilities, has emerged as the predominant adsorbent for the removal of various pollutants from aquatic environments, including PFASs. AC remains the workhorse technology for PFAS removal in municipal wastewater treatment facilities worldwide. Yu *et al.*[43] conducted a comparative study on the adsorption of PFOS and PFOA from water using powdered activated carbon (PAC) and granular activated carbon (GAC). Their adsorption kinetics analysis revealed that the granular porous adsorbent GAC exhibited a significantly slower adsorption rate for PFOS and PFOA, necessitating a minimum of 168 hours to reach equilibrium, whereas powdered activated carbon achieved equilibrium in approximately 4 hours. The adsorption capacities of GAC for PFOS and PFOA were measured to be 0.37 millimoles per gram (mmol g^{-1}) and 0.39 mmol g^{-1}, respectively, whereas PAC demonstrated higher capacities of 1.04 mmol g^{-1} and 0.67 mmol g^{-1} for these compounds. The adsorption process was influenced by the solution's pH, with an observed increase in adsorption as the pH decreased. In

addition to electrostatic interactions and ion exchange, hydrophobic forces contributed to the adsorption process. Yu concluded that, in comparison to GAC, an appropriately selected PAC presents a promising avenue for the effective removal of PFOS and PFOA. Furthermore, Zhang *et al.*44 discovered that the adsorption capacity of GAC varied significantly with PFAS concentration, with notable differences observed between lower and higher concentrations. In real-world aquatic environments, where PFAS concentrations are typically several orders of magnitude lower, the adsorption rate of GAC followed the order PFOS > PFOA > PFHpA.

In summary, extensive research has consistently demonstrated the effectiveness of PAC and GAC in the removal of PFASs from water systems, particularly in the efficient adsorption of long-chain PFASs.[56] However, the current limitations of activated carbon technology lie in its reduced efficacy in adsorbing short-chain PFASs. Long-chain PFASs exhibit strong hydrophobic properties, whereas short-chain PFASs possess a degree of hydrophilicity, which hinders their aggregation on the hydrophobic surfaces of GAC.[57] Furthermore, the presence of dissolved organic carbon (DOC) in water can diminish the adsorption capacity of GAC or reduce the overall removal efficiency of PFASs by desorbing previously adsorbed PFASs.[58] From a practical standpoint, while activated carbon offers the benefits of low cost and a considerable adsorption capability for long-chain PFASs compared to alternative adsorbents, the regeneration of spent activated carbon remains challenging, even with solvents like methanol or ethanol.[59] Consequently, the non-reusability of activated carbon necessitates the safe disposal of the spent material.

2.1.1.2 Biochar. Biochar, a non-toxic solid biofuel, is generated by the thermal breakdown of biomass under aerobic or anaerobic conditions. It is distinguished by its rich porosity, high carbon content, and significant calorific value. Nobuyoshi Yamashita *et al.*[45] developed Triporour rice husk activated carbon, which features a unique porous structure combining micropores, mesopores, and macropores. This material effectively adsorbs both short-chain and long-chain PFASs, demonstrating a maximum adsorption capacity for ultra-short-chain PFASs exceeding 95%. This discovery has led to the conceptualization of a novel rice cultivation system.

In a separate study, Du *et al.*[46] utilized bamboo-derived activated carbon (BAC) for the treatment of actual wastewater. They observed that the dosage of BAC had a pronounced impact on the efficacy of eliminating PFASs. As the BAC dosage increased from 0.1 g L^{-1} to 0.5 g L^{-1}, the PFOA removal efficiency increased from 33.2% to 96.6%, and remained stable at dosages exceeding 0.7 g L^{-1}. The efficiency of removing PFHxA and PFHpA slightly improved with the increase in the initial dosage. Notably, at a 0.3 g L^{-1} BAC level, the elimination percentage for PFHxA was merely 8.8%, while that of PFOA reached 88.4%, suggesting preferential adsorption of PFOA at lower adsorbent concentrations. The presence of cations in the wastewater enhanced the adsorption process, whereas anions inhibited it. The coexistence of other organic substances adversely affected the adsorption capacity of BAC. Over a broad pH range, BAC demonstrated high selective adsorption for

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Table 2 Comparative analysis of adsorption performance of various adsorbents for PFASs

Adsorbent	PFAS	Initial concentration (mg L⁻¹)	Equilibrium time (h)	Adsorption capacity/removal rate	References
Granular activated carbon (GAC)	PFOS	20–250	4	0.37 mmol g⁻¹	43
	PFOA	20–250	4	0.39 mmol g⁻¹	
Powdered activated carbon (PAC)	PFOS	20–250	168	1.04 mmol g⁻¹	
	PFOA	20–250	168	0.67 mmol g⁻¹	
GAC	PFOS	0.5–10	24	0.032 mmol g⁻¹	44
	PFOA	0.5–10	120	0.031 mmol g⁻¹	
	PFHpA	0.5–10	120	0.029 mmol g⁻¹	
Activated carbon derived from rice husks	15 kinds, including PFBA, PFOA, PFHxA, 6 : 2FTS, *etc.*	0.008	—	More than 95%	45
BAC	PFHxA	31.4	12.5	0.06 mmol g⁻¹	46
	PFHpA	40	12.5	0.18 mmol g⁻¹	
	PFOA	120	33.5	1.03 mmol g⁻¹	
AI400	PFOS	20–250	168	0.42 mmol g⁻¹	43
	PFOA	20–250	168	2.92 mmol g⁻¹	
Ion-exchange resin adsorption (IRA)67	PFOS	200	48	5.70 mmol g⁻¹	47
IRA958	PFOS	200	48	4.68 mmol g⁻¹	
IRA96	PFOS	200	168	3.82 mmol g⁻¹	
IRA900	PFOS	200	168	4.20 mmol g⁻¹	
IRA400	PFOS	200	168	0.53 mmol g⁻¹	
IRA410	PFOS	200	168	0.73 mmol g⁻¹	
IRA67	PFHxA	31.4	33.5	0.12 mmol g⁻¹	46
	PFHpA	40	33.5	0.53 mmol g⁻¹	
	PFOA	120	33.5	2.82 mmol g⁻¹	
IRA67	F-53B	200	48	4.2 mmol g⁻¹	48
	PFOS	175	20	5.5 mmol g⁻¹	
20%[NH₂]-COF	GenX	50	0.5	0.69 mmol g⁻¹	49
28%[NH₂]-COF	GenX	50	0.5	91%	
GAC	GenX	50	—	0%	
PAC	GenX	50	—	72%	
MELEM-COF	PFOA	1	1	6.04 mmol g⁻¹ (99.7%)	50
MEL-COF	PFOA	1	1	4.83 mmol g⁻¹ (99.3%)	
MELEM-COF	GenX, PFOA, PFOS, PFDA, PFBA, PFHA	Each 0.02	0.5	More than 97%	
MOF NU-1000	Groundwater containing PFCA, PFSA, FTS, *etc.*	0.19 ± 0.25	0.02	Anionic PFAS: 58% Non-ionic PFAS: 99%	51
MOF UiO-66	Groundwater containing PFCA, PFSA, FTS, *etc.*	0.19 ± 0.25	0.17	Anionic PFAS: 2% Non-ionic PFAS: 95%	
MOF ZIF-8	Groundwater containing PFCA, PFSA, FTS, *etc.*	0.19 ± 0.25	0.5	All less than 10%	
GAC	Groundwater containing PFCA, PFSA, FTS, *etc.*	0.19 ± 0.25	48	Anionic PFAS: 37% Non-ionic PFAS: 44%	

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Table 2 (*Contd.*)

Adsorbent	PFAS	Initial concentration (mg L⁻¹)	Equilibrium time (h)	Adsorption capacity/ removal rate	References
MOF NU-1000	PFOS, PFHxS, PFBS, PFDA, PFOA, PFHPA, PFPeA, PFBA, and TFA	Each 100	0.02–0.17	1.16–1.76 mmol g⁻¹	52
Pre-assembled modified MIL-101(Cr) MOF	PFOA	—	1	1.19 mmol g⁻¹	53
Synthesized and modified MIL-101(Cr) MOF	PFOA	—	1	1.89 mmol g⁻¹	
MIPs	PFOS	200	32	0.56 mmol g⁻¹	54
MWCNTs@MIPs	PFOA	0.1–20	1.33	0.03 mmol g⁻¹	55

PFOA while also effectively and consistently removing other PFASs. Consequently, BAC is considered particularly appropriate for the extraction of PFOA from actual wastewater, especially under high pH conditions. However, as it stands, the reusability of BAC is currently less than ideal.

2.1.2 Anion exchange resin. Presently, the predominant focus in the treatment of PFASs in water is on GAC. However, anion exchange resin (AER) technology is garnering growing interest.[60] A pivotal factor driving this shift towards AER is the significantly higher adsorption capacities of anion exchange resins for both short-chain and long-chain PFASs than that of GAC.[61] Anion exchange has emerged as a promising removal technology, as illustrated by reaction eqn (1) and (2), where [R4N+] and [R3N] denote the ion exchange sites.[62]

$$[R4N^+]Cl^- + PFAS^- \rightleftharpoons [R4N^+]PFAS^- + Cl^- \quad (1)$$

$$[R3N] + H^+ + PFAS^- \rightleftharpoons [R3NH^+]PFAS^- \quad (2)$$

In previous research, Yu[43] discovered that the AER AI400 demonstrated the greatest adsorption capacity for PFOA at 2.92 mmol g⁻¹, while its capacity for PFOS was lower. Achieving adsorption equilibrium required more than 168 hours. Ion exchange, electrostatic interactions, and hydrophobic interactions contributed to the sorption, with potential formation of hemi-micelles or micelles within the intraparticle pores. The variability in certain characteristics among different resins, including the polymer matrix, porosity, and functional groups, leads to differences in their efficiency in removing PFASs.[63]

Deng[47] found that AERs are effective in the removal of PFOS from wastewater. The efficiency and capacity for PFOS adsorption primarily rely on the polymer structure and porosity. Polyacrylic resins, such as IRA67 and IRA958, can rapidly remove PFOS, reaching adsorption equilibrium in about 48 hours, while polystyrene resins take 168 hours. The adsorption capacity on IRA67 and IRA958 was 4–5 mmol g⁻¹, which exceeded the amount of chloride liberated by the resin, indicating that there were other interactions in addition to anion exchange during the adsorption process. The solution pH had little effect on the adsorption of PFOS by IRA958. However, at a pH greater than 10, the deprotonation of the amine functionality led to the adsorption on IRA67 being significantly affected.

Gao *et al.*[48] undertook an investigation into the removal of F-53B and PFOS from electroplating wastewater using the AER IRA67. Their findings indicated that the adsorption capacities for F-53B and PFOS reached 4.2 and 5.5 mmol g⁻¹ pH was identified as a crucial factor influencing the adsorption process. Under acidic conditions, IRA67 exhibited superior adsorption capabilities for F-53B as well as PFOS. The adsorption capacity significantly decreased at pH levels exceeding 10. In actual wastewater scenarios, IRA67 exhibited the capability to concurrently extract F-53B and PFOS without favoring one compound over the other. However, the removal rate was subject to competitive effects, potentially impacting the overall efficiency of the process. The coexistence of sulfate and chromate in the wastewater collectively diminished the adsorption

capacity for both F-53B and PFOS. Du *et al.*[46] found that IRA67 benefits from requiring a low dosage and maintaining consistent removal throughout the adsorption cycle, and that ethanol solution or a mixed solution of NaCl and methanol could successfully regenerate the exhausted IRA67.

AER is currently being employed in actual wastewater treatment plants. A 15-month pilot-scale comparative study by Chow *et al.*[64] on PFAS adsorption revealed that AERs outperformed GAC during long-term operation of a pilot treatment plant. However, both AC and AER technologies face challenges such as competitive adsorption, low adsorption capacity for specific PFASs (like short-chain PFASs), and the high costs associated with them often necessitate regular chemical reactivation to rejuvenate the adsorbent or manage spent adsorbents. For example, spent resins typically undergo chemical reactivation with a blend of salts or alkalis and alcohols like methanol or ethanol, necessitating the treatment of the resulting toxic wastewater.[48] Some resins, such as the PS/G/bifunctional resin (A532E),[65] can only be directly incinerated after reaching a certain adsorption capacity for PFASs. Between 760 and 980 °C, the PFAS content decreases with the increase in incineration temperature, indicating that PFASs decompose more thoroughly at higher temperatures. However, the emission of gaseous PFASs remains a concern.[66] The current methods for regenerating PFAS-loaded resins involve the use of high-concentration alcohol cosolvents, such as 70% methanol, combined with saline. These methods require a separate distillation step to recover the cosolvent. Consequently, future research should focus on developing resins and treatment systems that are not only effective in removing PFASs but are also suitable for regeneration, thereby avoiding potential safety or toxicity issues during the regeneration process.[67]

2.1.3 Metal–organic frameworks (MOFs). MOFs, a category of inorganic–organic hybrid materials, are coordination polymers formed by metal ions or metal oxides serving as coordination centers and organic linkers as ligands.[68] MOFs are characterized by their high specific surface area, high porosity, and ease of functionalization,[69] which make them proficient in eliminating PFAS contaminants from water. Clark *et al.*[70] discovered that UiO-66 exhibited an adsorption rate for PFBS that was several orders of magnitude faster than that of GAC, other carbon-based materials and ion exchange resins. The substantial adsorption capacity and fast adsorption rates result from its higher internal surface area and increased density of coordinatively unsaturated Zr sites, which facilitate binding with the sulfonate headgroup. Hydrophobic interactions within UiO-66's pores likely contribute as well. Liu *et al.*[53] found that MIL101(Cr) demonstrated maximum adsorption capacities of 1.19 and 1.89 mmol L^{-1} for PFOA, with equilibrium times of less than 1 hour, indicating rapid adsorption rates and high adsorption capacities. Adsorption of PFOA anions onto the anion-exchanged MIL-101(Cr) MOF occurs primarily *via* direct coordination to the Cr(III) coordinatively unsaturated sites (CUS), with synergistic contributions from π–π interactions between the PFOA anions and the BDC (terephthalic acid) linkers. Rui *et al.*[51] evaluated the performance of three distinct MOFs—NU-1000, UiO-66, and ZIF-8—in removing eight types of

PFASs from groundwater. At PFAS concentrations of 190 ± 250 μg L^{-1}, NU-1000 showed a removal efficiency of 58% for anionic PFASs and achieved a near-quantitative removal rate of 99% for non-ionic PFASs. For non-ionic PFASs, UiO-66 exhibited analogous removal characteristics with a removal rate of 95%, yet it exhibited a significantly lower removal rate of merely 2% for anionic PFASs. ZIF-8 displayed low affinity for both anionic and non-ionic PFASs, with removal rates less than 10%. GAC exhibited removal efficiencies of 37% and 44% for anionic and non-ionic PFASs, respectively. In contrast, ZIF-8 displayed removal rates of less than 10%. Anionic PFAS adsorption on NU-1000 primarily occurs through ionic interactions. The mechanism involves anion exchange between PFAS carboxylate/sulfonate groups and the hydroxo ligands of NU-1000's Zr6-node $[Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(H_2O)_4(OH)_4(\text{-}CO_2)_8]$. This contrasts sharply with UiO-66, whose structurally similar Zr6-node lacks anion exchange capacity, explaining its poor anionic PFAS removal. However, UiO-66's robust framework with μ_3-bridging hydroxo groups facilitates effective adsorption of non-ionic PFAS species. For ZIF-8 systems, while amine groups of non-ionic PFASs can coordinate with exposed Zn sites, the material demonstrates limited PFAS removal overall. This stems from two key factors: (1) the absence of anion exchange capability in its Zn-node, and (2) the relatively weak interaction strength between Zn sites and PFAS functional groups. These structural differences highlight how subtle variations in MOF node chemistry dramatically influence PFAS adsorption performance.

Li *et al.*[52] investigated the adsorption of nine PFASs by NU-1000, revealing that this material demonstrates a significant adsorption capacity within an extremely short equilibrium period. NU-1000 stands out as one of the most effective adsorbents, rendering it an exemplary adsorbent for both short-chain and long-chain PFAS compounds. The adsorption capacity for short-chain PFBS was observed to be two orders of magnitude higher than that of activated carbon and resin materials, coupled with excellent regeneration and reusability, with near-complete removal and recovery efficiencies.

In comparison to conventional adsorbents, which are characterized by low adsorption capacities and prolonged equilibrium times, MOF materials exhibit superior capacity and efficiency in the removal of PFASs, thereby representing a novel direction in the research of PFAS removal technologies.

2.1.4 Covalent organic frameworks (COFs). COFs are a class of porous crystalline organic materials formed through covalent bonding between organic molecules. They are characterized by a large specific surface area, a crystalline network structure, an abundance of adsorption sites, and thermal stability.[71,72] By incorporating specific building blocks and functional groups, COFs enhance their interactions with target pollutants, making them highly efficient tools for the selective adsorption of pollutants, even in complex mixtures.[73] Compared to conventional adsorbents, COFs demonstrate superior extraction performance through π–π conjugation, hydrogen bonding, and hydrophobic interactions.[74]

Ji *et al.*[49] developed a COF material with *X*% amino groups, which interact with the anionic head groups of PFASs, and

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a substantial hydrophobic surface area, further enhancing its adsorption capabilities. The optimized material, with an amino loading of 20–28%, demonstrated high affinity and rapid kinetics for binding 13 different PFAS compounds. The 20% [NH$_2$]-COF variant exhibited the highest adsorption capacity for GenX at high concentrations, while the 28%[NH$_2$]-COF variant showed the fastest and highest adsorption capacity for GenX and 12 other PFASs under environmental conditions. The COF material's adsorption performance for short-chain PFASs, exemplified by GenX, was significantly superior to that of GAC and PAC, with adsorption levels of 91%, 0%, and 72%, respectively.

Zadehnazari et al.[50] synthesized COF nanoparticles, MELEM-COF and MEL-COF, which are highly crystalline and demonstrate excellent affinity for various anionic PFASs through electrostatic interactions. These nanoparticles can simultaneously remove multiple pollutants within 30 minutes, achieving removal efficiencies of 90.0–99.0%, including difficult-to-remove short-chain PFASs like PFBA and PFHA. Cationic MELEM-COF achieves a 2500 mg g^{-1} adsorption capacity via electrostatic and dipole interactions. Moreover, MELEM-COF demonstrated superior regenerability, allowing for multiple reuses through simple methanol washing at ambient temperature.

Incorporating functional groups within the material framework that enhance hydrogen bonding and electrostatic interactions increases the potential for selective capture and extraction of PFAS species. Precise control of the size and distribution of pores in porous materials can affect the adsorption kinetics of PFASs. In the nascent phase of COF application in PFAS elimination, modifying the COF skeleton with different ionic building blocks or functional groups, using fluorine and oxygen atoms, can significantly enhance the adsorption capacity for PFASs.In summary, COFs are at the cutting edge of research into PFAS removal.[75–77]

2.1.5 Molecularly imprinted polymers (MIPs). In the adsorption process within aquatic environments, particularly in wastewater, the presence of numerous compounds and colloids competes with anionic PFASs, thereby reducing the overall adsorption capacity. Consequently, selective adsorption is particularly appealing from water and wastewater. Researchers have utilized molecular imprinting technology to develop MIPs that exhibit high selectivity for PFASs.[78] The MIP technology for removing PFASs (Fig. 2) involves selecting a target PFAS molecule (e.g., PFOA/PFOS) or its structural analog as a template, followed by pre-assembly with functional monomers in a weak-polarity solvent (e.g., acetonitrile). A cross-linker (EGDMA) and

initiator are then added to polymerize the mixture, forming a rigid network that locks the template–monomer complex. Subsequent repeated washing with acidic methanol or mixed solvents (e.g., acetic acid–acetonitrile) thoroughly removes the template molecules, exposing specific cavities. These cavities enable highly efficient capture of PFAS "forever chemicals" through synergistic size/shape matching, fluorophilic interactions, and electrostatic forces. The primary advantage of MIPs lies in their high affinity and selectivity for the target compounds.[54]

Cao et al.[79] discovered that MIPs can effectively remove approximately 90% of PFOA from mixtures, with the advantage of rapid adsorption kinetics being particularly useful for the quick separation and enrichment of PFOA. Yu et al.[54] discovered that the adsorption capacity of MIPs is pH-dependent, with a decrease in adsorption capacity observed as the solution pH or ionic strength increases. Cao et al.[55] synthesized novel MWCNTs@MIPs using multi-walled carbon nanotubes as the supporting material. Their experiments revealed that PFOA reached adsorption equilibrium on MWCNTs@MIPs within approximately 80 minutes, significantly faster than resin and activated carbon adsorbents. There was no significant loss in adsorption capacity after five consecutive adsorption–desorption–adsorption cycles, and the adsorbent demonstrated a high selective recognition ability for PFOA. Owing to its high selectivity for PFOA and superior regenerative capabilities, the synthesized MWCNTs@MIPs are deemed a promising adsorbent for the extraction of PFOA from aquatic environments.

The rational design of MIPs necessitates ensuring that the structure of PFAS molecules aligns with the material properties, which is a key research direction for future MIP removal technology. Future research will focus on more detailed design based on the characteristics of PFAS molecules.

In conclusion, adsorption technology is widely applied for PFAS removal due to its operational simplicity and low cost. However, its core limitation lies in the selectivity-regeneration conflict. Conventional adsorbents suffer from low regeneration efficiency, and competitive adsorption compromises their practical efficacy. Future breakthroughs in emerging materials should focus on functionalized materials designed for synergistic selective adsorption and mild regeneration. This necessitates a focus on bifunctional material design (e.g., integrating ion-exchange groups with hydrophobic micropores), aiming to enhance selectivity for short-chain PFASs while reducing regeneration energy consumption through weak-bonding mechanisms.

2.2 Advanced oxidation technology

As the range of anthropogenic pollutants released into the natural environment rapidly expands, particularly the recognized persistent organic pollutants, the efficiency of physical purification methods is limited. This has led to a significant interest in typical chemical methods for decomposing pollutants. In 1987, Glaze et al. introduced the term "Advanced Oxidation Processes" (AOPs), which produce powerful oxidants such as hydroxyl radicals,[80,81] used in water treatment processes
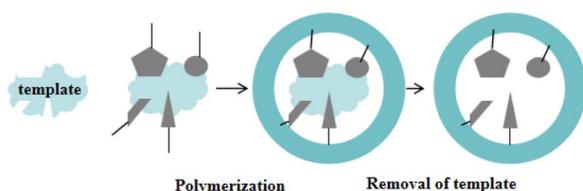

Fig. 2 The principle of PFAS removal by MIP technology.

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at room temperature.[82] Due to the slow reaction rate, high cost, and susceptibility to external factors of commonly used oxidants like ozone (O3) and hydrogen peroxide (H_2O_2) in AOPs, and the potential to generate short-chain PFASs during the oxidation process, which can contaminate water sources, this technology can be combined with other methods to remove PFASs.[83,84] In laboratory or industrial applications, a combination of oxidants with ultraviolet light, ultrasound, catalysts, or electrochemical reactions is utilized.[85,86] Advanced oxidation technology has been employed to degrade PFASs, offering advantages like conversion efficiency and straightforward manipulation. Certain technologies are capable of accomplishing full mineralization.[87]

2.2.1 Electrochemical technology. Electrochemical oxidation is a burgeoning advanced oxidation technology that offers the merits of high removal efficiency and potent oxidation capacity (Table 3). However, the high cost of electrode materials and the potential issue of electrode contamination have restricted their widespread application at present. The mechanism of electrochemical oxidation for removing PFASs entails oxidation occurring at the anode directly or *via* indirect action through reactive free radicals.[88] Due to its lack of secondary pollution and high energy efficiency, electrochemical oxidation has gained extensive application in wastewater management.[89]

The efficiency of removal is significantly influenced by the electron transfer capability, OH generation capability, and oxygen evolution potential (OEP) of the anode material. Schaefer et al.[90] investigated the effective treatment of PFOA and PFOS in chlorinated water and natural groundwater using boron-doped diamond (BDD) anodes. The use of a radical scavenger, *tert*-butanol (TBA), revealed no impact on the removal rate and corresponding defluorination rate of PFOA and PFOS, indicating that direct anode oxidation is the primary mechanism. Zhuo[91] employed a Ti/SnO$_2$–Sb–Bi electrode for degradation of PFOA. After 2 hours of electrolysis, over 99% of PFOA was degraded, and the F-concentration continued to increase, reaching a defluorination rate of 63.8% after 3 hours. Xiao et al.[92] utilized BDD electrodes fabricated on conductive single-crystal silicon substrates, achieving a PFOA removal rate of 93.6% and effective mineralization after 6 hours of degradation. Zhuo et al.[93] found that BDD anodes could degrade PFXA and PFXS, and the pseudo-first-order kinetic constants for PFXA and PFXS increased with the elongation of the carbon chain, attributing the rise to enhanced hydrophobicity. Increasing the current density from 0.12 mA cm^{-2} to 0.59 mA cm^{-2} resulted in a removal rate of up to 97.48% from 0%. The degradation rate of PFOA in acidic solutions was higher than that in alkaline solutions. Zhuo et al.[94] demonstrated that SnO$_2$–F modification could significantly enhance the electrochemical performance of BDD anodes. After fluorination of SnO$_2$ crystals, the SnO$_2$–F particles became smaller, the oxygen evolution potential increased by 0.13 V, and the F-53B degradation efficiency improved by 15.07%. Under optimal operating parameters, the removal rate of F-53B was 95.6% after 30 minutes of electrolysis, and the defluorination rate reached 61.39%.

Electrochemical oxidation is an advanced oxidation technology that can remove or even mineralize PFASs in wastewater,

Table 3 Comparative analysis of various electrochemical technologies for the removal of PFASs

Anode material	PFAS	Current density (mA cm^{-2})	Initial concentration	Electrolyte	Rate constant	Degradation rate and defluorination rate	References
BDD	PFOA	50	15 mg L^{-1}	1500 mg/LNa$_2$SO$_4$ + 167 mg L^{-1} NaCl	1.2 ± 0.047 h^{-1}	99% & 70%	90
BDD	PFOS	50	10 mg L^{-1}	1500 mg/LNa$_2$SO$_4$ + 167 mg L^{-1} NaCl	0.37 ± 0.017 h^{-1}	95% & 75%	
Ti/SnO$_2$–Sb–Bi	PFOA	14	50 mg L^{-1}	1.4 g L^{-1} NaClO$_4$	1.93 h^{-1}	99% & 63.8%	91
Si/BDD	PFOA	20	200 mg L^{-1}	0.05 mol L^{-1} Na$_2$SO$_4$	0.444 h^{-1}	93.6% & 90.2%	92
Si/BDD	PFBA	23.24	0.114 mmol L^{-1}	1.4 g L^{-1} NaClO$_4$	0.0332 min^{-1}	Not mentioned & ≈80%	93
	PFHxA				0.0335 min^{-1}	Not mentioned & ≈70%	
	PFOA				0.0428 min^{-1}	99% & ≈60%	
	PFDeA				0.0455 min^{-1}	Not mentioned & ≈50%	
	PFBS				0.0139 min^{-1}	Not mentioned & ≈50%	
	PFHxS				0.0223 min^{-1}	Not mentioned & ≈70%	
	PFOS				0.0357 min^{-1}	Not mentioned & ≈70%	
BDD	F-53B	30	100 mg L^{-1}	1 mol L^{-1} NaCl	0.0550 min^{-1}	80.54% & not mentioned	94
BDD/PbO$_2$					0.0742 min^{-1}	87.32% & not mentioned	
BDD/SnO$_2$					0.0641 min^{-1}	90.39% & not mentioned	
BDD/SnO$_2$–F					0.1097 min^{-1}	95.6% & 61.39%	

including most short-chain PFASs, in a short period of time. However, challenges persist, including the high cost, low activity, and short lifespan of electrode materials.[95] Up to now, most studies have been conducted on relatively pure reaction systems, which centered around using spiked deionized water with specific PFASs, and it is still in the phase of experimentation. Achieving the goal of cleaning up PFASs at extremely low concentrations ($ng\ L^{-1}$) remains a significant challenge.[96,97]

2.2.2 Photocatalytic technology. Photocatalytic degradation technology is a widely employed physicochemical treatment method in the fields of organic synthesis, materials science, and water purification treatment, and is regarded as an efficient and cost-effective approach (Table 4).[98] This method involves the decomposition and mineralization of organic compounds through the combined action of ultraviolet light and specific catalysts.[99] During this process, the energy from ultraviolet light induces water molecules to produce highly reactive substances such as hydrated electrons (e_{aq}^{-}), hydroxyl radicals (·OH), and hydrogen radicals (H·), which are essential in the decomposition of PFASs.[100]

Hori and colleagues[83] first investigated the photolytic decomposition of PFOA in water. They found that PFOA underwent complete decomposition in the presence of the catalyst phosphotungstic acid after 24 hours of irradiation with a 200 W xenon mercury lamp. The catalyst remained intact and could be reused in continuous operation. To generate sufficient e_{aq}^{-}, both the power and time of irradiation were significantly increased. Sun et al.[101] discovered the UV photodegradation of PFOS in the presence of iodide (I^{-}) and humic acid (HA). Without a catalyst, PFOS exhibited a moderately slow rate of direct photolysis; in the UV/KI process, the degradation velocity was moderate, but there was a significant lag phase in the defluorination process; the inclusion of HA in the UV/KI treatment process significantly enhanced the rate of degradation and defluorination, with the defluorination rate increasing by 11.6 times in 1.5 hours. This acceleration is attributed to HA reducing iodine (I_2), hypoiodous acid (HOI), iodate (IO_3^{-}), and triiodide (I_3^{-}) to iodide (I^{-}), thereby producing more e_{aq}^{-}. These e_{aq}^{-} are capable of cleaving the C–C and C–F bonds in PFOS, resulting in its complete mineralization. Ochiai et al.[102] studied the decomposition of PFOA in an aqueous suspension containing a TiO_2 photocatalyst. PFOA molecules adhered to the surface of TiO_2 following adsorption equilibrium, and the adsorbed PFOA molecules were readily decomposed by the holes and ·OH produced by TiO_2, ultimately producing CO_2 and F-. At a TiO_2 photocatalyst concentration of 1.5 wt%, almost all 5 mmol L^{-1} PFOA was decomposed during a 4-hour period of irradiation with a medium-pressure UV lamp at atmospheric pressure. Gu et al.[103] significantly enhanced the decomposition of PFOA by employing a high photon flux UV/sulfite system to promote the generation of e_{aq}^{-}. The product of sulfite after the reaction is sulfate, which has a much smaller adverse impact on the environment. In an experiment where the reaction time was increased from 30 minutes (98% of PFOS was decomposed) to 60 minutes, it was observed that the fluoride concentration in the test solution continued to increase, indicating a gradual defluorination. The final defluorination efficiency approached

Table 4 Comparative analysis of various photocatalytic degradation technologies for the removal of PFASs

Catalyst	PFAS	Light wavelength	Power	Reaction conditions	Reaction time	Degradation rate and defluorination rate	References
None	PFOA	UV254 nm	200 W	$C_0 = 1.35$ mmol L^{-1} pH = 3.0 (O_2 0.48 MPa)	72 h	89.5% & 33%	83
Phosphotungstic acid	PFOA	UV254 nm	200 W	$C_0 = 1.35$ mmol L^{-1} $C_{catalyst} = 6.68$ mmol L^{-1} pH = 1.8 (O_2 0.48 MPa)	24 h	100% & 70%	
None	PFOS	UV254 nm	14 W	$C_0 = 0.03$ mmol L^{-1} pH = 10	2 h	5.5% & 0.8%	101
I^{-}	PFOS	UV254 nm	14 W	$C_0 = 0.03$ mmol L^{-1} pH = 10	2 h	73.9% & 44.3%	
I^{-}/humic acid (HA)	PFOS	UV254 nm	14 W	$C_0 = 0.03$ mmol L^{-1} pH = 10	2 h	97.9% & 77.0%	
TiO_2	PFOA	MPUV 250–375	600 mW cm^{-2}	$C_0 = 5$ mmol L^{-1} TiO_2 nanoparticles (1.5–6.0 wt%)	4 h	100%	102
Na_2SO_3	PFOS	UV254 nm	250 W	$C_0 = 0.03$ mmol L^{-1} $C_{catalyst} = 10$ mmol L^{-1} DO = 5 mg L^{-1} pH = 9.2	0.5 h	98% & 70%	103
Na_2SO_3	F-53B	UV254 nm	16 × 8.0 mW cm^{-2}	$C_0 = 0.16$ mmol L^{-1} $C_{catalyst} = 20$ mmol L^{-1} pH = 10	1 min (removal rate of 99%)	100% & 85%	37
Na_2SO_3	PFOS	UV254 nm	16 × 8.0 mW cm^{-2}	$C_0 = 0.16$ mmol L^{-1} $C_{catalyst} = 20$ mmol L^{-1} pH = 10	2 h	100% & 70%	
Na_2SO_3	F-53	UV254 nm	16 × 8.0 mW cm^{-2}	$C_0 = 0.16$ mmol L^{-1} $C_{catalyst} = 20$ mmol L^{-1} pH = 10	3 h	100% & 70%	

70%. This suggests that after the complete decomposition of PFOS, other fluorinated intermediates were still undergoing defluorination reactions. Bao et al.[37] studied the removal of F-53B, PFOS, and F-53 by UV/sulfite reduction. F-53B was easily decomposed with the help of e_{aq}^-, with about 99% decomposition within 1 minute. PFOS disappeared within 2 hours, but about 10% of the remaining F-53 was still observable, requiring an additional hour for complete degradation. This indicates that the incorporation of an oxygen atom in the perfluoroalkyl chain reduces the interaction between F-53 and e_{aq}^-, thereby slowing down the molecular decomposition. The rapid degradation kinetics of F-53B suggests that chlorine atoms accelerate the decomposition of the molecule. Moreover, more than 90% of the fluorine from all studied compounds was reclaimed in the form of minerals; however, this process extended over a duration of 8 hours. Prominently, when PFOS was undetectable (2 hours), its defluorination rate reached about 85%, while at the same reaction time, the fluorine recovery rates for F-53B and F-53 were lower (about 70%).

Furtado et al.[104] demonstrated that PFOS at concentrations close to environmental levels (100 μg L^{-1}) can indeed be degraded using a TiO$_2$/UV system (25 °C, pH = 4, 1.45 g L^{-1} TiO2), achieving a substantial removal rate of 83% after 8 hours of treatment. Uwayezu et al.[105] employed a 185/254 nm UV, 6 W lamp under the condition of 5 g L^{-1} persulfate to treat industrial wastewater, groundwater, and landfill leachate for 4 hours. Their findings indicated that the main PFAS degradation rates in industrial wastewater were 57% for PFBA, 80% for PFOA, and 60% for PFOS; the main PFAS degradation rates in groundwater were 94% for 6–2 FTS, 75% for PFOA, 62% for PFOS, and 61% for PFHxS. The removal rates of the main compounds in landfill leachate were as high as 12% for PFHxA, 32% for PFPeA, 56% for PFOA, and 43% for PFOS.

In practical applications, photocatalytic technology gradually degrades high-fluorine PFASs into low-fluorine molecules such as trifluoroacetic acid (CF$_3$COOH), and then completely decomposes them into fluoride ions, achieving complete mineralization.[106,107] Nevertheless, the coexistence of other organic substances in wastewater may significantly diminish the effectiveness of PFAS removal processes.[108] Moreover, the photocatalytic degradation technology may face secondary pollution issues due to the addition of catalysts, which could limit its practical application. Despite challenges, photocatalytic degradation offers swift elimination and substantial treatment capacity, indicating significant promise for eliminating PFAS pollutants from aquatic environments.[109]

2.2.3 Ultrasonic oxidation. Ultrasonic waves (US), with a frequency range of 20 kHz to 2 MHz, are capable of degrading a variety of refractory organic pollutants, including certain types of PFASs.[110,111] When applied to a liquid, ultrasonic waves generate repetitive compression patterns, causing the nucleation, expansion, and implosion of cavitation bubbles. During the collapse of these bubbles, a local hot spot is formed; temperatures within the bubbles can surge to 5000–6000 K, and pressures can spike to 1000–2000 atm; meanwhile, the temperature at the bubble-liquid boundary stays at 1000–1500 K.[112] Consequently, the thermal pyrolysis of refractory organic

pollutants occurs inside the bubbles or at the bubble-liquid boundary. Additionally, ˙H and hydroxyl ˙OH radicals are generated within the cavitation bubbles, where they can either react immediately with gaseous volatile pollutants or diffuse into the bubble-liquid interface and the surrounding solution.[113]

Dannj et al.[114] discovered that in a saturated argon water solution, under ultrasonic irradiation at 640 kHz and 396 W, over 80% of GenX was degraded within 60 minutes, with the primary product being fluoride ions. Wood et al.[115] conducted degradation studies on PFOS at frequencies of 44, 400, 500, and 1000 kHz, and found that no degradation of PFOS was observed at 44 kHz. At 400, 500, and 1000 kHz, the degradation rates within 4 hours were 96.9%, 93.8%, and 91.2%, respectively, accompanied by a proportional release of fluoride, signifying the mineralization of PFOS molecules. Awoyemi et al.[116] treated aqueous film forming foam (AFFF) and foam fractionation (FF) under the conditions of 187.5 W, 580 kHz, and 3 hours. The total PFAS level in AFFF was reduced from approximately 2200 ppb to approximately 766 ppb, a reduction of about 65%. For FF, the total PFAS level was reduced from approximately 1950 ppb to approximately 60.8 ppb, a reduction of about 97%.

Ultrasonic waves represent a promising degradation technology due to their ease of application, ability to completely mineralize PFASs without producing short-chain PFASs, and requirement for minimal or no chemical additives, along with compatibility with various other technologies.[17,117] The key factor influencing the effectiveness of ultrasonic action is the intensity of cavitation, which is dependent on the ultrasonic frequency, power density, and the structure of PFASs. Ultrasonic technology is increasingly gaining attention. However, because of the intricacies of real-world scenarios and the high energy demands, there is still limited understanding of its scalability or field application.[118] Despite the high energy requirements and associated costs of ultrasonic irradiation (USI) for water treatment, USI holds promise as a viable method for the complete degradation of PFASs in pre-concentrated or highly concentrated wastewater.[119]

2.3 Bioremediation

Bioremediation technology offers unique advantages over physical and chemical methods, including environmental friendliness and cost-effectiveness, thus avoiding further damage to aquatic environments.[120]

Microbes and their enzymes represent the primary natural mechanism for degrading fluorinated compounds in contaminated environments, transforming and/or defluorinating organic substances through diverse metabolic pathways to obtain energy and nutrients. For a long time, the biodegradation of the exceptionally stable C–F bonds, particularly within the long-chain perfluoroalkyl moieties of PFASs, has been considered a major obstacle. This has made their complete biodegradation, especially defluorination, extremely challenging and resulted in slow progress. Consequently, PFASs exhibit significant resistance to mineralization. Only a limited number of microbial species can utilize them for growth. Most

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degradation occurs *via* co-metabolism, where an additional growth substrate provides the necessary energy and nutrients.[121] In contrast, polyfluoroalkyl compounds exhibit somewhat greater biodegradability than their perfluoroalkyl counterparts, as their non-fluorinated sites introduce potential points of enzymatic attack.

Previous research has primarily focused on the transformation of precursor substances: (1) perfluoroalkyl sulfonamide derivatives: these compounds serve as precursors for PFOS. Studies by Benskin *et al.*[122] and Mejia *et al.*[123] elucidated the transformation of *N*-ethyl perfluorooctane sulfonamidoethanol (EtFOSE). EtFOSE undergoes *O*-dealkylation to form *N*-ethyl perfluorooctane sulfonamide (EtFOSA), followed by *N*-deethylation to yield perfluorooctane sulfonamide (FOSA). FOSA is further oxidized *via* sulfonamide oxidation (nitrogen atom oxidation) to generate PFOS. Both dealkylation steps are catalyzed by monooxygenases, with no cleavage of C–S bonds occurring throughout the process. (2) Desulfonation of sulfonamide precursors: This process involves cleavage of C–S bonds in compounds such as 6 : 2 fluorotelomer sulfonamide (6 : 2 FTSA), generating fluorotelomer intermediates (*e.g.*, 6 : 2 fluorotelomer unsaturated carboxylic acid, 6 : 2 FTUCA). (3) β-Oxidation of hydrogen-containing precursors (*e.g.*, FTOHs): this pathway proceeds stepwise without C–F bond cleavage. Initial oxidation converts FTOHs to fluorotelomer aldehydes (FTALs), which are further oxidized to fluorotelomer carboxylic acids (FTCAs). Subsequent β-oxidation cycles entail dehydration to fluorotelomer unsaturated carboxylic acids (FTUCAs), hydration, and oxidative decarboxylation, yielding progressively shorter-chain perfluoroalkyl carboxylic acids (PFCAs). Kinetic constraints in terminal steps result in predominant accumulation of C4–C6 PFCAs (*e.g.*, PFBA, PFPeA, and PFHxA).Shaw *et al.*[124] demonstrated that the aerobic strain Gordonia sp. NB4-1Y efficiently transformed 6 : 2 FTAB and 6 : 2 FTSA within one week, achieving transformation rates of 85–88%. The primary metabolite was 5 : 3 fluorotelomer carboxylic acid (5 : 3 FTCA), with <2% combined yield of short-chain PFCAs (notably PFBA and PFPeA at detectable levels). Yang *et al.*[125] investigated the desulfonation and defluorination of 6 : 2 FTSA by *Rhodococcus jostii* RHA1. Their study revealed two major transformation products – 6 : 2 FTUCA and α-OH 5 : 3 FTCA-along with two minor products: 6 : 2 FTCA and PFHpA in RHA1 cultures grown in a sulfur-free medium supplemented with ethanol and 1-butanol, respectively. A substantial body of research has corroborated this process. While current investigations focus predominantly on the aerobic biotransformation of these precursor compounds, studies under anaerobic conditions remain scarce.[126–128] Yin *et al.*[129] found that EtFOSA in wetland microcosms was biotransformed aerobically with a half-life of 0.5 days but not biotransformed anaerobically. Yi *et al.*[130] found that under nitrate-reducing conditions with equivalent biomass, the anaerobic biotransformation rate of 6 : 2 fluorotelomer thioether amido sulfonate (FtTAoS) was approximately 10 times slower than that under aerobic conditions. Therefore, continued efforts should be dedicated to investigating anaerobic biotransformation, as these endeavors will facilitate the

development of remediation strategies tailored to specific electron-acceptor limiting environments.

While current literature predominantly examines precursor biotransformation to terminal products in environmental samples and microbial consortia, specific bacterial strains with defluorination capabilities for perfluorinated compounds including PFOA and PFOS, have been increasingly identified.[131] Yu *et al.*[132] reported C–F bond cleavage in two C6 PFASs through reductive defluorination by an organohalide-respiring microbial community. The major dechlorinating species in the seed culture, *Dehalococcoides*, was not responsible for the defluorination, as neither its growth nor reductive dehalogenase expression was detected. These findings suggest that minor phylogenetic groups within the community likely mediated the reductive defluorination. Huang *et al.*[133] investigated an acidophilic microorganism, strain A6, which utilizes PFOA/PFOS as electron acceptors under anaerobic conditions. Over 100–120 days, this strain achieved a PFOA removal rate of 46.2% and a PFOS removal rate as high as 40.1%. The detection of short-chain PFAAs (*e.g.*, PFPeA and PFHxA) and F⁻ provided direct evidence for the cleavage of C–F bonds (evidenced by F⁻ release) alongside C–C bond cleavage—a significant breakthrough. These short-chain products are likely transient intermediates.

Constructed wetlands (CWs) represent an eco-friendly ecological remediation technique,[134] leveraging the natural functions of wetland plants, soils, and associated microbial networks to facilitate the purification of wastewater.[135] Their advantages, including low energy consumption, simple operation, and minimal maintenance, have demonstrated great potential for CWs in remediating PFAS-contaminated water. Gkika *et al.*[136] explored the bioaccumulation of PFASs in macrophytes (*Myriophyllum spicatum*) and sediment-dwelling invertebrates (*Lumbriculus variegatus*). Initially, the study identified 18 PFAS compounds at a concentration of 4.06 ng g⁻¹. Following a 56-day exposure involving the aquatic plants, PFAS concentrations had dropped to 32% of their original levels and the number of detectable PFAS compounds was reduced to 8. The coexistence of macrophytes and sediment-dwelling invertebrates resulted in an additional reduction of PFAS levels to 25% of the starting concentration, reaching 1.03 ng g⁻¹. However, the organisms were sensitive to environmental changes and did not achieve complete mineralization. Li *et al.*[137] discovered that constructed wetlands utilizing two typical macrophytes, *Potamogeton wrightii* and *Ceratophyllum demersum*, achieved a removal of 33.59–88.99% of PFASs through sediment adsorption, plant extraction, and microbial bioaccumulation. Wang *et al.*[138] found that the symbiotic relationship between arbuscular mycorrhizal fungi and wetland vegetation (*Iris pseudacorus* L.) not only boosts plant growth and photosynthetic capabilities but also heightens the plants' resilience to oxidative stress caused by PFASs, thereby enhancing the contaminant elimination efficiency of CWs. Ji *et al.*[139] discovered that the CW microbial fuel cell system effectively removed PFOA and PFOS with an efficiency exceeding 96%, indicating a broad application prospect for CWs in removing PFASs. Nevertheless, chronic exposure to PFASs can harm plant growth and microbial diversity,[140] which may

further affect the stability of CWs and reduce their ability to remove pollutants. Grasping and alleviating the adverse effects of PFAS stress on plant development and microbial community composition is vital for enhancing the enduring efficacy and sustainability of CWs in environmental restoration.

Anthropogenic pollutants often introduce novel chemical structures, demanding that microorganisms possess the capability to degrade these new compounds. While this holds true for organochlorides, which generally exhibit favorable biodegradability, the case for organofluorine compounds—particularly polyfluorinated structures—is distinct. Although microbial degradation of such compounds is documented, it occurs infrequently in natural environments. This scarcity arises because the dominant dechlorinating species within microbial communities are not responsible for reductive defluorination. Consequently, the microorganisms capable of actual defluorination likely represent low-abundance populations. Therefore, it is reasonable to expect that microorganisms enriched or isolated specifically for defluorination will exhibit significantly higher defluorination activity and possess a broader substrate range for fluorinated compounds. Thus, future research must focus on enriching or isolating microorganisms responsible for reductive defluorination, followed by characterizing their physiological properties within highly enriched cultures or pure isolates. Bioremediation, including the study of PFAS removal in constructed wetlands, remains in its infancy and has encountered numerous constraints and obstacles. Identifying microorganisms with high PFAS mineralization capabilities and plant species that can accumulate PFASs effectively, as well as comprehending their absorption mechanisms for various PFAS configurations, and bolstering the synergy between these biological elements to improve the removal rate of PFASs remain significant challenges.[141,142]

2.4 Membrane separation technology

Although adsorption technology is more economical than high-pressure membranes for treating long-chain PFASs, high-pressure membranes might be a superior option for treating short-chain PFASs given the difficulty of removing short-chain PFASs with adsorbents.[143] Membrane separation is a technique that selectively partitions mixtures according to the varying abilities of particles in the solution to traverse the membrane based on their size, with each membrane having a different pore size and being capable of separating different substances. Reverse osmosis (RO) membranes and nanofiltration (NF) membranes demonstrated efficacy in the removal of PFASs under various water source conditions.[144]

Tang et al.[145] investigated the potential of reverse osmosis membranes for the treatment of PFOS-contaminated wastewater, discovering that the retention rate of PFOS exceeded 99% for a broad spectrum of initial concentrations (0.5–1500 mg L^{-1}). No distinct correlation was found between the membrane flux and the initial membrane potential. However, an increase in PFOS concentration was associated with a reduction in membrane flux. Liu et al.[146] found that under all operating conditions and in evaluated water matrices, NF

membranes exhibited a very high retention rate (about 97%) for the selected 10 PFASs. Ma et al.[58] studied the retention or removal effects of commercial RO and NF membranes on PFASs. The study also delved into the impact of surfactants, ionic valence, and solution temperature, which have not been fully explored. The study revealed that cationic surfactants (CTAB) could effectively enhance the filtration efficiency of negatively charged PFASs, while anionic surfactants (SDS) could also improve filtration performance by increasing electrostatic repulsion. Furthermore, the study indicated that the filtration efficiency of PFASs improves with increasing ionic valence, with aluminum (Al^{3+}) and phosphate (PO$_4^{3-}$) ions showing outstanding performance. At the same time, it was found that higher temperatures could lead to membrane pore expansion, thereby reducing the filtration efficiency of PFASs. Sadia et al.[147] found that reverse osmosis membranes might inherently contain PFASs, which have the potential to leach into the treated drinking water. Leaching tests and direct total oxidizable precursor analysis indicated the presence of PFOS (branched and linear), PFBA, PFHxA, PFNA, and PFOA in five selected commercial reverse osmosis membranes, with leaching potential. This resulted in the release of tens of milligrams of PFASs from each membrane element used for drinking water production.

Membrane separation demonstrates good removal efficiency for both long-chain and short-chain PFASs, but it remains a physical method that does not alter the structure of PFASs. The high-concentration PFAS wastewater produced still necessitates subsequent treatment. Additionally, the composition of real wastewater is exceedingly complex, and the dissolved organic matter present in the wastewater can affect membrane flux due to particle size, which may lead to a decrease in the removal efficiency of PFASs. In practice, pretreatment steps are necessary to mitigate the influence of other organic contaminants on the treatment process. Consequently, the high operating costs and maintenance requirements of membrane separation technologies limit their widespread application in actual water treatment.

2.5 Comparative analysis of technologies for PFAS removal

As shown in Table 5, various PFAS remediation technologies currently have their own advantages and disadvantages. Current large-scale technologies for PFAS removal include activated carbon adsorption, anion exchange resins, and membrane separation. However, their cost-effectiveness requires enhancement through optimized regeneration processes. Meanwhile, electrochemical and photocatalytic techniques are advancing from laboratory research to the pilot-scale stage. In contrast, other approaches—such as novel adsorption methods and ultrasonic technology—remain predominantly at the bench-scale research phase. Significant research gaps persist in microbial remediation, necessitating the isolation and characterization of microorganisms/enzymes with enhanced defluorination capabilities, along with elucidation of the detailed molecular mechanisms and enzymatic basis of reductive defluorination.

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Table 5 Comparative analysis of various PFAS remediation technologies

Remediation technology	Material	Process	Advantages	Disadvantages	References
Adsorption	Carbon adsorption materials (activated carbon and biochar)	Selecting different types of adsorbents for the adsorption and removal of PFASs	Effective removal, simple operation, low cost, and widespread application	Only involves adsorbing PFASs from the liquid phase without degradation and difficult to remove short-chain PFASs, and is greatly affected by organic matter in wastewater. Most carbon adsorption materials cannot be reused, and the subsequent safe disposal remains a problem	59 and 148
	Anion exchange resin		Superior removal efficiency to activated carbon, simple operation, and capable of removing some short-chain PFASs	Only involves adsorbing PFASs from the liquid phase without degradation. The adsorption time is long, and it cannot effectively remove non-ionic PFASs, and the recovery and regeneration have certain difficulties	149
	MOFs and COFs		Superior adsorption kinetics and capacity compared to currently implemented large-scale technologies, particularly for targeted removal of short-chain PFASs, enhancing their potential for ionic contaminant analysis applications	Only involves adsorbing PFASs from the liquid phase without degradation. High cost, still in the laboratory research stage	74
	MIP		Exhibits selective adsorption and excellent regeneration capacity	Only involves adsorbing PFASs from the liquid phase without degradation. The adsorption capacity is relatively weak, still in the laboratory research stage	150
Advanced oxidation technology	Electrodes (BDD, lead dioxide, titanium dioxide, tin dioxide, etc.)	Direct oxidation at the anode or indirect oxidation through active free radicals transforms PFASs into non-toxic, biodegradable byproducts	High removal efficiency(≥80%) and short reaction time	The reaction process will produce short-chain PFASs and toxic byproducts, and the high cost, low activity, and short lifespan of electrode materials make it temporarily difficult to achieve the goal of cleaning up PFASs at extremely low concentrations (ng L^{-1})	87, 151 and 152
	Ultraviolet light	The energy of ultraviolet light causes water molecules to produce hydrated electrons (e$_{aq}^{-}$), hydroxyl radicals ($\cdot$OH), and hydrogen radicals (H$\cdot$), which work together with specific catalysts to achieve the decomposition and mineralization of PFASs	Strong removal capacity(≥70%), environmentally friendly, and can reduce secondary pollution	High cost and high energy consumption, currently not suitable for large-scale use	107, 153 and 154

Table 5 (*Contd.*)

Remediation technology	Material	Process	Advantages	Disadvantages	References
	Ultrasonic waves	Using ultrasonic irradiation to form high-temperature bubbles and highly oxidative substances to degrade PFASs	Easy to apply, capable of complete PFAS mineralization without producing short-chain PFASs, requiring less or no chemicals, and compatible with other technologies	The energy demand is high, and the cost is high, currently not suitable for large-scale use	17, 113, 117 and 155
Bioremediation	Microorganisms and constructed wetlands	Using microorganisms with high PFAS mineralization capabilities and plant species with high PFAS accumulation capabilities to remove PFASs	Environmental friendliness and economic efficiency, avoiding further damage to the aquatic environment	The reaction time is long, and the removal rate is not high. In the future, it is still necessary to understand their absorption mechanisms for different PFAS structures and enhance the interactions between these biological components to improve the removal rate of PFASs	141 and 142
Membrane separation technology	NF membranes, RO membranes, *etc.*	Using RO membranes and NF membranes to separate PFASs	Effective removal (≥90%) and simple operation	The replacement of membranes and the treatment of high-concentration retention fluid will increase costs	146 and 147

3 Conclusions and perspectives

PFASs are highly stable chemicals that resist degradation under typical environmental conditions, making them persistent and challenging to remediate. This article compares various treatment technologies and demonstrates that adsorption, electrochemical oxidation, photocatalytic degradation, ultrasound, biodegradation, and membrane filtration technologies exhibit certain removal effects on PFASs.

Considering removal efficiency, treatment time, energy consumption, and cost, adsorption is the most widely used technology for effectively removing PFASs. However, the long adsorption cycle, difficulty in removing short-chain PFASs, and unsatisfactory regeneration capacity are the main challenges. Emerging materials such as MOFs, COFs, and MIPs, with their selective adsorption and excellent regeneration and reusability characteristics, are important research directions for PFAS adsorption technology in the future. Electrochemical, photocatalytic, and ultrasound degradation technologies offer the advantages of high removal efficiency and short reaction time. They can degrade short-chain PFASs and have a mineralizing effect, making them important development directions for PFAS removal. However, the requirements for complete mineralization are high, and so far, most treatment technologies have only reported partial defluorination (*i.e.*, removing fluorine atoms from PFAS molecules). Although the degradation rate (such as the truncation of COOH) can reach 100%, the short-chain intermediates produced, which contain multiple C–F bonds, may be more difficult to degrade and toxic than the precursor molecules. Consequently, the ultimate objective of PFAS remediation should be complete defluorination, where all C–F bonds are decomposed into benign inorganic substances, thereby achieving a zero toxicity level. Biodegradation technology has garnered attention due to its good environmental friendliness, but currently discovered microorganisms and plants exhibit low absorption and mineralization effects on PFASs, and the reaction time is long. Identifying microorganisms with high PFAS mineralization capabilities and plant species with high PFAS accumulation capabilities is a crucial aspect. Membrane separation is a technology for efficient PFAS enrichment, yet the complexity of actual wastewater composition presents challenges. Dissolved organic matter in wastewater can hinder membrane flux due to particle size, which in turn diminishes the removal efficiency of PFASs. Additionally, the cost associated with this technology is comparatively high.

It is worth mentioning that these techniques come with a mix of pros and cons for potential use. In addition, due to the different branching and linear isomers, ionic states, and molecular weights of various PFASs, each with distinct environmental destinies and transformation pathways, it is a great challenge to remediate various PFASs using only a single method. Therefore, it is advisable to tailor the choice of technologies to the properties of PFASs, taking into account the pros and cons of different methods. Future research should concentrate on the following aspects: (a) addressing the issue of extended treatment time and the limited regenerative

capabilities of adsorption materials; it is necessary to modify the functional groups of adsorption materials to improve electrostatic interactions and hydrophobicity, thereby increasing the adsorption efficiency and the rate of short-chain PFASs. (b) Innovatively designing short-chain PFAS remediation by altering electrodes and catalysts and developing advanced oxidation technologies with low carbon, low energy consumption, high degradation efficiency, and adaptability to low-concentration PFASs. (c) In light of the escalating issue of short-chain PFAS contamination in potable water, it is essential to develop advanced treatment technologies for real-world groundwater and surface water scenarios, and exploring novel adsorption materials, electrode materials, and catalysts is vital to effectively eliminate low levels of short-chain PFASs amidst the complex compositions found in actual water bodies. (d) Short-chain PFASs exhibit greater resistance to degradation compared to their long-chain homologs. Integrative technologies that leverage concentration and degradation recycling can be devised, including the sequential use of adsorption or membrane separation followed by advanced oxidation and reduction technologies, to effectively remove short-chain PFASs from actual water.

Author contributions

The authors confirm their contribution to the paper as follows: Hao Zang contributed to the conceptualization, methodology, and writing-original draft. Yingming Feng contributed to data curation & supervision. Shengyuan Gao contributed to formal analysis & writing-original draft. Xiangfeng Chen and Qiyan Feng contributed to supervision & conceptualization. Mangmang Su contributed to writing-review & editing.

Conflicts of interest

There are no conflicts to declare.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

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