



Chain-length dependent behavior of per- and polyfluoroalkyl substances (PFASs): Environmental risks, migration patterns, remediation strategies and decontamination mechanisms

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ABSTRACT

Per- and polyfluoroalkyl substances (PFASs), characterized by their persistent perfluoroalkyl backbone and functional terminal groups, have emerged as global contaminants of critical concern due to their detrimental impacts on human health and ecosystem integrity. While short-chain PFASs derivative have been increasingly adopted as alternatives to long-chain homologs, their heightened aqueous solubility and environmental mobility have facilitated widespread aquatic contamination. Despite extensive research on PFASs generally, systematic comparisons of environmental distribution patterns, transport mechanisms, and transformation pathways between long- and short-chain variants remain notably lacking. This comprehensive review analyzes global contamination profiles and environmental fate dynamics of PFASs compounds, with particular emphasis on human exposure pathways and toxicological consequences. We critically evaluate current remediation strategies, including: 1) Methodical examination of physical removal technologies with detailed analysis of material-specific adsorption characteristics and underlying molecular interaction mechanisms, 2) Comparative assessment of advanced oxidation/reduction processes (AO/RPs), particularly addressing chain-length dependent degradation efficiencies and mechanistic pathways, 3) Technological viability analysis for short-chain PFASs elimination, incorporating performance benchmarking across treatment modalities. Through systematic integration of contaminant behavior analysis and technological efficacy evaluation, this work advances predictive understanding of PFASs environmental dynamics while establishing a robust decision-making framework for selecting context-appropriate remediation solutions targeting both conventional and emerging PFASs contaminants.

1. Introduction

Per- and polyfluoroalkyl substances (PFASs) constitute a class of synthetic organic compounds characterized by at least one perfluorinated methyl ($-\text{CF}_3$) or methylene ($-\text{CF}_2-$) moiety. This diverse family encompasses perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkyl sulfonic acids (PFSA), fluorotelomer alcohols, and perfluoroalkyl sulfonamides [1,2]. The unique amphiphilicity of PFAS arises from their molecular architecture: a non-polar hydrophobic fluorocarbon chain coupled with a polar hydrophilic functional group. Exceptional chemical stability and thermal resistance derive from the formidable C-F bond energy (~ 536 kcal/mol) [2,3], while pronounced hydrophobicity and oleophobicity have driven their industrial adoption in water-repellent textiles, non-stick coatings, and food contact

materials. Global environmental contamination has emerged from pervasive PFASs utilization, with detectable concentrations documented in aquatic systems (such as rivers, lakes, groundwater), terrestrial matrices (soil), atmospheric compartments, and biota including human [1]. Their environmental persistence enables bioaccumulation through resistance to metabolic breakdown, coupled with demonstrated toxicological effects [4]. Particular concern focuses on perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), recognized as priority contaminants through their inclusion in the Stockholm Convention on Persistent Organic Pollutants alongside perfluorohexanesulfonic acid (PFHxS) derivatives [5,6].

Current regulatory frameworks define short-chain PFAS as perfluoroalkyl carboxylic acids ($\leq \text{C}_7$) and sulfonic acids ($\leq \text{C}_5$). Marketed as safer alternatives following long-chain PFAS restrictions, these

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substitutes retain comparable surfactant properties (insulation capacity, hydrophobicity) while exhibiting enhanced aqueous solubility [7]. Contrary to initial assumptions about reduced bioaccumulation potential, emerging evidence reveals that short-chain variants demonstrate environmental persistence comparable to legacy long-chain compounds, enabling prolonged environmental residence and continuous biogeochemical cycling [2]. Structural modifications, such as reducing the fluorocarbon chain length, enhance hydrophilicity and decrease the propensity for micellization. This leads to increased mobility in aqueous solutions, reduced sorption affinity for sedimentary and soil matrices, and enhanced long-range transport capacity [6]. These physicochemical properties significantly elevate exposure risks across ecological compartments and human populations.

The structural configurations and carbon chain characteristics of predominant perfluoroalkyl carboxylic acids (PFCAs) and sulfonic acids (PFSA) are systematically cataloged in Table 1. A comparative analysis of typical concentration ranges for individual PFASs in surface water systems was conducted to evaluate their environmental impact potential [8]. This comparative analysis incorporates quantitative structure-activity relationship (QSAR)-derived toxicological parameters, including bioconcentration factors (BCFs), acute mammalian toxicity (LD₅₀ Oral rat, mg/kg·bw), and aquatic lethality thresholds (96-hr LD₅₀ Fathead minnow 96 hr mg/L).

Significant research efforts have focused on developing remediation strategies for PFASs-contaminated matrices [7,9]. Adsorption emerges as a particularly promising approach due to its operational efficiency and cost-effectiveness. Engineered adsorbents demonstrating PFASs removal capacity include: granular activated carbon (GAC) [10], ion exchange resins [2], carbon nanotubes [11], chitosan-based composites [12] and mineral substrates [13]. The dual hydrophilicity (functional groups) and hydrophobicity/oleophobicity (fluorocarbon chains) of PFAS molecules engender complex adsorption mechanisms requiring molecular-level interrogation [2]. Full-scale implementations frequently employ pressure-driven membrane processes (reverse osmosis, nanofiltration) [14] and coagulation-flocculation systems [15], though efficacy varies with PFAS chain length. Significant advances have been made in developing advanced oxidation/reduction technologies (AO/RPs) for achieving effective degradation and defluorination of per- and polyfluoroalkyl substances (PFAS), with promising approaches including persulfate activation [16], Fenton-based processes [17], catalytic ozonation [18], photolytic/photocatalytic systems [19], electrocatalytic oxidation [20], thermal decomposition [21], and ultrasonic treatment [22]. Complementary reduction strategies utilizing hydrated electrons (e_{aq}^-) and hydrogen radicals ($H\cdot$) have demonstrated particular efficacy in PFAS mineralization [23], offering new pathways for breaking recalcitrant carbon-fluorine bonds.

The review systematically examines the environmental prevalence and human exposure pathways of PFASs across multiple matrices. The paper comprehensively analyzes contamination levels in aquatic systems, terrestrial soils, atmospheric environments, and biological matrices, while elucidating their spatial distribution characteristics and bioaccumulation patterns. The published treatment technologies for PFASs with different chain lengths were summarized, including adsorption, membrane separation, flocculation and advanced oxidation/reduction technology. The adsorption mechanism involved in the adsorption process and the degradation pathway of the oxidation/reduction process were explained. In particular, the impact of the chain length of PFASs on the pollution and degradation of PFASs was evaluated. The adaptability and degradation history of various treatment technologies to short-chain PFASs were compared to provide a scientific basis for the efficient treatment and disposal of PFASs.

The dataset originates from globally distributed peer-reviewed studies encompassing laboratory simulations, pilot-scale experiments, and field monitoring investigations. Geographically representative samples span North America (United States, Canada), Europe (Germany, Netherlands), Asia (China, Japan), Oceania (Australia), and Africa

(South Africa), covering multiple environmental matrices including surface water, groundwater, soil, atmospheric deposition, and biotic specimens. Temporally, the scope integrates longitudinal monitoring of legacy long-chain PFASs (e.g., PFOS/PFOA) regarding bioaccumulation and toxicity profiles, while incorporating emerging contamination data on short-chain PFASs (GenX, PFBS). Selection criteria prioritized studies demonstrating clear environmental relevance through documented PFASs concentration ranges, accounting for chain-length-dependent variations in source characteristics and environmental partitioning behaviors. Particular emphasis was placed on critical performance parameters of contemporary treatment technologies to reflect cutting-edge developments in remediation methodologies.

2. Environmental risks and migration patterns of PFASs

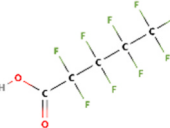
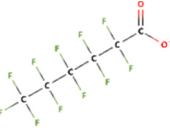
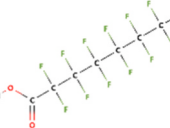
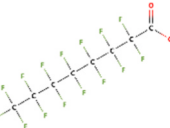
2.1. Distribution of PFASs in the environment

PFASs exhibit ubiquitous distribution across environmental matrices including aquatic systems, terrestrial substrates, and atmospheric compartments [24] with documented presence extending to biological specimens and food products [25,26]. Toxicological investigations reveal concerning endpoints such as reproductive impairment, neurotoxic effects, and immune system disruption in model organisms [27]. The environmental persistence of PFAS facilitates their continuous cycling through ecological systems, consumer products, and ultimately human populations. Contemporary monitoring data confirm PFAS contamination across multiple reservoirs: atmospheric particulates [28], aqueous environments [29], sedimentary deposits [30], and pedospheric systems [31]. Industrial effluents, agricultural runoff, and municipal wastewater discharges constitute primary vectors for PFAS introduction into surface waters, groundwater aquifers, and potable water supplies [29,32,33]. Comparative toxicological assessments indicate heightened bioaccumulation potential and adverse effects associated with long-chain PFASs ($C \geq 8$) relative to their short-chain counterparts ($C < 8$) [3,34]. Despite increasing regulatory pressure on long-chain variants, the chemical industry shift toward short-chain alternatives presents emerging concerns. While marketed as environmentally preferable substitutes, short-chain PFASs demonstrate bioaccumulative tendencies and toxicological profiles that may pose equivalent or novel human health risks [2], necessitating urgent investigation into their environmental fate and transformation pathways.

2.1.1. Aquatic distribution of PFASs contamination

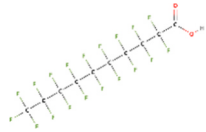
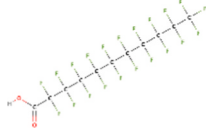
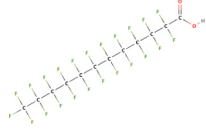
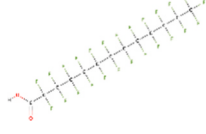
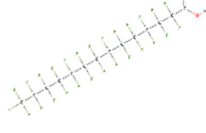
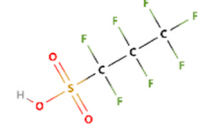
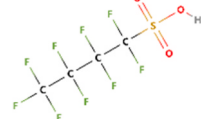
The unique physicochemical properties of PFASs, particularly their pronounced aqueous solubility and environmental mobility, have established aquatic environments and sedimentary deposits as primary reservoirs for these persistent contaminants [29]. Hydrological interactions between surface water and groundwater systems facilitate PFASs transport during aquifer recharge processes [35]. This perpetual input has resulted in progressive PFASs accumulation across freshwater resources, compromising both ecological integrity and human drinking water security. A landmark investigation of 25 U.S. drinking water treatment plants (DWTPs) revealed ubiquitous PFASs contamination (17 target compounds, total concentrations: $<1\text{--}1102\text{ ng/L}$), with six riverine facilities exhibiting distinct chemical signatures - three dominated by perfluorooctanoic acid (PFOA) and three by perfluorobutyric acid (PFBA) [36]. Median total PFAS concentrations measured 21.4 ng/L in source water and 19.5 ng/L in treated water, with one facility exceeding the outdated 2016 U.S. EPA health advisory threshold of 70 ng/L for combined PFOA/PFOS. These results expose significant gaps in conventional treatment technologies, particularly as the EPA's 2022 updated advisory limits now mandate drastically lower thresholds: 0.004 ng/L for PFOA and 0.02 ng/L for PFOS. The persistent presence of PFAS underscores the urgent need to modernize water infrastructure and align regulations with contemporary toxicological insights on these enduring contaminants.

Table 1
Chemical structures and prediction of toxicity of common long/short chain PFASs.

	Short name	Long name/ Formula	Chemical Structure	Short/ Long chain	Carbon Atoms	C-F	Concentration range (ng/L)	Bioconcentration factor*	LD50 Oral rat (mg/kg bw)	LD50 Fathead minnow 96 hr (mg/L)
ω	TFA	Trifluoroacetic acid CF ₃ COOH		Short chain	2	1	82.44–641.34	1.43	169.98	363.09
	PFPrA	Perfluoropropanoic acid CF ₃ CF ₂ COOH		Short chain	3	2	0.12–2.18	1.44	564.26	342.59
	PFBA	Perfluorobutanoic acid CF ₃ (CF ₂) ₂ COOH		Short chain	4	3	2.54–14.95	8.74	1713.11	369.83
	PFCAs PFPeA	Perfluoropentanoic acid CF ₃ (CF ₂) ₃ COOH		Short chain	5	4	0.03–4.66	50.75	1563.74	97.46
	PFHxA	Perfluorohexanoic acid CF ₃ (CF ₂) ₄ COOH		Short chain	6	5	1.2–6.19	71.57	779.08	85.59
	PFHpA	Perfluoroheptanoic acid CF ₃ (CF ₂) ₅ COOH		Short chain	7	6	0.83–4.22	179.68	221.55	36.92
	PFOA	Perfluorooctanoic acid CF ₃ (CF ₂) ₆ COOH		Long chain	8	7	2.82–45.83	217.38	176.24	32.52

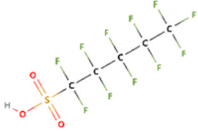
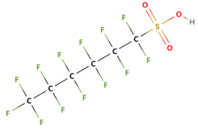
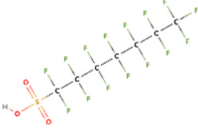
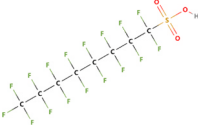
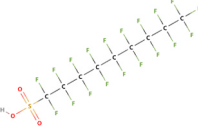
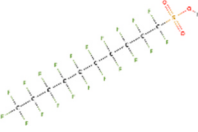
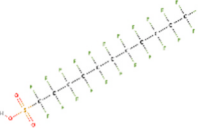
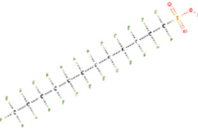
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Table 1 (continued)

	Short name	Long name/ Formula	Chemical Structure	Short/ Long chain	Carbon Atoms	C-F	Concentration range (ng/L)	Bioconcentration factor*	LD50 Oral rat (mg/kg bw)	LD50 Fathead minnow 96 hr (mg/L)
	PFNA	Perfluorononanoic acid CF ₃ (CF ₂) ₇ COOH		Long chain	9	8	0.09–0.75	324.85	174.74	14.03
	PFDA	Perfluorodecanoic acid CF ₃ (CF ₂) ₈ COOH		Long chain	10	9	0.05–0.81	518.55	478.92	0.37
	PFUnDA	Perfluoroundecanoic acid CF ₃ (CF ₂) ₉ COOH		Long chain	11	10	<LOD	808.85	448.43	-
	PFDoDA	Perfluorododecanoic acid CF ₃ (CF ₂) ₁₀ COOH		Long chain	12	11	0.03–0.16	602.26	-	-
	PFTTrDA	Perfluorotridecanoic acid CF ₃ (CF ₂) ₁₁ COOH		Long chain	13	12	<LOD	707.35	-	-
	PFTeDA	Perfluorotetradecanoic acid CF ₃ (CF ₂) ₁₂ COOH		Long chain	14	13	0.03–3.15	-	-	-
	PFSAs	PFPrS	Perfluoropropanesulfonic acid CF ₃ (CF ₂) ₂ SO ₃ H		Short chain	3	3	0.03–0.13	36.01	534.27
PFBS		Perfluorobutanesulfonic acid CF ₃ (CF ₂) ₃ SO ₃ H		Short chain	4	4	0.09–19	124.13	1082.36	40.14

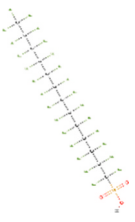
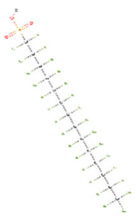
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Table 1 (continued)

Short name	Long name/ Formula	Chemical Structure	Short/ Long chain	Carbon Atoms	C- F	Concentration range (ng/L)	Bioconcentration factor*	LD50 Oral rat (mg/ kg bw)	LD50 Fathead minnow 96 hr (mg/L)
PFPeS	Perfluoropentanesulfonic acid CF ₃ (CF ₂) ₄ SO ₃ H		Short chain	5	5	0.18–0.62	203.46	400.85	28.95
PFHxS	Perfluorohexanesulfonic acid CF ₃ (CF ₂) ₅ SO ₃ H		Short chain	6	6	0.55–2.96	344.58	284.37	16.85
PFHpS	Perfluoroheptanesulfonic acid CF ₃ (CF ₂) ₆ SO ₃ H		Long chain	7	7	0.03–0.14	900.15	283.34	14.67
PFOS	Perfluorooctanesulfonic acid CF ₃ (CF ₂) ₇ SO ₃ H		Long chain	8	8	0.88–5.38	921.82	235.73	18.58
PFNS	Perfluorononanesulfonic acid CF ₃ (CF ₂) ₈ SO ₃ H		Long chain	9	9	<LOD	2338.39	245.85	-
PFDS	Perfluorodecanesulfonic acid CF ₃ (CF ₂) ₉ SO ₃ H		Long chain	10	10	<LOD	2571.77	325.41	-
PFUnDS	Perfluoroundecanesulfonic acid CF ₃ (CF ₂) ₁₀ SO ₃ H		Long chain	11	11	-	3942.59	-	-
PFDoDS	Perfluorododecanesulfonic acid CF ₃ (CF ₂) ₁₁ SO ₃ H		Long chain	12	12	-	648.34	-	-

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Table 1 (continued)

Short name	Long name/ Formula	Chemical Structure	Short/ Long chain	Carbon Atoms	C- F	Concentration range (ng/L)	Bioconcentration factor*	LD50 Oral rat (mg/kg bw)	LD50 Fathead minnow 96 hr (mg/L)
PFTrDS	Perfluorotridecanesulfonic acid $\text{CF}_3(\text{CF}_2)_{12}\text{SO}_3\text{H}$		Long chain	13	13	-	-	-	-
PFTeDS	Perfluorotetradecanesulfonic acid $\text{CF}_3(\text{CF}_2)_{13}\text{SO}_3\text{H}$		Long chain	14	14	-	-	-	-

*Bioconcentration factor, LD50 Oral rat and LD50 Fathead minnow 96 hr are calculated by the QSAR-based toxicity prediction tool T.E.S.T. (Toxicity Estimation Software Tool). T. E.S.T. is a software developed by the United States Environmental Protection Agency (US EPA) to evaluate the acute (short-term) toxicity and chronic (long-term) toxicity of chemical substances.

In recent years, researchers have studied the distribution characteristics and pollution levels of PFASs in surface water, groundwater and sediments. The summary of results was shown in Table 2. Short-chain PFASs, such as perfluorobutyric acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorobutane sulfonic acid (PFBS), and perfluorohexane sulfonic acid (PFHxS), were detected in surface water in many countries such as the United States, China, Germany, and Japan at different concentrations [37,38]. Research resulted on long-chain and short-chain PFASs in various environmental media found that the concentration of short-chain PFASs has significantly exceeded that of traditional long-chain PFASs, and more and more types of them have been detected [7]. In some areas, PFOS, PFOA and short-chain carboxylic acids with 5–7 carbon atoms have dominated the water environment. Similar results were also found in the sediment, with the values of short chains PFASs being higher.

Li et al. [7] summarized the occurrence and distribution of short-chain PFASs in the aquatic environment. From the perspective of chemical substances, PFBA, PFBS, PFPeA, PFHxA and PFHpA were the short-chain PFASs with the widest detection range, among which PFBA and PFBS account for more than 50 %. Among them, the concentration of PFBA fluctuated greatly. From the perspective of regional distribution, the coastal areas of the United States and Canada [36,39], the Rhine River in Germany [40], China [41], India [42] and other regions were the most severely affected.

Municipal wastewater treatment facilities and industrial effluents are globally acknowledged as principal vectors for PFASs contamination. Nguyen et al. [43] conducted PFAS analysis on influent samples from 76 municipal wastewater treatment plants (WWTPs) servicing approximately 53 % of Australia population. Among the 14 targeted PFAS compounds, 12 analytes were detected, comprising six C5–C10 PFCAs, four C4–10 PFASs, and two fluorotelomer sulfonates (6:2 and 8:2 Fluorotelomer sulfonic acid). PFOS, PFHxS, and PFHxA exhibited the highest median concentrations. The estimated background release of $\Sigma 12$ PFAS in Australian WWTP influent was quantified at 8.1–24 $\mu\text{g/day}$ per person. Furthermore, a statistically significant positive correlation ($p < 0.05$) was observed between industrial site density and per capita mass loads of $\Sigma 12$ PFAS, conclusively identifying industrial activities as a principal contamination source for wastewater-borne PFASs

2.1.2. Atmospheric distribution of PFAS contamination

Atmospheric transport constitutes a critical pathway for global PFASs dispersion through aerosol-bound association and particulate matter interactions. Short-chain PFASs exhibit enhanced atmospheric mobility due to their elevated vapor pressure compared to long-chain analogs, facilitating aquatic-to-atmospheric transfer and subsequent long-range transport [57]. Volatile perfluorinated compound precursors (PFCPs) further contribute to atmospheric loading through gas-phase oxidation during atmospheric transit, ultimately generating stable PFASs deposition [58]. Long-chain PFAS (such as PFOA and PFOS) were adsorbed on atmospheric particulate matter (PM_{2.5}/PM₁₀), and PFASs in aerosols entered water bodies and soil during precipitation or dry-wet sedimentation. The detection of new types of PFASs such as GenX (hexafluoropropylene dimer acid) and ADONA (perfluoroadipic acid) in the atmosphere has gradually attracted attention. The concentrations of these new compounds in the atmosphere were on the rise. The transport and deposition processes of the new type of PFASs in the atmosphere were similar to those of the traditional PFASs [59].

Urban centers, characterized by dense populations and concentrated industrial activity, serve as primary atmospheric PFAS emission sources. Contaminant distribution demonstrates strong seasonal correlations with temperature variations, particularly influencing transport mechanisms: winter temperature inversions enhance atmospheric stability and near-surface pollutant retention, while summer conditions promote longitudinal contaminant redistribution [60]. Air quality parameters

Table 2

Global distribution and contamination levels of per-and polyfluoroalkyl substance in surface water, groundwater, drinking water and sediments.

Region/Country	Water type	PFASs	Concentration (ng/L or ng/g)	Long/Short chain	C-F	Possible source	Refs	
North America	USA	Drinking Water	PFOA	21–57 ng/L	Long chain	7	Firefighting foams, Paper and cardboard coating materials in food packaging	[5]
	USA	Drinking Water	PFOS	61 ng/L	Long chain	8		[5]
	USA	Drinking Water	PFHxA	62 ng/L	Short chain	5		[5]
	USA	Surface Water	PFOA	349 ng/L	Long chain	7	Fluorochemical facility, Military training sites, AFFF ^a	[44]
	USA	Surface Water	PFOS	1800 ng/L	Long chain	8	Fluorochemical facility, AFFF ^a	[44]
	USA	Surface Water	PFNA	56 ng/L	Long chain	8	Industrial sites	[44]
	USA	Groundwater	PFOA	25.2 ± 27.4 ng/L	Long chain	7	JBCC ^b Military facilities	[45]
	USA	Groundwater	PFHxS	158.2 ng/L	Long chain	6	AFFF ^a in JBCC ^b	[45]
	USA	Groundwater	PFHxA	25.0 ± 37.2 ng/L	Short chain	5	Industrial products, Precursor degradation	[45]
USA	Groundwater	PFBA	6.0 ± 6.6 ng/L	Short chain	3	JBCC ^b Military facilities, Precursor degradation	[45]	
Europe	Netherlands	Drinking Water	PFOA	4.08 ng/L	Long chain	7	Electrochemical fluorination, Telomerization	[8]
	Netherlands	Drinking Water	PFOS	1.70 ng/L	Long chain	8		[8]
	Netherlands	Drinking Water	PFHpA	2.39 ng/L	Short chain	6		[8]
	Netherlands	Drinking Water	PFHxA	4.07 ng/L	Short chain	5	/	[8]
	Netherlands	Drinking Water	PFBA	7.26 ng/L	Short chain	3		[8]
	France	Surface Water	PFOA	36 ng/L	Long chain	7	PVDF ^c synthesizing fluorochemical plants	[46]
	France	Surface Water	PFOS	173 ng/L	Long chain	8	Diffuse sources	[46]
	France	Sediment	PFOA	0.05 ± 0.58 ng/g	Long chain	8	Industrial/urban zones, WWTPs ^d , AFFF ^a used at airport, Precursor transformation	[47]
	France	Sediment	PFHpA	0.04 ± 0.12 ng/g	Short chain	6	/	[47]
	Sweden	Surface Water	PFOA	60 ng/L	Long chain	7	AFFF ^a	[48]
	EU	Groundwater	PFOA	39 ng/L	Long chain	7	Leakages from industrial sites and sewage wastewaters	[49]
	EU	Groundwater	PFOS	135 ng/L	Long chain	8	Sewage related sources	[49]
	EU	Groundwater	PFHxS	19 ng/L	Long chain	6		[49]
	EU	Groundwater	PFHpA	21 ng/L	Short chain	6	/	[49]
Asia	Japan	Drinking Water	PFOS	22 ng/L	Long chain	8	Emissions from fluorochemical factory or WWTPs ^d	[50]
	Japan	Drinking Water	PFOA	84 ng/L	Long chain	7		[50]
	China	Surface Water	PFOA	77.01 ng/L	Long chain	7	Electrochemical fluorination, Telomerization	[51]
	China	Surface Water	PFOS	9.5 ng/L	Long chain	8	Electrochemical fluorination	[51]
	China	Surface Water	PFOA	83.4 ng/L	Long chain	7	Wastewater discharge from municipal and industrial drain outlets	[52]
	China	Surface Water	PFOS	6.80 ng/L	Long chain	8		[52]
	China	Groundwater	PFBA	0.3 ng/L	Short chain	3	/	[53]
	China	Groundwater	PFHxA	0.75 ng/L	Short chain	5	New material in manufacturing industry	[53]
China	Groundwater	PFOA	0.95 ng/L	Long chain	7	Precursor degradation, Industrial sources	[53]	
Oceania	Australia	Surface Water	PFOA	6.4 ng/L	Long chain	7	/	[54]
	Australia	Surface Water	PFOS	21 ng/L	Long chain	8		[54]
	Australia	Drinking Water	PFPrS	0.02 ng/L	Short chain	3	AFFF ^a , Industrial/urban wastewater discharge	[54]
	Australia	Surface Water	PFPrS	68 ng/L	Short chain	3		[54]
	Australia	Surface Water	PFEtS	12 ng/L	Short chain	2	Byproduct from electrochemical fluorination, AFFF ^a , Industrial wastewater discharge	[54]
	Australia	Groundwater	PFEtS	162 ng/L	Short chain	2		[54]
	Australia	Groundwater	PFPrA	567 ng/L	Short chain	2	/	[54]
	Australia	Groundwater	PFPrS	8100 ng/L	Short chain	3	AFFF ^a , Industrial/urban wastewater discharge	[54]
	Australia	Sediment	PFOA	8.3 ng/g	Long chain	7	Food packaging, Paper, Personal care products, Textiles, Carpet, Clothing	[55]
	Australia	Sediment	PFHxA	9.2 ng/g	Short chain	5	Biodegradation of 6:2 FTS ^e	[55]
	Australia	Sediment	PFBA	11.3 ng/g	Short chain	3	Atmospheric transport deposition, Consumer products impurities, By-products of PTFE ^f manufacturing	[55]
	Australia	Sediment	PFHxS	2.9 ng/g	Long chain	6	AFFF ^a , Metal plating, Carpet treatments, Curatives, Industrial coatings, Printing inks	[55]
Africa	South Africa	Surface Water	PFOA	4.2 ng/L	Long chain	7	Contaminated tributaries (mining, heavy industry, WWTPs ^d)	[56]
	South Africa	Surface Water	PFOS	34.5 ng/L	Long chain	8	Point source	[56]
	South Africa	Surface Water	PFHpA	1.2 ng/L	Short chain	6	/	[56]
	South Africa	Surface Water	PFHxA	38.5 ng/L	Short chain	5		[56]

^a AFFF: aqueous film-forming foam; ^b JBCC Joint Base Cape Cod; ^c polyvinylidene fluoride; ^d Wastewater treatment plants; ^e 6:2 FTS: 6:2 Fluorotelomer Sulfonate; ^f PTFE: Polytetrafluoroethylene

significantly modulate dispersion patterns, with studies revealing positive correlations between $PM_{2.5}$ concentrations and particulate-bound PFAS levels. Global atmospheric monitoring has ubiquitously detected short-chain PFAS in particulate matter, exemplified by Chen et al. [61] findings near chemical industrial zones ($\Sigma PFASs = 1400 \pm 3000 \text{ pg} \cdot \text{m}^{-3}$), where C4-C8 compounds (PFPeA, PFHxA, PFOA, PFOS) demonstrated $> 70\%$ detection frequencies, reflecting regional industrial usage patterns.

Some studies have reported the distribution of PFASs in atmospheric particles and gas phases, indicating that the concentration of PFASs in the global atmosphere has increased year by year [62], and ionizable PFASs showed a stronger affinity for atmospheric particles than neutral PFASs. However, existing studies only focus on traditional PFASs, such as PFCAs, PFASs, fluorotelomer alcohols (FTOHs), perfluorooctane sulfonamide (FOSA) and perfluorooctane sulfonamide ethanol (FOSE), and have not investigated the distribution of new PFASs in the air, particularly the gas phase of air. Recent methodological advancements by Yu et al. [63] employing cryogenic air sampling (CAS), nanoparticle fractionation (NPS), and non-targeted ultrahigh-resolution mass spectrometry (NTS) have identified > 100 PFAS species in ambient air, including volatile precursors that facilitate the global redistribution of persistent compounds like PFOS and PFCAs through atmospheric transformation pathways.

2.1.3. Edaphic distribution of PFAS contamination

Soil serves as a long-term reservoir for PFASs contamination, exhibiting notably elevated concentrations due to cumulative inputs from atmospheric deposition, rainfall, surface runoff, and sedimentation. These contaminants undergo continuous biogeochemical cycling, migrating between soil and adjacent compartments (surface water, groundwater, and atmosphere) via diffusion, leaching, and volatilization. Widespread PFASs detection in agricultural, industrial, and remote soils highlights their environmental ubiquity, with short-chain variants increasingly displacing long-chain homologs as dominant pollutants. Li et al. [64] emphasized the critical role of soil physicochemical properties in PFAS distribution, noting that pH fluctuations and cation exchange capacity significantly modulate contaminant behavior [65]. In addition, the chemical properties of specific PFASs may affect the distribution to the soil. Short-chain PFAAs were not as well bound to soil as long-chain PFAAs, and there were signs that the molecular structure controls the adsorption behavior of cationic and zwitterionic PFASs [66]. Due to its stronger hydrophobicity, long-chain PFASs still exhibited a higher sedimental-water partition coefficient (K_d), indicating that hydrophobic partition remained the main adsorption mechanism even in a low organic carbon environment. High calcium ion concentration may promote adsorption by neutralizing charges, reducing the electrostatic repulsion between PFAS and sediments, especially for long-chain PFAS. Long-chain PFASs were positively regulated by the content of organic carbon and the concentration of cations. The low hydrophobicity and strong electrostatic repulsion of short-chain PFASs caused the high migration [66].

Research on the adsorption behavior of PFASs has mainly focused on Perfluoroalkyl acids (PFAAs) [67]. Due to concern about bioaccumulation, the production of long-chain PFASs, especially 8 or more perfluorocarbons ($-CF_2$ groups), has been reduced and replaced [64]. However, research on the behavior of PFASs substitutes, such as Hexafluoropropylene oxide dimer acid (GenX) and 4,8-Dioxo-3H-perfluorononanoic acid (ADONA) and 9-chlorohexadecafluoro-3-oxanonane-1-sulfonate (9Cl-PF₃ONS, PFOS substitute used in China) in soil environments was still limited [68, 69]. 6:2 chlorinated polyfluorinated ether sulfonates (6:2 Cl-PFESA) was commonly found in municipal sewage sludge in China, with an average concentration (2.15 ng/g) comparable to that of PFOS (3.19 ng/g) [70]. New PFASs were widely present in soil, with 6:2Cl-PFESA [$n.d.$ – 1.20 ng/g] at concentrations similar to those of PFOS ($n.d.$ – 0.55 ng/g) in agricultural soils collected from the Beijing-Tianjin-Hebei region in northern China [71]. The concentrations and detection frequencies of short-chain PFAAs

($0.375 \pm 0.509 \text{ ng/g}$, 100 %) and chlorinated polyfluorinated ether sulfonates (Cl-PFESAs) ($0.216 \pm 0.306 \text{ ng/g}$, 98.9 %) were significantly higher than those of PFOS ($0.193 \pm 0.502 \text{ ng/g}$, 85.4 %). perfluoro-2-propoxypropanoic acid (HFPO-DA) ($0.019 \pm 0.104 \text{ ng/g}$, 40.5 %) was also frequently detected in residential soils collected from 89 cities in China [72].

PFASs have been widely detected in water bodies, soil, atmosphere and living organisms. Long-chain PFASs ($C \geq 8$) have become the focus of control due to their strong bioaccumulation and toxicity. Although short-chain PFASs ($C < 8$) has stronger mobility as a substitute, its pollution range has expanded due to high water solubility and atmospheric transport potential (such as 50 % of GenX wet deposition), and its global surface water concentration has exceeded that of traditional PFASs. New substitutes (such as 6:2 Cl-PFESA, ADONA, etc.) are widespread in the environment but their behavioral mechanisms are unclear. There was an urgent need to construct multi-media regression models and improve the global control system.

The differential bioaccumulation behaviors between short- and long-chain PFASs stem from their molecular architectures and physicochemical interactions. Long-chain analogues exhibit pronounced hydrophobicity and lipophilicity due to extended perfluorinated chains, enabling passive diffusion into lipid bilayers of cellular membranes and adipose tissues. Their strong binding to hydrophobic domains of serum albumin significantly prolongs biological half-lives, while concurrent inhibition of hepatic metabolic enzymes establishes self-reinforcing accumulation cycles. In contrast, short-chain PFASs demonstrate reduced hydrophobicity and enhanced aqueous solubility, facilitating rapid renal clearance via glomerular filtration and organic anion transporter-mediated excretion, accompanied by substantially diminished trophic transfer efficiencies. This chain length-dependent accumulation paradigm provides critical insights for ecological risk assessment and regulatory strategy formulation.

2.2. Migration and transformation patterns of PFASs

PFASs contamination originates from both point and non-point sources, exhibiting distinct migration patterns contingent on environmental conditions [73]. Short-chain PFAS demonstrate heightened environmental mobility relative to long-chain analogs due to their shorter fluorocarbon chains, which amplify hydrophilicity while diminishing hydrophobic interactions. This structural characteristic inhibits aqueous aggregation and enhances transport potential, as evidenced by ubiquitous PFASs detection across firefighting facilities, landfills, wastewater treatment plants, industrial sites, groundwater reservoirs, and drinking water systems [24]. Existing research has also shown that precursor compound degradation and chain-shortening transformations generate secondary short-chain PFASs, thereby amplifying environmental cycling and human exposure risks via drinking water contamination [2]. Contaminant dispersion occurs through multiphase transport mechanisms including surface runoff, groundwater infiltration [35], and atmospheric deposition [58], with short-chain variants exhibiting exceptional environmental persistence and elevated migration capacity [7]. Although short-chain PFASs display reduced bioaccumulation potential compared to long-chain counterparts, their resistance to degradation and weak sorption to soils/sediments facilitate widespread environmental propagation. Current analytical limitations persist in detecting novel short-chain fluorinated substitutes, obstructing comprehensive assessments of their environmental prevalence and ecological impacts.

PFASs have a significant impact on health after being ingested by the human body. It was of great significance to clarify the environmental behaviors of PFASs such as migration, adsorption, desorption, and distribution in water and sediments. In recent years, the migration and distribution behaviors of PFASs in water and sediments have attracted more and more attention. Migration and transformation of PFASs in the ecological environment is shown in Fig. 1, PFASs migrated and degraded

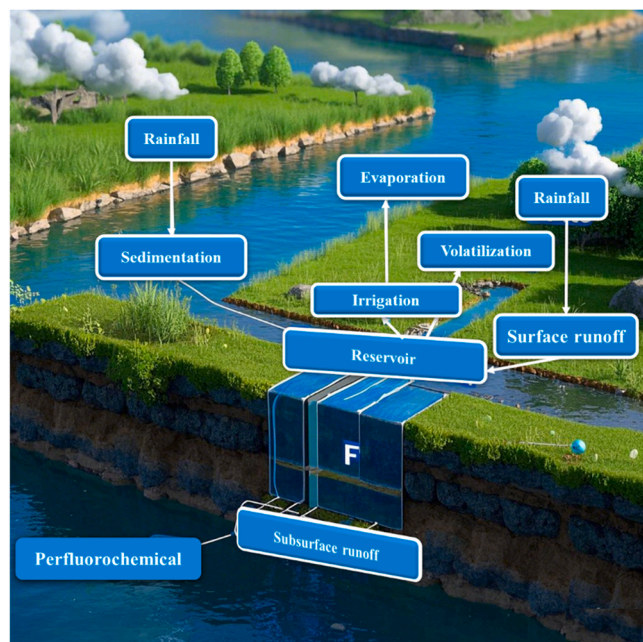


Fig. 1. Migration and transformation of PFASs in the ecological environment.

in different water environments, undergo adsorption and desorption, percolation and volatilization in soil, and transform precursors and dust deposition in atmosphere.

The mutual transport of liquid-solid-gas made PFASs circulate globally and maintained mass balance. The environmental transport and distribution characteristics of PFASs in aquatic systems, sedimentary environments, and soil matrices demonstrate several distinctive patterns.

(1) Chain-Length and Functional Group Dependencies in Aquatic Systems

The migration and distribution dynamics of PFAS in aqueous environments are fundamentally governed by molecular architecture, particularly carbon chain length and functional group composition. The length of the carbon chain was the main factor affecting the adsorption of PFASs in sediments, and the adsorption amount increases with the increase of the carbon chain length [74]. PFASs with more than 6 carbon atoms, such as PFOA, 6:2 fluoropolymer sulfonic acid, 8:2 fluoropolymer sulfonic acid showed similar migration characteristics. Sulfonic acid-functionalized PFAS demonstrate enhanced sediment affinity relative to carboxylate congeners, a phenomenon corroborated by Nguyen et al. [75] through comparative adsorption studies of sulfonic vs carboxylic PFAS derivatives.

(2) Hydrochemical Controls on Contaminant Mobility

The migration and distribution behavior of PFASs in the water environment was related to the physical and chemical properties of water and sediments. The surface charge of the sediment, pH, and ionic strength in the water can affect the adsorption and distribution of PFASs in water and sediments. The ionic strength and dissolved organic matter in the water body have an important influence on the migration and distribution of PFASs. The increased ionic strength and changed cation type have a stronger inhibitory effect on the migration of PFOS to the sediment [76]. The surface charge of sediments also affected the migration behavior of PFASs in sediments. Since the functional groups of PFASs themselves were negatively charged, the pH of the sediment decreased, resulting the negative charge in the sediment decreased. So the amount of PFASs adsorbed by the sediment increased. The change of soil pH affected the adsorption of PFASs in soil. Nickerson et al. [77] compared the influence of sediments under different pH conditions on the adsorption performance of 4:2 fluoromodulonic acid and found that the change of pH affected the charge distribution of soil, which the

adsorption of PFASs in soil affected.

(3) Sediment Matrix Composition Effects

The migration and distribution dynamics of PFAS in sedimentary environments are governed by synergistic interactions between organic matter and mineral constituents. Organic carbon content serves as a critical determinant of contaminant retention, with humic acid acting as a multifunctional sorbent through electrostatic and hydrophobic binding mechanisms [78]. Milinovic et al. [79] demonstrated strong positive correlations ($R^2 > 0.89$) between sediment organic carbon levels and adsorption capacities for PFOA, PFOS, and perfluoroheptanesulfonic acid (PFHpS). Uwayezu et al. [80] revealed enhanced PFOS adsorption (42–65 % increase) in goethite-humic acid composite systems compared to single-component matrices, attributed to ligand-bridging and surface complexation effects.

Contemporary contamination patterns reflect a global shift toward short-chain PFAS utilization, as evidenced by Li et al. [72] findings of predominant short-chain contamination (mean concentration: 375 ± 509 pg/g) over PFOS (193 ± 502 pg/g) in Chinese residential soils. This trend extends to wastewater infrastructure, where urban sewage sludge exhibits elevated short-chain PFASs levels [81], and even remote atmospheric samples from the Qinghai-Tibet Plateau demonstrate detectable concentrations [82]. Geospatial analysis identifies severe contamination hotspots along China eastern coastline, mirroring industrial production and consumption patterns. Severely contaminated areas with PFASs were mainly distributed along the eastern coast of China. The concentration level of short-chain PFASs (375 ± 509 pg/g) was higher than the detected PFOS (193 ± 502 pg/g), which indicated that short-chain PFASs was used as a substitute and its impact has exceeded that of long-chain PFOS [72]. Since the shorter the carbon chain of PFASs, the stronger its water solubility, the content of short-chain PFASs was higher in water bodies, such as PFBS and PFBA.

Cousins et al. [83] collected data on PFOS, PFOA, PFNA, and PFHxS in rainwater from many places around the world and found that the levels of PFOA and PFOS in rainwater far exceeded the EPA recommended drinking water safety values. In addition, these four PFASs formed non-point source pollution of global soil and surface water as they fall with rainwater. The global diffusion in the atmosphere also led to a global chemical pollution cycle. In a study on the migration of PFASs from groundwater to five tributaries near the Cape Fear River produced by a fluoride manufacturing plant in Carolina, USA [84], about (32 ± 7) kg of PFASs were discharged from groundwater to five tributaries each year, eventually reaching the Cape Fear River, causing long-term pollution of surface water and affecting downstream drinking water supply.

Environmental mobility disparities between PFASs homologues arise from chain length-governed physicochemical properties. Long-chain variants, characterized by elevated Log Kow values and soil organic carbon adsorption coefficients (Koc), are preferentially adsorbed onto soil particles and sediments, exhibiting restricted mobility and localized accumulation near contamination sources while undergoing bio-magnification through food webs. Conversely, short-chain counterparts display heightened Henry's Law Constants, reduced molecular weights, and increased polarity, enabling groundwater infiltration, atmospheric volatilization, and penetration through conventional water treatment barriers. Their weak soil/sediment binding facilitates hydrological remobilization during precipitation events, ultimately driving widespread environmental distribution, whereas long-chain PFASs persist in localized reservoirs.

2.3. Health effects of PFAS exposure in humans and biological samples

PFASs are ubiquitously detected across human biomonitoring matrices including blood, urine, semen, follicular fluid, nails, and hair. Their persistent bioaccumulation stems from slow metabolic clearance rates, rendering blood serum/plasma the primary analytical medium for long-chain PFASs. However, the increased hydrophilicity and enhanced

renal excretion of short-chain alternatives position urine as a preferential matrix for emerging substitutes. Epidemiological studies reveal gender-based exposure disparities, with males exhibiting higher serum PFASs concentrations than females [85]. Vertical transmission pathways further amplify exposure risks, as maternal PFASs loads transfer transplacentally and via lactation, correlating with impaired neonatal development indices [86]. While over 4700 PFASs are registered for industrial use, analytical methodologies currently quantify fewer than 100 variants in biological samples, underscoring critical gaps in understanding cumulative exposure health impacts.

The detection and quantification of PFASs in human biological matrices predominantly utilize blood-derived samples (plasma, serum), urine, breast milk, and keratinous tissues (hair, nails), each offering distinct temporal resolution for exposure assessment. Blood and urine analyses provide insights into recent PFASs exposure (hours to weeks), while keratinous biomarkers archive cumulative exposure over months. Breast milk serves as a critical matrix for evaluating gestational and lactational exposure windows, reflecting contaminant transfer during specific developmental periods.

Human PFAS exposure pathways are primarily mediated through dietary intake (contributing 55–75 % of total burden) [87], atmospheric inhalation [88] and dermal absorption [89], with aqueous ingestion emerging as a pivotal vector for short-chain variants. The heightened hydrophilicity of short-chain PFAS facilitates their preferential migration into drinking water systems, enabling bioaccumulation even at trace concentrations. Pharmacokinetic modeling demonstrates nonlinear bioamplification. Steady-state pharmacokinetic studies can predict that the average increase in blood PFOA in adults was more than 100 times the concentration in drinking water. Specifically, a 1 µg/L increase in aqueous PFOA correlates with a 114 µg/L elevation in serum concentrations [90].

2.3.1. Blood PFASs exposure profiling

Blood PFAS concentrations serve as direct biomarkers of systemic absorption, though venipuncture sampling poses challenges related to invasiveness, procedural complexity, and ethical constraints. Despite global regulatory phaseouts, PFOS and PFOA persist as dominant analytes in serological screenings, albeit with declining detection frequencies paralleled. Correspondingly, the detection frequency of short-chain PFASs alternatives was increasing [91,92].

The National Health and Nutrition Examination Survey (NHANES) has documented declining serum concentrations of legacy PFASs (PFOA, PFOS, and PFHxS) in U.S. populations, reflecting regulatory phaseout impacts [93]. Parallel investigations by Canadian researchers reveal gender-specific partitioning in blood PFASs profiles, with males exhibiting elevated PFOA and PFHxS levels compared to higher PFDA (perfluorodecanoic acid) and PFUnDA (perfluoroundecanoic acid) concentrations in females [94]. Longitudinal analyses of Danish maternal cohorts demonstrate progressive reductions in PFNA (perfluorononanoic acid), PFDA, and PFUDA (perfluoroundecanoic acid) over time, though PFOS persists as the dominant contaminant in serum samples [95]. Demographic stratification further identifies significant exposure disparities, with males consistently showing higher serum PFAS burdens than females, while elderly populations exhibit elevated concentrations relative to younger adults [96].

Comparing the detection status and exposure level of PFASs in the blood of occupational groups with that of the general population, the concentration of PFASs in the blood of occupational groups is 1–2 orders of magnitude higher than that of the general population. The detection frequency and concentration of PFOA and PFOS in the blood of both groups of people were at a high level. Some scholars have studied the correlation between the exposure level of PFOA in the blood of residents living around fluorine chemical plants. The results showed that the PFOA concentration is the highest in residents whose residential addresses were 1 km away from the plant, with a median concentration of 10.20 ng/mL and a maximum detection concentration of 147 ng/mL

[97].

2.3.2. Urinary PFASs exposure profiling

Urinary excretion serves as a critical elimination pathway for systemic PFASs burdens, with noninvasive sampling advantages including operational feasibility, large sample volumes, and ethical acceptability for population-scale exposure assessments. Urine emerges as a pragmatically superior matrix for large-scale biomonitoring due to noninvasive collection and volumetric advantages. Urinary PFASs concentrations typically occur at trace levels (ng/L range) [98], reflecting both metabolic clearance rates and renal susceptibility to PFASs induced toxicity.

The kidneys, as primary target organs, face elevated risks of metabolic dysfunction under high PFASs exposure conditions. He et al. [99] investigated urinary PFASs utility in correlating renal effects through a cohort study of 72 occupational workers and 153 residents near a fluororochemical plant in Hubei, China. Serum and urine analyses quantified 23 PFAS subtypes: 9 PFCAs, 8 PFASs, 4 fluorotelomer sulfonic acids (6:2 FTS), and 2 Cl-PFESAs. Workers exhibited significantly elevated burdens (serum $\sum 23\text{PFASs}$: 5.43 ± 1.02 µg/mL; urinary $\sum 23\text{PFASs}$: 201 ± 46.9 ng/mL) compared to residents (urinary $\sum 23\text{PFASs}$: 6.18 ± 0.76 ng/mL), with strong serum-urine correlations ($r = 0.57\text{--}0.93$) validating urinary PFASs as reliable exposure biomarkers. Metabolomic profiling identified 1773 urinary metabolites (803 positive/970 negative ion mode), revealing 78 significantly altered metabolites in workers, including 24 PFASs associated variants and 8 directly linked to renal biochemical parameters [99].

The average concentrations of PFBA and PFOA in urine of people in Barcelona, Spain were 545 ng/L and 824 ng/L, respectively, while the average concentration of PFHxS was as high as 11889 ng/L [100]. In South Korea, Kim et al. found that PFPeA was the main pollutant in urine samples, and the average concentrations of PFPeA in children and adults were 2340 ng/L and 2490 ng/L, respectively. Therefore, the types and concentration levels of PFASs detected in urine samples of people in different countries and regions show certain spatial differences [101].

2.3.3. Breast milk PFASs exposure profiling

PFAS in breast milk represent a critical exposure pathway for infants through maternal transfer, with current concentrations generally below thresholds for immediate health risks [102]. However, the detection rate and concentration of PFASs in breast milk have increased in recent years, and the potential risks to infants still need to be taken seriously. Zhang et al. [103] conducted longitudinal analyses of 31 PFAS variants across maternal blood and lactation stages (colostrum, transitional milk, mature milk) in 76 postpartum women. High detection rates (>50 %) were observed for L-PFHxS, L-PFOS, PFOA, PFDA, and N-Methyl perfluorooctane sulfonamidoacetic acid (N-MeFOSAA) in all milk phases, paralleling maternal blood contamination profiles (1.31–100 % detection). The detection rates of 30 PFASs in maternal postpartum peripheral blood ranged from 1.31 % to 100 %. The detection rates of 28 PFASs detected in breast milk fifteen days after delivery ranged from 1.31 % to 96.1 %, and the detection rates of 30 PFASs detected in breast milk at 1 month and 3 months ranged from 1.31 % to 98.7 % and 1.31–100 %, respectively. The PFASs concentration in breast milk was significantly correlated with the PFASs concentration in maternal peripheral blood.

Zheng et al. [104] detected and analyzed 39 PFASs in 50 breast milk samples from the United States. A total of 16 PFASs were detected. The concentration of $\sum 16$ PFASs in breast milk ranged from 52 to 1850 ng/L, with PFOS (median: 30.40 ng/L–1) and PFOA (median: 13.90 ng/L) having the highest content; two short-chain PFHxA and PFHpA were also detected in most samples, with median values of 9.69 ng/L and 6.10 ng/L, respectively.

Jin et al. [105] studied the concentration of PFASs in breast milk and its relationship with infant growth and development. They detected and analyzed 16 PFASs in the breast milk of 174 women, which explored the relationship between PFASs in breast milk and infant growth and

development after birth. It was the first time reported for the exposure level of Cl-PFESAs in breast milk of the Chinese population. The results showed that the PFOA content in breast milk was the highest, with an average concentration of 87 ng/L, followed by PFHxS and 6:2 Cl-PFESAs with average concentrations of 41 ng/L and 28 ng/L, respectively. The concentrations of PFOA, PFDA, PFNA and 6:2Cl-PFESAs in breast milk were negatively correlated with infant height and weight gain rates, while exposure to higher levels of 8:2 FTOH was associated with a decrease in infant weight gain rates. These findings constitute the first empirical evidence of lactation-mediated developmental impacts from five PFAS compounds, establishing critical exposure thresholds for neonatal health risk assessments.

2.3.4. Biological samples PFASs exposure profiling

Extensive evidence has established the bioaccumulation and bio-magnification potential of PFASs [106]. Long-chain analogues (carbon chain length ≥ 7) demonstrate pronounced trophic transfer characteristics through food webs with significant biological retention [107]. Carnivores exhibit significantly higher hepatic accumulation levels compared to herbivores, indicating dietary exposure as the predominant pathway. While short-chain PFASs (e.g., PFBA) demonstrate enhanced mobility in plant-soil systems resulting in elevated concentrations in herbivore muscle and milk tissues compared to long-chain PFASs, their bioaccumulation factors remain substantially lower than long-chain PFASs.

PFASs accumulation in aquatic organisms generally escalates with compound chain length and trophic level [108]. Short-chain PFASs exhibit limited bioaccumulation potential, typically maintaining muscle tissue concentrations below 1 ng/g. Jiao et al. [109] detected PFOA, PFOS, and PFHxS in hepatic and muscular tissues of fish species from Yangtze River in China, demonstrating bioaccumulation factors (BAFs) exceeding 5000 L/kg. In contrast, Casal et al. [110] observed low short-chain PFASs in marine mammals, though elevated detection frequencies in coastal populations like porpoises, which suggest terrestrial pollution inputs. Zooplankton predominantly accumulate short-chain PFASs through surface seawater exposure, while benthic crustaceans and mollusks exhibit significantly higher total PFASs burdens than fish due to sediment ingestion pathways. Notably, detections of PFPeA in Beibu Gulf marine organisms (gastropods, crabs, plankton and laver) indicate short-chain PFASs bioaccumulation and long-range transport capacities [111]. Although urban/industrial proximity correlates with PFASs exposure, atmospheric deposition mediates contamination in remote areas. Canadian freshwater fish monitoring programs revealed perfluoro-1-butananesulfonamide (FBSA) detection in 32 out of 33 sampled specimens [112]. Although concentrations remained substantially lower than those documented in industrialized aquatic systems such as the St. Lawrence River and Great Lakes, this persistent detection establishes FBSA as an emerging bioaccumulative contaminant of ecological concern.

Plant exposure studies reveal preferential short-chain PFASs accumulation in root systems. Griffin et al. [113] detected 12 PFAS compounds (including PFOA, PFOS, and PFBA) across aquatic plant communities (macroalgae, wetland macrophytes, and free-floating species) in Florida, with total concentrations ranging from 0.18 to 55 ng/g. Qian's investigations [114] demonstrated differential accumulation patterns between legacy (PFOA/PFOS) and emerging PFASs (HFPO-DA, 6:2 fluorotelomer sulfonate) in terrestrial plants, where long-chain analogues become preferentially retained in root epidermis, while short-chain variants exhibit enhanced vascular translocation capacity.

Table 3 synthesizes distribution data on PFASs bioaccumulation across trophic levels, revealing distinct patterns between short-chain ($C \leq 6$) and long-chain ($C \geq 7$) PFASs. Short-chain PFASs (PFHxA, PFHpA, PFHxS, PFPeA) are ubiquitously detected but typically occur at lower concentrations (e.g., 0.097–0.14 ng/g in Copepoda, ND–0.74 ng/g in *Gammarus* pp.). Their prevalence in lower trophic organisms

(zooplankton, polychaetes, crustaceans) and benthic species reflects enhanced mobility and bioavailability in aqueous systems. However, their bioaccumulation factors (BAFs) remain limited, as muscle concentrations consistently below 1 ng/g in most fish species (e.g., ND–0.65 ng/g in *Platichthys flesus*). Conversely, long-chain PFASs (PFOA, PFOS) dominate in higher trophic organisms and exhibit significant biomagnification. PFOS concentrations escalate dramatically in marine mammals (e.g., 160–220 ng/g in harbor seals, 170 ng/g in white-tailed eagles) and piscivorous birds (390 ng/g in common guillemot), exceeding those in fish and invertebrates by orders of magnitude. This trophic amplification underscores the persistence and protein-binding affinity of long-chain compounds. Notably, legacy long-chain PFAS (PFOS, PFOA) remain the primary contaminants in top predators despite regulatory phaseouts [115–118].

2.4. Toxicological impacts of PFASs

PFASs pose significant global health risks due to bioaccumulative persistence and multi-organ toxicity, with heightened vulnerability observed in susceptible populations (pregnant individuals, neonates, elderly cohorts, and immunocompromised subgroups). Physiological alterations in these groups amplify sensitivity to PFASs exposure, notably elevating risks of gestational hypertension, diabetes mellitus, and placental transfer-mediated fetal developmental abnormalities including neurotoxicity, growth retardation, and reproductive dysfunction. Postnatal exposure further disrupts central nervous system gene expression while exacerbating chronic conditions such as asthma, atherosclerosis, and metabolic disorders. Mechanistic toxicology studies reveal PFASs induced pathologies in vulnerable subpopulations primarily through oxidative stress induction, immune dysregulation, cellular metabolic interference, and gut microbiome perturbations [119].

Emerging epidemiological evidence confirms adverse health outcomes from chronic PFAS exposure, including reproductive impairments [120], hepatotoxicity [121], immunotoxicity, and tumorigenesis [122], with short-chain analogs demonstrating equivalent hazard potential to legacy long-chain compounds. Weatherly et al. [121] established PFBA-mediated hepatotoxicity and dermal toxicity in murine models through histopathological, immunophenotypic, and transcriptomic analyses, revealing systemic effects from sustained dermal exposure. These findings underscore the necessity for revised risk assessments incorporating cumulative and synergistic toxicities across PFAS homologs.

Jia et al. [123] demonstrated distinct pharmacokinetic behaviors between short- and long-chain PFAS in a 5-month longitudinal study of elderly Chinese populations, revealing significant concentration variability in short-chain PFCAs (C4–C7) compared to persistent enrichment of long-chain PFAS (PFOS, PFOA) in serum. These observations reflect the reduced bioaccumulation potential of short-chain analogs, attributable to faster absorption rates, reduced tissue accumulation, and enhanced renal clearance mechanisms that lower internal exposure burdens [124].

Du et al. [125] further elucidated PFASs mediated endocrine disruption through a 6 month cohort study of 318 healthy Shanghai residents (aged 11–80 years, all participants underwent thyroid ultrasound examination), employing weighted quantile regression (WQS) and Bayesian kernel machine regression (BKMR) models to analyze thyroid function parameters. *In vitro* experiments using Nthy-ori3–1 cells exposed to median serum concentrations of PFOA, PFOS, PFHxS, PFNA, PFDA, PFHpA, and PFUnDA revealed PFASs mixture dose-dependent effects on thyroid-stimulating hormone (TSH) and thyroid peroxidase antibodies (TPOAb), with significant inverse correlations to free triiodothyronine (FT3) and complex interactions with free thyroxine (FT4). Transcriptomic analyses identified PFAS-induced dysregulation of thyroid-associated signaling pathways and gene expression profiles.

Human toxicity studies corroborate developmental risks, with

Table 3

Concentrations of long/short-chain PFASs in biological samples and sampling locations.

Biological samples	PFASs	C-F	Long/Short chain	Concentration (ng/g)	Time	Sampling location	Refs
Carcinus maenas	PFHpA	6	Short chain	0.22–1.4			[115]
	PFHxS	6	Short chain	0.26–0.59			[115]
Nereis	PFHpA	6	Short chain	0.71–1.7			[115]
diversicolor	PFHxS	6	Short chain	0.21–1.17			[115]
Copepoda, ind.	PFHpA	6	Short chain	ND–0.45			[115]
	PFHxS	6	Short chain	0.097–0.14			[115]
Gammarus spp.	PFHpA	6	Short chain	ND–0.74			[115]
	PFHxS	6	Short chain	0.19–0.33	May to November, 2012	French Atlantic coast, the Gironde estuary (SW France)	[115]
Sole	PFHpA	6	Short chain	ND–0.39			[115]
	PFHxS	6	Short chain	ND–1.3			[115]
Platichthys flesus	PFHpA	6	Short chain	ND–0.050			[115]
	PFHxS	6	Short chain	ND–0.65			[115]
Argyrosomus regius	PFHpA	6	Short chain	ND–0.098			[115]
	PFHxS	6	Short chain	ND–0.22			[115]
Dicentrarchus labrax	PFHpA	6	Short chain	ND–0.16			[115]
	PFHxS	6	Short chain	ND–0.12			[115]
	PFHxA	5	Short chain	-			[116]
	PFHpA	6	Short chain	-			[116]
	PFOA	7	Long chain	0.0238–0.0292		Arctic (Norway)	[116]
Zooplankton	PFBS	4	Short chain	0.0078–0.7356	June, 2018	Four representative stations located in the fjord system (the Adventfjord and Isfjord)	[116]
	PFHxS	6	Short chain	0.0131		Svalbard airport with two firefighting training stations (FFTS)	[116]
	PFOS	8	Long chain	0.0046–0.2270			[116]
	6:2 FTS	6	Short chain	0.1667–1.87			[116]
	PFHxA	5	Short chain	-			[116]
	PFHpA	6	Short chain	0.1176			[116]
	PFOA	7	Long chain	0.0665–0.1602		Arctic (Norway)	[116]
Polychaete	PFBS	4	Short chain	0.0621–0.1543	June, 2018	Four representative stations located in the fjord system (the Adventfjord and Isfjord)	[116]
	PFHxS	6	Short chain	0.2056–1.01		Svalbard airport with two firefighting training stations (FFTS)	[116]
	PFOS	8	Long chain	0.2630–4.54			[116]
	6:2 FTS	6	Short chain	0.0675–0.5971			[116]
	PFHxA	5	Short chain	-			[116]
	PFHpA	6	Short chain	-			[116]
	PFOA	7	Long chain	0.018–0.040		Arctic (Norway)	[116]
Carb	PFBS	4	Short chain	0.309–4.50	June, 2018	Four representative stations located in the fjord system (the Adventfjord and Isfjord)	[116]
	PFHxS	6	Short chain	0.144		Svalbard airport with two firefighting training stations (FFTS)	[116]
	PFOS	8	Long chain	0.158–0.312			[116]
	6:2 FTS	6	Short chain	0.66			[116]
	PFHxA	5	Short chain	0.134			[116]
	PFHpA	6	Short chain	-			[116]
	PFOA	7	Long chain	0.025–0.247		Arctic (Norway)	[116]
Liver of fish	PFBS	4	Short chain	0.027–0.066	June, 2018	Four representative stations located in the fjord system (the Adventfjord and Isfjord)	[116]
	PFHxS	6	Short chain	0.445–3.02		Svalbard airport with two firefighting training stations (FFTS)	[116]
	PFOS	8	Long chain	0.993–2.812			[116]
	6:2 FTS	6	Short chain	-			[116]
	PFHxS	6	Short chain	< 0.075			[117]
Viviparous eelpout	PFOS	8	Long chain	0.49	2015–2016	Darsser Ort, Arkona Basin	[117]
	PFHpA	6	Short chain	< 0.05			[117]
	PFOA	7	Long chain	< 0.05			[117]
	PFHxS	6	Short chain	< 0.62			[117]
Atlantic herring	PFOS	8	Long chain	8.1	2014–2016	Byxelkrok, Western Gotland Basin	[117]
	PFHpA	6	Short chain	< 0.07			[117]
	PFOA	7	Long chain	1.0			[117]
	PFHxS	6	Short chain	0.77			[117]
Grey seal	PFOS	8	Long chain	200	2006–2010	Åland Sea ; Northern Baltic Proper; Western Gotland Basin	[117]
	PFHpA	6	Short chain	< 0.07			[117]
	PFOA	7	Long chain	0.78			[117]
	PFHxS	6	Short chain	1.2			[117]
Harbor seal	PFOS	8	Long chain	160	2012–2016	Western Gotland Basin; Eastern Gotland Basin	[117]
	PFHpA	6	Short chain	< 0.07			[117]
	PFOA	7	Long chain	1.2			[117]
	PFHxS	6	Short chain	0.67			[117]
Harbor porpoise	PFOS	8	Long chain	220	2006–2012	Eastern Gotland Basin	[117]
	PFHpA	6	Short chain	0.31			[117]
	PFOA	7	Long chain	0.25			[117]
	PFHxS	6	Short chain	0.90			[117]
Common eider	PFOS	8	Long chain	17	2015–2016	Christiansø, Bornholm Basin	[117]
	PFHpA	6	Short chain	< 0.07			[117]
	PFOA	7	Long chain	0.22			[117]

(continued on next page)

Table 3 (continued)

Biological samples	PFASs	C-F	Long/Short chain	Concentration (ng/g)	Time	Sampling location	Refs
Common guillemot	PFHxS	6	Short chain	1.2	2015–2016	Western Gotland Basin	[117]
	PFOS	8	Long chain	390			[117]
	PFHpA	6	Short chain	< 0.07			[117]
	PFOA	7	Long chain	0.34			[117]
White-tailed eagle	PFHxS	6	Short chain	1.1	2015–2016	Stockholm/Uppsala Counties, Åland Sea; Kalmar/Blekinge Counties, Western Gotland Basin	[117]
	PFOS	8	Long chain	170			[117]
	PFHpA	6	Short chain	< 0.07			[117]
	PFOA	7	Long chain	0.84			[117]
<i>G. vulgaris</i>	PFOS	8	Long chain	0.167–3.57	November and December, 2018	10 sites were sampled in the Belgian part of the North Sea and the Western Scheldt estuary	[118]
	PFOA	7	Long chain	0.156–0.64			[118]
<i>M. merlangus</i>	PFOS	8	Long chain	0.299–18.4			[118]
	PFOA	7	Long chain	0.134–0.888			[118]
<i>P. platessa</i>	PFOS	8	Long chain	0.617–107			[118]
	PFOA	7	Long chain	0.060–11.3			[118]
<i>S. solea</i>	PFOS	8	Long chain	0.302–78.6			[118]
	PFOA	7	Long chain	0.113–4.03			[118]
<i>C. harengus</i>	PFOS	8	Long chain	0.216–16.7			[118]
	PFOA	7	Long chain	0.12–25.8			[118]
<i>A. laterna</i>	PFOS	8	Long chain	1.56–24.5			[118]
	PFOA	7	Long chain	0.141–2.93			[118]
<i>M. surmuletus</i>	PFOS	8	Long chain	0.663–37.3			[118]
	PFOA	7	Long chain	0.202–8.16			[118]
<i>L. holsatus</i>	PFOS	8	Long chain	0.301–5.61			[118]
	PFOA	7	Long chain	0.128–4.35			[118]
<i>C. crangon</i>	PFOS	8	Long chain	0.292–4.55			[118]
	PFOA	7	Long chain	0.132–1.58			[118]

prenatal exposure to short-chain PFBS and PFHpA linked to fetal gonadotropin axis disruption and altered free androgen levels [126]. These compounds exhibit higher placental transfer efficiency than PFOA/PFOS, enabling elevated fetal exposure that impairs growth trajectories [127]. PFBS specifically induces multiorgan toxicity, manifesting as offspring weight loss, developmental delays, reproductive impairments, and hepatic/renal pathologies via thyroid hormone modulation and cellular ultrastructural changes.

PFASs exhibit high binding affinity for serum albumin, fatty acid-binding proteins (FABP), renal organic anion transporters (OATs), and hepatic FABP [128], facilitating their accumulation in protein-rich tissues such as liver and blood. In aquatic organisms, crustacean and bivalve proteins serve as critical binding targets for PFASs, with fish tissues demonstrating highest accumulation levels in hepatic systems compared to muscular compartments [110,129]. Regarding phytotoxicity, short-chain PFASs inhibit photosynthetic efficiency in freshwater algae (e.g., *Scenedesmus obliquus*) at $\mu\text{g/L}$ concentrations, manifested through reduced chlorophyll-a content and impaired photosystem II (PSII) activity. Liu et al. [130] documented significant growth inhibition in *Chlorella pyrenoidosa* under PFBA and FBSA exposure, accompanied by disrupted physiological processes including photosynthesis, reactive oxygen species (ROS) metabolism, and DNA replication. Gonzales et al. [33] observed leaf morphogenesis alterations in *Lemna minor* under low dose PFOA exposure, while chlorophyll biosynthesis and ROS regulation remained unaffected.

3. Physical removal technology and adsorption mechanism of PFASs

The bond energy of the carbon-fluorine bond in PFASs was very high (110 kcal/mol), and its chemical stability was extremely strong. Therefore, PFASs were difficult to degrade and can resist traditional chemical actions, microbial actions and their biological metabolic processes [131]. Currently, the technologies for effectively removing PFOS were mostly focused on physical separation and chemical degradation. However, these technologies still need to be improved, because there were problems such as high energy consumption, complex operation, and potential threats of secondary pollution. Surfactants such as PFOA cannot be properly treated by traditional treatment methods because

traditional treatment methods were energy-intensive, difficult to operate, and may cause secondary pollution. Notably, surfactants like PFOA remain inadequately addressed by conventional treatment methods, which are inherently energy-intensive, technically demanding, and environmentally risky.

3.1. Adsorption

Adsorption technology was an efficient and feasible method for removing PFASs. Mineral materials such as activated carbon, ion exchange resins, carbon nanotubes, zeolites, and organic polymer materials were often used as adsorbents [132]. The adsorption method used the selective adsorption of pollutants by adsorbents to separate pollutants from water bodies to achieve the purpose of removal. It has the characteristics of low cost, high efficiency, easy operation and renewable cycle. The principles of adsorption for removing PFASs from water bodies include hydrophobic effect, electrostatic effect, hydrogen bonding effect, van der Waals force, which the adsorption process includes one or more of them [2]. Several major adsorbent materials for removing PFASs and their corresponding adsorption mechanisms are summarized in Fig. 2. A large number of scholars have conducted research on the adsorption process and mechanism of PFASs. As shown in Table 4, the adsorption performance of various adsorbents on PFASs was summarized. The adsorption capacity and mechanism of different types of adsorbents were not exactly the same. Therefore, the adsorbents previously reported for the degradation of PFASs were sorted out, and the interaction between PFASs and adsorbents and the adsorption process were explained.

3.1.1. Activated carbon

Activated carbon (AC) filtration was the most common and widely adopted treatment method for treating water contaminated with PFOS [133]. Previous studies have demonstrated that granular activated carbon (GAC) and powdered activated carbon (PAC) have strong adsorption capacity for PFOA and PFOS [134,135]. Yu et al. [10] compared the adsorption performance of powdered activated carbon and granular activated carbon. The adsorption capacities of powdered activated carbon for PFOA and PFOS were 0.67 and 1.04 mmol/g, respectively, and the adsorption equilibrium time was about 4 h. The adsorption

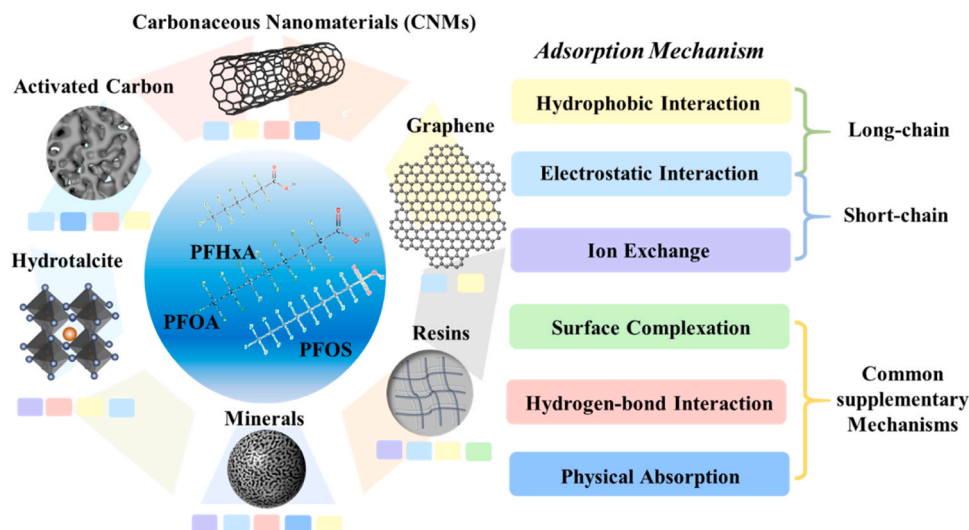


Fig. 2. Adsorbent materials and adsorption mechanisms of removed PFASs.

capacities of granular activated carbon were 0.39 and 0.37 mmol/g, respectively, and the adsorption equilibrium time was at least 168 h.

While activated carbon demonstrates effectiveness in removing long-chain PFASs such as PFOS and PFOA, its removal efficiency for short-chain PFASs (PFCA <C7; PFSA <C6) has been consistently reported as low [7]. Although hydrogen bonding and nonspecific van der Waals interactions contribute to the adsorption process, hydrophobic and electrostatic interactions are identified as the dominant mechanisms governing PFAS adsorption on GAC [10]. Hydrophobic interactions primarily occur between the nonpolar carbonaceous surface of GAC and the fluorinated alkyl tails of PFAS molecules [136], while electrostatic interactions arise between the anionic functional groups of PFASs and charged sites on the GAC surface. Comparative studies indicate that adsorption of more hydrophilic short-chain PFASs is predominantly governed by electrostatic interactions, whereas hydrophobic interactions play the principal role in the adsorption of long-chain PFASs on GAC [2]. The pH value significantly influences the adsorption behavior and capacity of activated carbon towards PFASs through distinct mechanisms. For long-chain PFASs such as PFOS and PFOA, hydrophobic interactions dominate the adsorption process, while electrostatic forces play a more critical role in short-chain PFASs adsorption. This differential behavior originates from the zero charge point (pH_{PZC}) of activated carbon. Specifically, when the solution pH deviates from this critical threshold, the modified surface charge state of activated carbon significantly alters its electrostatic interactions with short-chain PFASs. Under acidic conditions, the activated carbon surface typically acquires positive charges, thereby enhancing electrostatic attraction with negatively charged PFASs and improving adsorption efficiency. Conversely, in alkaline environments, the surface tends to become negatively charged or electrically neutral, resulting in increased electrostatic repulsion and subsequent adsorption reduction. This diminished electrostatic interaction consequently elevates the relative contribution of other intermolecular forces in the adsorption process, potentially altering the overall adsorption mechanism for different PFAS species under varying pH conditions.

When treating PFASs with activated carbon, the adsorption process exhibits prolonged equilibration periods, while the hydraulic retention time of GAC in practical applications is often constrained. The slow adsorption kinetics enable premature breakthrough of PFOA and PFOS through the adsorption layer before saturation is achieved. Studies have shown that PFASs in drinking water can quickly penetrate activated carbon filters, thereby affecting the removal of pollutants. Some shorter carbon chain PFASs may penetrate granular activated carbon faster than longer carbon chain PFASs [137].

3.1.2. Resins

Compared to granular activated carbon (GAC), certain ion exchange resins demonstrate superior adsorption efficiency for PFASs (PFCs). Senevirathna et al. [138] evaluated the adsorption performance of GAC, ion exchange resins, and non-ionic polymers for PFOS, revealing that non-ionic polymers exhibited higher adsorption capacity than other adsorbents at PFOS concentrations below 100 ng/L. However, based on adsorption isotherm and kinetic analyses, ion exchange resins proved more effective for PFOS removal in the ng/L concentration range. Gagliano et al. [2] conducted a comparative analysis of adsorption mechanisms and performance between ion exchange resins and activated carbon for PFASs. Mesoporous and macroporous adsorbents (e.g., activated carbon and resins) displayed high adsorption capacities, particularly favoring long-chain PFASs due to enhanced accessibility.

Long-chain PFASs (such as PFOA and PFOS) have larger molecular sizes and are more easily captured by adsorbents with macroporous and mesoporous structures. Short-chain PFASs (such as PFBA and PFBS) have smaller molecular sizes and were more easily captured by microporous adsorbents. The pore size of microporous adsorbents was relatively small, but their specific surface area was large, which can provide more adsorption sites. Anion exchange resins outperformed activated carbon in removing both long- and short-chain PFASs, though short-chain PFASs consistently exhibited lower adsorption capacities across all adsorbent types, rendering their removal more challenging. Long-chain PFASs molecules were larger, they were more easily captured by adsorbents through hydrophobic interaction and pore structure. The limited adsorption of short-chain PFASs may correlate with insufficient active pore site availability, as their molecular structure prevents micelle formation required for multilayer adsorption. Additionally, coexisting organic matter further reduces short-chain PFAS adsorption by competing for active sites. In contrast, long-chain PFAS adsorption likely involves surface aggregate formation, potentially enhancing efficiency through hydrophobic interactions [139].

Carter et al. [140] reported that resin-based PFOS adsorption achieved equilibrium significantly faster (10 h) than conventional GAC (50 h). Zaggia et al. [141] investigated three anionic resins—A532E (highly hydrophobic), A520E (moderately hydrophobic), and A600E (non-hydrophobic)—for PFOA and PFOS removal in drinking water. The equilibrium adsorption capacities for PFOA were 142.1, 134.7, and 125.2 mg/g, while PFOS capacities reached 260.5, 210.4, and 186.2 mg/g, respectively. These results underscore the critical role of resin hydrophobicity in PFAS adsorption capacity, directly linked to the surfactant properties of PFASs.

Table 4

Adsorption effects and kinetics of various adsorbents on long/short chain per-and polyfluoroalkyl substance.

Adsorbent		Adsorbate	C- F	Long/ Short chain	C ₀ (mg/ L)	Equilibrium time(h)	Kinetics		Refs
							q _m (mg/g)	k ₂ (g/mg/h)	
Activated carbons (AC)	Powder AC	PFOA	7	Long chain	50	2–3	183.12–344.44	1.18×10^{-2} $\sim 3.19 \times 10^{-2}$	[10]
	Powder AC	PFOS	8	Long chain	50	3–4	322.80–371.22	9.09×10^{-3} $\sim 1.01 \times 10^{-2}$	[10]
	Granular AC	PFOA	7	Long chain	50	90–168	130.80–165.68	1.61×10^{-4} $\sim 8.49 \times 10^{-4}$	[10]
	Granular AC	PFOS	8	Long chain	50	~168	220.58–274.38	1.12×10^{-4} $\sim 1.30 \times 10^{-4}$	[10]
	Granular AC	PFHpA	6	Short chain	0.05	24	52.5	0.3	[154]
	Granular AC	PFHpA	6	Short chain	0.05	24	51	2.0	[154]
	Granular AC	PFHpA	6	Short chain	0.05	24	43	3.75	[154]
	Granular AC	PFBS	4	Short chain	0.05	24	53.0	0.7	[154]
	Granular AC	PFBS	4	Short chain	0.05	24	52.5	2.25	[154]
	Granular AC	PFBS	4	Short chain	0.05	24	49	4.0	[154]
	Granular AC	PFBS	4	Short chain	1	96	128.1	-	[155]
	Bamboo-derived AC	PFHpA	6	Short chain	1	12	46.8	-	[156]
	Bamboo-derived AC	PFHpA	6	Short chain	1	12	46.8	-	[156]
	Activated carbon	PFBA	3	Short chain	6,4	24	14,7	-	[157]
	Activated carbon	PFPrA	2	Short chain	6.4	24	10.88	-	[157]
	Activated carbon	PFBS	4	Short chain	6.4	24	39.66	-	[157]
	Ordered mesoporous carbon	PFOA	7	Long chain	10	1	82.5	1.51	[158]
	Reed straw-derived biochar	PFOA	7	Long chain	0.1	20	17.91	9.61×10^{-4}	[159]
	Reed straw-derived biochar	PFOS	8	Long chain	0.1	20	34.62	8.38×10^{-4}	[159]
	Vitis vinifera leaf litter AC	PFOA	7	Long chain	0.125	1	119.12	0.74	[160]
Vitis vinifera leaf litter AC	PFOS	8	Long chain	0.125	1.5	66.01	2.08	[160]	
Resins	Anion-exchange resins	PFOA	7	Long chain	50	168	789.16–1478.04	2.29×10^{-5} $\sim 4.59 \times 10^{-5}$	[10]
	Anion-exchange resins	PFOS	8	Long chain	50	48	182.92–193.68	$2.23 \times 10^{-4} \sim 2.97 \times 10^{-4}$	[10]
	Anion-exchange resins	PFBS	4	Short chain	1000	50–80	34.6 ~ 109.2	-	[141]
	Anion-exchange resins	PFBA	3	Short chain	6,4	24	5.006	-	[157]
	Anion-exchange resins	PFPrA	2	Short chain	6.4	24	1.245	-	[157]
	Anion-exchange resins	PFBS	4	Short chain	6.4	24	6.100	-	[157]
	Anion-exchange resins	PFBA	3	Short chain	6,4	24	2.272	-	[157]
	Anion-exchange resins	PFPrA	2	Short chain	6.4	24	2.020	-	[157]
	Anion-exchange resins	PFBS	4	Short chain	6.4	24	7.849	-	[157]
	Anion-exchange resins	PFOS	8	Long chain	200	48–168	210–2575	$1.3 \times 10^{-5} \sim 3.2 \times 10^{-4}$	[161]
	Graphene oxide	PFOA	7	Long chain	10	48	10.17	11.81×10^{-2}	[162]
	Graphene oxide	PFOA	7	Long chain	1000	48	424.1	5×10^{-3}	[162]
Carbonaceous nanomaterials	Carbon Nanoparticles	PFHxA	5	Short chain	1	2	42	-	[163]
	Carbon Nanoparticles	PFBA	3	Short chain	0.1	2	7.4	-	[163]
	Carbon nanotubes	PFOA	7	Long chain	0.218	5	0.8284	-	[143]
	Carbon nanotubes	PFOS	8	Long chain	0.269	5	1.0491	-	[143]

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Table 4 (continued)

Adsorbent	Adsorbate	C-F	Long/Short chain	C ₀ (mg/L)	Equilibrium time(h)	Kinetics		Refs
						q _m (mg/g)	k ₂ (g/mg/h)	
Mineral materials	Carbon nanotubes	PFOS	8 Long chain	100	2	237	1.83×10^{-2}	[11]
	Carbon nanotubes	PFHxA	5 Short chain	-	2	23.2	0.259	[143]
	Hydrotalcite	PFOA	7 Long chain	1000	1	1033	31.77	[164]
	Hydrotalcite	PFOS	8 Long chain	1000	1	998	6.39	[164]
	Zeolites	PFOA	7 Long chain	300	3	37	7.92	[165]
	Zeolites	PFOS	8 Long chain	300	3	126	3.69	[165]
	Zeolites	PFBA	3 Short chain	50	144	7.72	0.314	[166]
	Zeolites	PFBA	3 Short chain	50	144	8.74	-0.580	[166]
	Montmorillonite	PFOS	8 Long chain	50–500	24	83–99	5×10^{-3}	[167]
	Metal-organic frameworks	PFOS	8 Long chain	5–100	3.5	154.56	2.51×10^{-3}	[168]
Chitosan	Magnetic bead-type chitosan material	PFOA	7 Long chain	20	120	16.150	8.22×10^{-1}	[169]
		PFOA	7 Long chain	0.2	4	99.2	1.38×10^{-1}	[153]
	Chitosan /covalent organic framework	PFOS	8 Long chain	0.2	4	86.8	7.8×10^{-2}	[153]
		GenX	5 Short chain	0.2	4	82.3	3.84×10^{-2}	[153]
	Chitosan-based molecularly imprinted polymer	PFOS	8 Long chain	0.05	32	275.27	6.00×10^{-4}	[170]
	non-imprinted polymer	PFOS	8 Long chain	0.05	32	122.98	7.00×10^{-3}	[170]

3.1.3. Carbonaceous nanomaterials (CNMs)

Carbonaceous nanomaterials (CNMs), particularly nanocarbons including carbon nanotubes (CNTs), graphene, carbon nanospheres, and fullerenes, exhibit high specific surface area, porosity, and adsorption capacity for both anionic and cationic species. Their nanoscale properties—such as elevated surface activity, quantum size effects, and interfacial interactions enable CNMs to overcome limitations inherent to conventional adsorbents. Furthermore, CNMs can be functionally tailored through surface modifications to enhance performance, circumventing challenges associated with traditional adsorbents like regeneration difficulties, slow kinetics, and limited functionalization potential [137].

Carbon nanotubes (CNTs), characterized by their hollow nanostructure, demonstrate exceptional hydrophobicity and high specific surface area, providing substantial adsorption capacity across their cylindrical surfaces. Chen et al. [11]. observed rapid PFOS adsorption equilibrium (2 h) on CNTs, significantly faster than activated carbon (384 h) or fly ash (48 h), attributed to synergistic electrostatic attraction and hydrophobic interactions with PFASs. Bei et al. [142] investigated PFAS adsorption mechanisms on CNT variants, revealing that adsorption capacity increased with fluorocarbon chain length for compounds sharing functional groups. Hydroxyl- and carboxyl-functionalized CNTs (CNT-OH, CNT-COOH) exhibited markedly reduced adsorption compared to pristine CNTs, confirming hydrophobic interactions as the dominant mechanism, with electrostatic repulsion suppressing PFAS adsorption. pH-dependent declines in adsorption rates further indicated minimal hydrogen bonding contributions.

Deng et al. [143] reported superior PFOA adsorption on single-walled carbon nanotubes (SWCNTs, 0.259 mmol/g) versus multi-walled counterparts (MWCNTs, 0.028 mmol/g), driven by SWCNTs enhanced surface area and unique physicochemical properties. At a low pH value, the carboxyl group (-COOH) and sulfonic acid group

(-SO₃H) of PFOA were not completely ionized, and PFOA existed in a neutral or weakly polar form. At high pH values, these groups were completely ionized, and PFOA existed in the form of anions. When the pH value exceeds 3.4, the surface of CNT all shows a negative charge. When the pH value increases, the electrostatic interaction between the adsorbent and the /PFOA anion changes from attraction to repulsion. This electrostatic repulsion prevented the PFOA anion from approaching the surface of the adsorbent, thereby reducing the adsorption effect. In addition, rapid removal (>95 % for PFOA/PFOS within 5 h) contrasted with limited PFBS adsorption (7.5 % after 48 h), yielding the adsorption hierarchy: PFOS > PFOA > PFHxS > PFHxA > PFBS > PFBA, underscoring PFAS chain length as a critical determinant [143]. Functionalized MWCNTs (MWCNTs-pri, MWCNTs-COOH, MWCNTs-OH) achieved 30 % PFBS removal, declining below 20 % in the presence of humic acid (HA) and phenol, reflecting PFBS weak hydrophobicity relative to long-chain PFASs [144]. Johnson et al. [145] was investigated the influence of different ions on degradation. It observed 15–30 % reductions in PFOS removal by CNTs with increasing concentrations of sulfate (SO₄²⁻), chloride (Cl⁻), and dichromate (Cr₂O₇²⁻) ions. Conversely, elevated Cu²⁺ and Pb²⁺ concentrations enhanced removal via metal ion bridging between PFOS and CNTs, with divalent cations potentially forming complexes with negatively charged PFOS molecules.

3.1.4. Minerals

Mineral materials encompass natural or modified minerals with exploitable physicochemical properties, offering advantages such as cost-effectiveness, abundant reserves, structural diversity, and broad applicability [146]. Mineral materials such as goethite, silica, kaolinite, zeolite, boehmite, alumina, and montmorillonite possess tunable mesoporous or layered structures, substantial specific surface areas, and functional groups, making them widely employed for PFAS adsorption and removal [147]. Their adsorption mechanisms primarily involve

electrostatic interactions, hydrophobic forces, hydrogen bonding, surface complexation, and ion exchange [13]. Natural minerals like hematite typically exhibit positively charged surfaces under ambient conditions, enabling electrostatic adsorption of anionic PFASs. Hydroxalite, a layered double hydroxide (LDH) clay material, features positively charged hydroxide sheets with interlayers occupied by anions and water molecules. PFASs are adsorbed onto hydroxalite surfaces and/or intercalated within its layers. The introduction of anionic surfactants or other anions into hydroxalite interlayers can further enhance PFAS adsorption efficiency [13].

Zhao et al. [13] investigated the adsorption of four PFASs (including PFOA and PFOS) on montmorillonite, kaolinite, and hematite, observing the adsorption hierarchy: hematite > kaolinite > montmorillonite. Adsorption capacity diminished with increasing solution pH, correlating with the pH-dependent surface charge of these minerals (pH_{PZC} values: montmorillonite 7.2, kaolinite 3.6, hematite 5.9). At pH levels below their pH_{PZC} , mineral surfaces become protonated and positively charged, fostering strong electrostatic attraction with anionic PFASs. As pH rises, surface charge transitions to neutral or negative, eliminating electrostatic attraction and amplifying repulsive forces, thereby reducing PFAS adsorption. In addition, the promoting effect of Ca^{2+} on the adsorption of PFOAs was significantly stronger than that of Na^+ , even if its concentration is only 1/10 of that of Na^+ . This difference not only stems from the regulation of electrostatic interaction by ionic strength, but was also closely related to the unique cation bridging effect of Ca^{2+} . Chen et al. [11] evaluated the adsorption of PFOS by materials such as corn straw ash (MA). The pseudo-second-order kinetic model fitted the adsorption kinetics well. According to the adsorption isotherms, MA has a high adsorption capacity (more than 700 mg/g). Due to the positively charged surface of MA, there were hydrophobic interactions and attractions, and the formation of hemi-micelles enhanced the adsorption. MA's cost-effectiveness and abundance position it as a highly efficient method for aqueous PFOS removal.

Wang et al. [148] engineered carnitine- and choline-modified montmorillonite as a therapeutic adsorbent to reduce human PFASs uptake via contaminated water and food. The modified clay effectively bound PFOA, PFOS, GenX, and PFBS. Langmuir-model adsorption under simulated gastric conditions demonstrated high binding capacity, affinity, and enthalpy for PFOA/PFOS, with limited desorption in intestinal environments. Hydrophobic, electrostatic, and hydrogen-bonding interactions drove PFASs immobilization in clay layers. Molecular dynamics simulations confirmed fluorinated carbon chains as primary adsorption sites, with PFOA/PFOS exhibiting stronger binding than GenX/PFBS. Similarly, Hearon et al. [149] enhanced montmorillonite's hydrophobicity and interlayer spacing via carnitine/choline modification. Langmuir-type adsorption at pH 7 and ambient temperature yielded higher capacities for PFOA (0.51–0.71 mol/kg) and PFOS compared to unmodified clay (0.37–0.49 mol/kg). Soil and plant studies demonstrated that 2 % adsorbent inclusion reduced PFASs bioavailability in soil (up to 74 %) and residues in cucumber plants ($p \leq 0.05$).

3.1.5. Chitosan

Chitosan was one of the most widely used natural biopolymers and was usually prepared from chitin by alkaline deacetylation. It was a unique alkaline polysaccharide in nature. Moreover, chitosan has excellent properties, such as biocompatibility, non-toxicity, and high hydrophilicity [150]. Chitosan contained a large number of amino, acetyl amino, primary hydroxyl, and secondary hydroxyl groups, which were highly active and can easily become good chelating sites for target pollutants. These groups also made chitosan extremely easy to chemically modify. Therefore, chitosan has been widely studied as a potential adsorbent for removing pollutants from water [151].

The abundant hydroxyl and amine groups in chitosan (CS) and chitin (CT) were conducive to hydrogen bonding and electrostatic interactions, which were suitable for the removal of persistent pollutants in drinking water. Castrillo et al. [12] prepared porous CS cryogels by acetic acid

dissolution, solidification and subsequent freeze-drying, and then obtained CT cryogels by acetylation. The ability to quickly remove per- and polyfluoroalkyl substances (PFASs) reached 451 mg/g. Zhang et al. [152] synthesized a quaternary amine COF with a positive surface charge, which adsorbed perfluorooctanoic acid through electrostatic interaction. COF was then combined with chitosan (CS) through a simple dissolution-evaporation process to form a composite gel material COF@CS. The results showed that COF@CS significantly exceeded the original COF and CS. According to the Langmuir model, the maximum capacity of COF@CS for perfluorooctanoic acid was 2.8 mmol/g at pH 5. In addition, the adsorption rate increased significantly to 6.2 mmol/g/h, while that of COF was 5.9 mmol/g/h and that of CS was 3.4 mmol/g/h. COF@CS has a good removal effect on the other 10 per- and polyfluoroalkyl substances. In addition, COF@CS was successfully regenerated in a mixed solution of 70 % ethanol and 1 % (mass fraction) NaCl and can be stably reused 5 times. The quaternary amine functional groups in COF were the main adsorption sites of the composite gel material, while the protonated amino groups on CS enhance the adsorption of perfluorooctanoic acid through electrostatic effects. He et al. [153] developed a new type of fluorine-functionalized covalent organic framework (F-COF). A layer of chitosan was modified on the surface of F-COF by cross-linking polymerization, and the resulting chitosan/F-COF had ideal hydrophilicity, high specific surface area and surface wettability. Chitosan/F-COF showed high adsorption capacity for perfluorinated compounds such as perfluorooctane sulfonic acid, perfluorooctanoic acid and GenX, and it was believed that electrostatic interactions, hydrogen bonding interactions, fluorine-fluorine interactions and channel size selection play a major role in the adsorption mechanism. The maximum adsorption capacity (q_{max}) for perfluorooctane sulfonic acid and perfluorooctanoic acid was 8307.1 mg/g and 6177.1 mg/g¹, respectively. This showed that chitosan and its composites can be used to remove perfluorinated compounds.

3.2. Membrane filtration

High-pressure membrane processes such as nanofiltration (NF) and reverse osmosis (RO) are widely employed for PFAS removal from water [14]. Membrane separation technology offers high efficiency and stable effluent quality by selectively separating solution components based on particle size, categorized into ultrafiltration, nanofiltration, and reverse osmosis by pore dimensions. With molecular weights of 498 g/mol (PFOS) and 414 g/mol (PFOA), common PFASs fall within the molecular weight cutoff range of NF membranes. RO membranes, featuring smaller pores than NF, achieve ultra-high PFAS retention while concurrently removing low-valent salts and small organic molecules [171]. In contrast, ultrafiltration and microfiltration membranes, with larger pore sizes than PFOS/PFOA, exhibit poor PFAS removal despite higher flux and lower operational costs.

Nanofiltration (NF), a pressure-driven technology leveraging sieving and charge effects, operates between ultrafiltration and RO in pore size. It effectively removes divalent/multivalent ions and 200–1000 Da organics, with its dual sieving-Donnan mechanisms making it particularly suitable for addressing emerging contaminants like PFASs in drinking water [172]. Hosseinzadeh et al. [173] applied seven machine learning algorithms to model PFOS removal via NF, identifying random forest, XGBoost, and AdaBoost as the most robust predictors. Pressure, initial PFOS concentration, and membrane type emerged as critical operational parameters.

Like other membrane separation technologies, nanofiltration also has problems such as membrane fouling and trade-off effect. The main research directions of nanofiltration treatment of PFASs were still the preparation and modification of membrane materials, water quality process parameters, etc., in order to improve the separation performance, retention rate and membrane flux of nanofiltration. Liu et al. [174] studied the retention process of PFASs by NF270 nanofiltration membrane and ESPA reverse osmosis membrane, respectively, and

explained the adsorption effect of membrane materials and membrane systems on PFASs. The retention rates of nanofiltration membrane and reverse osmosis membrane for 42 PFASs exceeded 97 %. After 13 days of continuous operation, the retention rate of PFASs by nanofiltration membrane was still over 98 %.

Liu et al. [175] investigated PFAS removal via nanofiltration (NF) in the presence of three natural organic matter (NOM) types: bovine serum albumin (BSA), humic acid (HA), and sodium alginate (SA). Their study focused on how PFAS molecular structures and coexisting NOM influence NF-mediated PFAS transfer and adsorption. Results demonstrated NF's efficacy in removing ether-linked and precursor PFASs, though NOM-induced fouling—particularly from SA—significantly reduced membrane flux. HA and BSA enhanced PFAS removal, while PFAS permeability inversely correlated with perfluorocarbon chain length and molecular weight. Steric hindrance and hydrophobic interactions were identified as critical retention mechanisms. Li et al. [176] compared dense (NF90) and loose (NFG) nanofiltration membranes for six anionic PFASs, revealing that NFG's PFOS removal relied predominantly on electrostatic and hydrophobic interactions, whereas these mechanisms contributed less than 10 % for NF90. The larger pore size and surface charge distribution of NFG also enhanced its adsorption capacity relative to NF90.

Griffin et al. [177] used nanofiltration (NF) for PFASs removal from semiconductor manufacturing wastewater and PFASs-related industrial wastewater. Compared with adsorption, membrane filtration was less sensitive to different water qualities and specific PFASs. The NF90 (compact NF) membrane has superior performance compared to the NF270 (loose NF) membrane, and the NF90 has a retention value of more than 97 % for all evaluated PFASs, including ultra-short trifluoromethanesulfonic acid (TFMS). In a semi-batch configuration, fab wastewater containing high concentrations of PFCAs, including trifluoroacetic acid (TFA: 96413 ng/L), perfluoropropionic acid (PFPrA: 11796 ng/L), and perfluorobutyric acid (PFBA: 504 ng/L), was treated, and the retention rate of all PFASs was ≥ 92 %, while achieving a water recovery rate of 90 % [178].

Reverse osmosis (RO) is a membrane separation process utilizing transmembrane pressure differentials to overcome solvent osmotic pressure, enabling selective solvent permeation through semipermeable membranes. RO achieves near-complete rejection of suspended solids, organic compounds, and low-valent salts, rendering it particularly suitable for seawater desalination, water reuse, and drinking water purification. In addition to PFAS removal, RO concurrently eliminates colloids, inorganic salts, and other organic contaminants. Despite high operational costs and significant concentrate generation, RO serves as an effective advanced treatment for drinking water facilities. Hara-Yamamura et al. [179] evaluated chlorine-treated Dow FILMTEC™ SW30HR RO membranes for retaining PFOA and PFOS, two representative PFASs. Salt retention rates (12.66 %) were measured to simulate membrane permeability variations. Cross-flow filtration tests demonstrated > 85 % PFOA/PFOS retention by damaged RO membranes at 39–66 % salt passage rates. Post-characterization revealed size exclusion and electrostatic repulsion as dominant retention mechanisms, even in compromised membranes.

3.3. Flocculation

The flocculation process mainly removes PFCs pollution in the water environment by adsorbing the flocculant itself and the flocs and suspended matter produced by the flocculant. Hubert et al. [15] used coagulation and flocculation to treat PFASs pollution in soil leachate. Six coagulants and flocculants were evaluated, including polyaluminum chloride (PACl), zirconium oxychloride octahydrate, cationic and anionic polyacrylamide, Polyclay 685 and Perfluor Ad®. Among them, Perfluor Ad® was a specially designed coagulant with the highest removal efficiency for all long-chain (>99 %) and short-chain PFA (>68 %). The removal efficiency of PFASs varied widely depending on

the coagulant/flocculant dosage and the target PFASs. All tested coagulants/flocculants achieved turbidity reductions greater than 95 %. Cationic polyacrylamide polymers achieved an average removal of up to 80 % for long-chain PFASs, while the average removal of short-chain PFASs was lower (<30 %). Two metal-based coagulants, PACl and Zr, achieved an average removal of 61 % for long-chain PFASs and 48 % for short-chain PFASs. Polyclay 685, a mixture of powdered activated carbon (PAC) and aluminum sulfate, achieved 90 % removal of long-chain PFASs and an average removal of 76 % for short-chain PFASs when a very high coagulant dosage (2000 mg/L) was used. The flocculation removal efficiency of long-chain and short-chain PFASs was highly correlated with chain length and head group. The removal of short-chain PFASs relied on electrostatic interactions with precipitated flocs, while for long-chain PFASs, hydrophobic interactions between flocs formed by coagulants/flocculants, dissolved organic matter, and suspended matter and lipid functional groups played a major role.

Maroli investigated cationic surfactant-enhanced coagulation for PFAS removal. Batch experiments utilizing a jar test unit evaluated the elimination of two short-chain and two long-chain PFASs (initial concentration: 10 $\mu\text{g/L}$) through cetyltrimethylammonium chloride (CTAC) supplementation. Results demonstrated that introducing coagulants (60 mg/L alum or 100 mg/L FeCl_3) combined with 1 mg/L CTAC significantly improved removal efficiencies for both short-chain (PFBS >40 %) and long-chain PFASs (PFOA/PFOS >80 %). FeCl_3 exhibited superior performance relative to alum. Sulfonates (PFBS, PFOS) displayed greater removal efficiency than carboxylates (PFBA, PFOA), attributed to their heightened hydrophobicity facilitating enhanced floc interactions. Notably, CTAC combined with powdered activated carbon (PAC) achieved PFOA, PFBS, and PFOS removal rates exceeding 98 % [180].

Deng et al. [181] employed polyaluminum chloride (PAC) for PFOA treatment in surface water, examining the effects of solution pH, PAC dosage, turbidity, and temperature on removal efficiency using PFOA and suspended solids removal rates as evaluation metrics. Results indicated a positive correlation between PAC dosage (up to 10 mg/L) and PFOA removal efficiency, achieving >90 % removal at maximum dosage. The mechanism involved PAC cations functioning as flocculants to adsorb PFOA anions through electrostatic interactions. PFOA hydrophobic nature further enhanced its adsorption onto suspended solids, enabling substantial removal through solid-liquid separation. Optimal adsorption occurred under low pH and low temperature conditions. Pre-flocculation supplementation of 1–16 mg/L PAC in wastewater containing 0.5–3.0 mg/L PFOA reduced residual concentrations to <1 $\mu\text{g/L}$, demonstrating PAC's efficacy in rapid PFOA elimination.

Bao et al. observed enhanced PFOS removal under acidic coagulation conditions, reflecting differential adsorption behaviors between PFOS and PFOA on flocs. This disparity stemmed from distinct functional group characteristics and molecular dimensions. Under standardized conditions (10 mg/L kaolin turbidity, 1 mmol/L NaHCO_3 alkalinity, 1 mmol/L NaCl ionic strength), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ dosing at 50 mg/L yielded 32 % PFOS removal versus 12 % PFOA removal. Despite identical $-\text{CF}_2$ chain lengths, PFOS's sulfonic acid groups exhibited stronger affinity for oxidized floc surfaces compared to PFOA's carboxylic acid groups, explaining the removal efficiency discrepancy [182].

Electrofloculation represents an eco-friendly electrochemical technology that utilizes continuously dissolving anode-generated metal ions as flocculants. The iron anode undergoes oxidation to release metal ions, which under aerobic conditions subsequently form insoluble iron hydroxide precipitates, enabling PFOS adsorption onto their surfaces. Concurrently, Li et al. [183] demonstrated that iron ions from electro-flocculation could activate peroxymonosulfate (PMS), generating hydroxyl radicals ($\cdot\text{OH}$) that effectively degrade PFOS.

4. Advanced oxidation/reduction processes and degradation pathways of PFASs

4.1. Oxidative degradation

The distinct stability profiles between short-chain and long-chain PFASs originate from their structural characteristics, with shorter homologues exhibiting higher C-F bond dissociation energies that confer enhanced chemical resistance. This molecular stability is reflected in environmental persistence metrics: while PFOS demonstrates biological half-lives of 4–5 years in humans and environmental persistence exceeding four decades, emerging research confirms that short-chain analogues maintain comparable or superior resistance to chemical/biological degradation. Their reduced adsorption potential in subsurface matrices enhances environmental mobility, facilitating widespread groundwater contamination. Photocatalytic degradation mechanisms reveal critical chain-length dependencies - during PFOA decomposition via sequential CF₂ elimination [2], the resultant short-chain PFCAs demonstrate exponentially increasing resistance to further mineralization. This degradation bottleneck manifests experimentally as elevated activation energy requirements for short-chain PFASs photolysis, exemplified by direct UV irradiation achieving only 16.3 % and 24.3 % removal efficiencies for PFBA (C4) and PFPeA (C5) respectively under identical reaction conditions, contrasting sharply with long-chain degradation kinetics[7]

4.1.1. Fenton oxidation

Iron ion-catalyzed Fenton oxidation represents an economical and effective method for degrading persistent organic pollutants. Despite the strong C-F bond stability in PFCs, hydroxyl radicals ($\cdot\text{OH}$) remain crucial in Fenton-mediated PFC decomposition. Mitchell et al. [184] demonstrated this through PFOA removal experiments using a Fenton system containing 1 mol H₂O₂ and 0.5 mmol Fe³⁺, achieving 89 % PFOA degradation within 150 min. The removal efficiency significantly decreased to 24 % when 2-propanol ($\cdot\text{OH}$ scavenger) was introduced, confirming $\cdot\text{OH}$ essential role in PFOA decomposition.

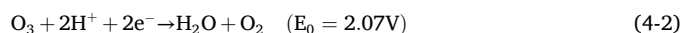
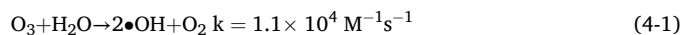
The conventional Fenton process faces limitations including pH dependency, catalyst loss, and toxic byproduct generation. Gokhale [185] developed a novel heterogeneous zwitterionic hydrogel catalyst containing iron ions within a porous scaffold, enabling Fenton degradation under neutral pH conditions through complexed iron ions. This catalyst maintained compatibility with UV-Fenton processes and achieved rapid degradation of xenobiotics (including PFASs) across multiple cycles, demonstrating enhanced operational stability. In addition, due to the extremely high hydrophobicity of long-chain PFAS, it is more inclined to co-precipitate with Fe(OH)₃ flocs. This co-precipitation mechanism favors long-chain PFAS removal through physical entrapment. Short-chain PFAS show lower affinity for floc adsorption due to higher hydrophilicity. Their degradation relies primarily on direct $\cdot\text{OH}$ oxidation rather than physical separation.

The combination of light radiation (such as ultraviolet light and visible light) and Fenton increased the oxidation activity of the system, reduce the amount of Fenton reagent. Schlesinger et al. [186] used nano-Fe₃O₄ to catalyze the ROS produced by UV-Fenton in an aqueous environment to degrade a variety of PFASs compounds, with a degradation rate of more than 90 %. They used fluorescent probes to confirm the presence of reactive oxygen in the reaction solution. As the pH value increases, the destruction efficiency of PFASs increases, achieving high-efficiency removal under neutral pH conditions. Nano-Fe₃O₄ still maintained its oxidation state and catalytic efficiency after multiple PFASs destruction.

4.1.2. Ozone oxidation

Ozone oxidation represents an efficient and low-residual water treatment technology with broad applications. The process operates through two primary mechanisms: (1) direct molecular interaction be-

tween ozone (O₃) and organic pollutants, and (2) indirect degradation via hydroxyl radicals ($\cdot\text{OH}$) generated from ozone decomposition [187], as exemplified in Equation 4–1. Characterized by secondary rate constants ranging from < 0.1 M/s to 7 × 10⁹ M/s, ozone predominantly acts as an electrophilic or nucleophilic agent depending on its electronic configuration and molecular structure. Despite its potent oxidative capacity (see Equation 4–2), ozone exhibits limited aqueous stability due to pH-dependent decomposition kinetics [185]. As a cornerstone of advanced oxidation processes (AOPs), ozone catalysis primarily enhances organic degradation through $\cdot\text{OH}$ generation, while alternative pathways involve catalyst-mediated complex formation to accelerate pollutant breakdown. This dual functionality underpins its widespread use in drinking water disinfection, micropollutant mineralization, and inorganic contaminant removal.



The ozone dosage critically determines oxidation efficiency and radical generation dynamics in PFASs degradation processes. This operational parameter governs reaction kinetics through two principal mechanisms. Increased ozone input enhances oxidative capacity by providing additional reactive oxidants for direct PFASs decomposition while simultaneously regulating $\cdot\text{OH}$ production via concentration-dependent decomposition pathways. Elevated ozone concentrations accelerate $\cdot\text{OH}$ formation through intensified O₃ autolysis and amplify chain reaction propagation by supplying surplus reactants for secondary radical generation including O₂^{•−} and ¹O₂. Empirical studies however reveal a paradoxical concentration threshold where excessive ozone dosing induces competitive scavenging effects. In such scenarios, superfluous radicals engage in mutual quenching reactions rather than targeting PFASs molecules[18]. Particularly in complex environmental matrices like landfill leachate, hyper-concentrated ozone and its derived reactive oxygen species have been identified as key drivers transforming PFAS precursors into detectable terminal products.

Ozone oxidation demonstrates significant potential for PFOS removal in water treatment applications. Thompson et al. [188] quantified PFAS concentrations in Australian water recycling facilities, detecting 3.7 ng/L PFOS and 16 ng/L PFOA in influent streams (secondary treated wastewater). Post-ozonation achieved effluent reductions to 0.7 ng/L PFOS and 12 ng/L PFOA, revealing differential removal efficiencies between PFAS species. Vo et al. [18] developed an ozone foam fractionation technique for PFAS removal from landfill leachate, achieving > 90 % long-chain PFAS elimination. The optimized system operated at 1 L/min ozone flow rate with 43 mg/L dosage, maintaining 4 % foam wettability while reducing foam volume by 2–4-fold through interfacial adsorption equilibrium analysis.

Dai et al. [189] systematically compared PFAS removal efficiencies across treatment modalities: UV irradiation alone (16.8 %), UV/O₃ integration (73 %), conventional air fractionation (81 %), and O₃-assisted air fractionation (>95 %). The superior performance of ozone-enhanced fractionation stemmed from $\cdot\text{OH}$ radical enrichment in microbubbles. Notably, perfluoroalkyl sulfonic acids (PFASs) exhibited higher removal than carboxylic analogs (PFCAs) due to enhanced hydrophobicity, while short-chain PFASs demonstrated exponentially decreasing removal efficiency with carbon chain reduction.

Huang et al. [19] developed a photocatalysis-ozone integrated system for PFOA degradation, demonstrating 99.1 % removal efficiency with 44.3 % defluorination after 4 h treatment—a marked improvement over standalone ozonation achieving merely 0.5 % defluorination under equivalent conditions. The hybrid process mechanistically resembles photo-Kolbe reactions through three sequential stages: (1) PFOA anion oxidation via carboxyl-to-photogenerated hole (h⁺) electron transfer generating PFOA radicals; (2) radical decarboxylation forming C₇F₁₅• intermediates; (3) $\cdot\text{OH}$ -mediated oxidation (from ozone-trapped photoelectrons) yielding thermally unstable C₇F₁₅OH, which subsequently

converts to $C_6F_{13}COF$ through β -scission and ultimately hydrolyzes to $C_6F_{13}COO^-$. Ozone supplementation enhanced quantum efficiency by 78 % through preferential hole-PFOA interaction over electron-hole recombination [190]. This synergistic mechanism enabled sustained radical generation, achieving near-complete mineralization while maintaining catalytic stability over multiple cycles.

4.1.3. Persulfate catalyzed oxidation

Persulfates constitute a class of compounds containing the persulfate anion ($S_2O_8^{2-}$), with common variants including ammonium ($(NH_4)_2S_2O_8$), potassium ($K_2S_2O_8$), and sodium ($Na_2S_2O_8$) salts. While stable at ambient conditions, the inherent peroxy ($-O-O-$) bond confers strong oxidative potential, evidenced by a standard redox potential ($E_0 = +2.01$ V) comparable to ozone ($+2.07$ V) [191]. Upon activation, persulfates generate sulfate radicals ($SO_4^{\cdot-}$) with elevated redox potential (2.5–3.1 V) capable of cleaving C-F bonds in PFASs [16]. However, unactivated persulfates exhibit limited PFAS degradation efficiency, necessitating activation strategies for enhanced reactivity.

Thermal activation (>140.2 kJ/mol energy input) cleaves the persulfate O-O bond to yield dual $SO_4^{\cdot-}$ radicals. Although elevated temperatures and concentrations accelerate radical generation and organic degradation, excessive heat promotes undesirable side reactions. Santos et al. [192] demonstrated complete defluorination of 0.1 mM PFOA within 18 h using 100 mM thermally activated persulfate (343.15 K), yet highlighted the economic and environmental impracticality of sustained thermal treatment. Their optimized system incorporated humic acid (HA, 600 mg/L) and Fenton reagents (165 mM H_2O_2 , 3 mM Fe^{3+}), achieving quantitative PFOA sequestration through HA-Fenton oxidation complexes. Under neutral pH, residual Fe^{3+} facilitated coagulation of HA-PFOA precipitates, while mechanistic studies revealed a stepwise decomposition pathway yielding shorter-chain PFOA ($PFHpA \rightarrow PFHxA \rightarrow PFPA \rightarrow PFBA$).

Photo-activation employs ultraviolet/visible irradiation to stimulate persulfate decomposition. Hori et al. [193] demonstrated that ultraviolet radiation (<270 nm) induces persulfate ($S_2O_8^{2-}$) photolysis, generating sulfate radicals ($SO_4^{\cdot-}$) with 11-fold enhanced PFOA degradation kinetics compared to direct photolysis. Using a 200 W xenon-mercury lamp, near-complete degradation of 1.35 mmol/L PFOA was achieved within 4 h irradiation.

Transition metal activation was the process of using transition metal ions (such as Ag^+ , Fe^{2+} , Co^{2+} , Zn^{2+} , Mn^{2+} , Ni^{2+} , etc.) to react with persulfate, so that the persulfate obtained an electron and was activated to produce sulfate free radicals. Taking ferrous ion (Fe^{2+}) as an example, the reaction equation for activating persulfate was shown in Eq (4–3). This activation method can be carried out at room temperature, and the operation was relatively simple. It was considered to be a common and effective method for producing sulfate free radicals. However, a single metal ion may encounter difficulties in the cyclic activation process, and the residual metal ions may cause secondary pollution to the environment [4].



Gevaerd et al. [194] developed reactive activated carbon (RAC) through zero-valent iron (ZVI, Fe^0) impregnation on granular activated carbon (GAC), establishing an adsorption-mediated PFAS degradation system. Experimental parameters including reaction temperature (60 °C), persulfate (PS) dosage, and soil composition were systematically evaluated for their impacts on PFAS removal. The RAC-PS system achieved complete catalytic oxidation of three carboxylate PFASs at 60 °C, generating short-chain derivatives through radical-mediated pathways. Sulfonate PFASs were effectively removed via adsorption, whereas carboxylate PFASs required combined physical adsorption and chemical decomposition. Carbon mass balance analysis revealed synergistic interactions between PFAS mineralization and ZVI oxidation through radical exchange mechanisms.

4.1.4. Photo-catalytic oxidation

The basic principle of photocatalytic degradation of PFASs was based on semiconductor photocatalytic theory [195]. When the photocatalyst was exposed to light with an energy greater than its bandgap width E_g , the electrons e^- in the valence band VB were excited to jump to the conduction band CB, leaving holes h^+ in the valence band to form electron-hole pairs. For example, the bandgap width of TiO_2 was about 3.2 eV. When it was irradiated with ultraviolet light with a wavelength less than 387 nm, electrons were excited to generate electron-holes. Photogenerated electrons and holes can undergo redox reactions with substances adsorbed on the surface of the photocatalyst. During the PFASs degradation process, photogenerated holes have strong oxidizing properties and oxidize water molecules or OH^- adsorbed on the catalyst surface to $\cdot OH$. They then undergo hydrogen abstraction, addition and other reactions with PFASs molecules, attacking the C-F bonds in the PFASs molecules, thereby degrading PFASs. At the same time, photogenerated electrons have reducing properties and can react with electron acceptors such as oxygen O_2 dissolved in water to generate active oxygen species such as superoxide radicals $\cdot O_2^-$ [196].

The direct action of sunlight or ultraviolet light on pollutants to decompose them was called photolysis. However, direct photolysis was usually slow and inefficient in degrading stable pollutants such as PFOA and PFOS. Therefore, it was necessary to add catalysts or combine with other technologies to enhance degradation. It was reported that under 254 nm ultraviolet light irradiation, the decomposition efficiency of PFOA reaches 17.5 % within 4 h, and the defluorination rate reaches 8.3 % [19]. The photon energy value of 254 nm ultraviolet light irradiation was 471.1 kJ/mol [197], while the energy value of a single F bond was (530 kJ/mol). Therefore, it was difficult for a single F bond to break under 254 nm ultraviolet light irradiation [198].

Cao et al. [199] synthesized $BiOI_{1-x}$ with abundant iodine vacancies by solvothermal and calcination methods, and degraded PFASs with a low-power ultraviolet light source. $BiOI_{1-x}$ has higher photocatalytic activity against PFOA. Under 5 W LED illumination, the degradation rate of PFOA by $BiOI_{1-x}$ calcined at 440 °C reached 51.9 % within 5 h. Active species capture, electron paramagnetic resonance spectroscopy and electrochemical analysis showed that the main active species in the system were photogenerated holes, followed by $\cdot OH$. The presence of iodine vacancies significantly improved the separation efficiency of carriers and improved the photocatalytic performance. And the degradation pathway of PFOA in this system was further proposed.

Banayan et al. [200] systematically compared photo-chemical/catalytic oxidation versus reduction mechanisms for diverse PFAS structures, evaluating the effects of redox mediators including inorganic ions (persulfate/sulfite), organic solutes (amino-polycarboxylic acids), and photocatalysts. The study identified distinct degradation pathways: oxidative processes dominated by sulfate radicals ($SO_4^{\cdot-}$) and photogenerated holes (h^+) versus reductive pathways mediated by hydrated electrons (e_{aq}^-). Oxidative degradation proceeded through three concurrent mechanisms: (1) single-electron transfer to photoinduced oxidants, (2) functional group desorption, and (3) perfluorocarbon chain shortening. Conversely, reductive decomposition involved: (1) C-F bond cleavage, (2) functional group dissociation with subsequent chain truncation, and (3) central C-C/C-O bond scission through e_{aq}^- -mediated reactions. These differential pathways exhibited strong structural dependency, particularly regarding functional group chemistry and carbon chain length.

Long-chain PFASs (such as PFOA) were mainly degraded through $SO_4^{\cdot-}$ and h^+ . The degradation efficiency of short-chain PFASs was usually lower than that of long-chain PFASs because of their shorter carbon chains and the limited attack sites. The disparity arises from differential adsorption on photocatalysts, hydrophobic long-chain PFASs readily concentrate on catalyst surfaces, enhancing radical exposure. Short-chain PFASs exhibit weaker adsorption due to higher hydrophilicity, reducing interfacial reaction efficiency.

4.1.5. Electrochemical oxidation

Electrochemical oxidation (EO) was a promising technology for degrading PFASs, which produces strong oxidants through in-situ electrolysis to oxidize pollutants, especially $\cdot\text{OH}$. Electrocoagulation (EC) relied on electrolytic dissolution to form insoluble metal hydroxides and other hydroxyl metal compounds, leading to the formation of flocs. However, EO and EC have inherent problems such as electrode passivation, anode poisoning, and electrolytic sludge. Due to the chemical and physiological inertness of PFASs, electrochemical advanced oxidation processes offered the advantage of synergistic effects.

The electrocatalytic system usually consists of an anode and a cathode. When an external power supply applies voltage, an electric field was formed in the system [201]. In the electrochemical oxidation process of PFASs, the anode material was the main factor affecting the oxidation process. Anode materials with high oxygen evolution potential and good stability were very necessary. Otherwise, due to a large amount of O_2 precipitation, the current efficiency was low and no effective electrochemical reaction will be carried out [202]. Typical anode materials that can effectively oxidize PFCs were usually boron-doped diamond (BDD) and some undoped or doped oxides (PbO_2 , SnO_2 , RuO_2 , IrO_2 , TiO_2) [203].

In addition to the electrode material, factors such as electrolyte type, current density, and initial pH value of the solution also affected the oxidation effect. For example, when the electrolyte was NaClO_4 , active chlorine species with strong oxidizing properties, such as $\cdot\text{Cl}$, $\cdot\text{Cl}_2$, HClO and ClO_3^- , will be produced during the electrolysis process, promoting the electrochemical degradation reaction [204]. The current density affected the degradation and defluorination rate of PFOA, mainly affecting the electron transfer capacity of the electrolysis system and the generation of hydroxyl radicals. In general, the removal rate increased with the increase of current density. It was more suitable for the degradation of PFOA under acidic conditions [203]. Under acidic conditions, the oxygen evolution potential was higher, and the oxygen evolution side reaction was not easy to occur, which increased the $\cdot\text{OH}$ yield. Under alkaline conditions, OH^- will adsorb on the electrode surface and lose electrons due to electrostatic force. OH^- competed with $\text{CF}_3(\text{CF}_2)_6\text{COO}^-$ anions for active sites and inhibited the decarboxylation reaction [202]. Long-chain PFASs were more prone to electrochemical oxidation because their C-F bonds were more likely to be broken. The removal efficiency of short-chain PFASs was relatively low and require higher current density or longer reaction time [205]. Long-chain PFASs preferentially accumulate at electrode interfaces due to hydrophobic interactions, concentrating oxidation targets. Short-chain PFASs analogs exhibit weaker adsorption and higher mobility in aqueous matrices, reducing electrode contact frequency.

Pierpaoli et al. [20] used PFOA and PFOS as representatives of landfill leachate and conducted a decomposition experiment of PFASs on a boron-doped diamond electrode (BDD). It was found that low-doped BDD had a good removal effect on COD (removal rate was 59 % after 8 h). When the current density was 75 Ma/cm, the average removal rates of PFOA and PFOS were 80 % and 78 %, respectively. The presence of degradation intermediates during the electrolysis process was also monitored. After 8 h of electrolysis of landfill leachate, the presence of long-chain degradation products C_6F_{13} and $\text{C}_6\text{F}_{13}\text{COO}^-$ was observed only in the 10 k BDD-PFOA test.

4.1.6. Thermal catalytic oxidation

Most chemical treatments cannot completely break the C-F bond in PFASs, so for the treatment of PFASs, more attention should be paid to its mineralization efficiency. High temperature can provide energy for the thermal decomposition of PFASs, and as the reaction temperature increases, the degradation efficiency of PFASs increases. There were also studies on the degradation of PFASs by low-temperature thermal treatment. Although temperatures below 80 °C were extremely unfavorable for PFOA degradation, after the addition of persulfate, the degradation rate and defluorination rate of PFOA after 6 h of reaction were as high as

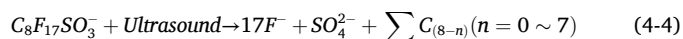
more than 99 % and 77.5 %, respectively [206]. It was also found that the addition of activated carbon to the thermally activated persulfate system was conducive to the defluorination and degradation of PFOA at relatively low temperatures (25 °C–45 °C). After 12 h of reaction (25 °C), the degradation rate and defluorination rate of PFOA reached 68.2 % and 54.9 %, respectively, which are 5 times and 18 times that of persulfate alone (15.1 % and 3.1 %) [21]. In the thermally activated persulfate system, PFSA was oxidized to generate PFCA at a temperature of 120 °C and when $\text{pH} > 12$, which was further deeply defluorinated under the action of UV-sulfite with a defluorination rate of up to 92 % [207].

For PFASs, hydrothermal technology was a very promising treatment technology with great potential for degrading pollutants. The energy required heating water to a subcritical state was less than that for low-temperature evaporation, and the dielectric constant of water will also drop from 80 (25 °C) to 20 (350 °C), which was more conducive to the degradation of PFASs [208]. Hori et al. [209] treated PFASs in water under subcritical conditions at a reaction temperature of 350 °C. In the absence of a catalyst, the defluorination rates of PFHxS and PFOS were only 3.27 % and 0.16 %, and the degradation rates were only 7.6 % and 9.7 %. After adding zero-valent iron, the defluorination rates increased to 40.3 % and 51.4 %, respectively, and the degradation rates reached 86.8 % and more than 99 %. The process was accompanied by the generation of a small amount of CHF_3 . It was found that Fe had a much higher effect on PFOS in subcritical water than Zn and Cu, while Al had almost no catalytic effect.

The effect of acidity and alkalinity on the hydrothermal degradation of PFASs was also very significant. Wu et al. [210] added 1 mol·L⁻¹ NaOH to the hydrothermal system at 350 °C. After 90 min, the defluorination rate of PFOS reached 80 %, and the degradation rate reached about 90 %, which was much higher than the defluorination and degradation effect without NaOH. At the same time, a small amount of short-chain PFAC was also detected. Based on this, Hao et al. [211] used alkaline hydrothermal method to treat mixed PFASs in aqueous film-forming foam (AFFF). It found that when the NaOH concentration was 1 mol/L, the concentration of most PFASs was lower than the detection limit after 15 min of reaction at 350 °C. When the NaOH concentration was increased to 5 mol/L, the defluorination effect of nearly 100 % could be achieved after 90 min of reaction.

4.1.7. Ultrasonic catalytic oxidation

Ultrasonic treatment operates through cavitation bubble formation in liquids. During bubble collapse, substantial energy release creates transient localized conditions (4000 K, 1800 atm) that thermally dissociate water molecules into hydroxyl radicals ($\cdot\text{OH}$) and hydrogen radicals ($\text{H}\cdot$) within the cavitation zone. Moriwaki et al. [212] demonstrated PFOS degradation via sonolysis proceeds through two phases: initial chain-shortening to fluorinated intermediates, followed by complete mineralization to fluoride (F^-) and sulfate (SO_4^{2-}) ions, as mechanistically described in Equation (4–4).



Shende et al. [22] investigated ultrasonic degradation of PFOA and PFOS under 575 kHz frequency and 77 W/L power density, demonstrating superior degradation efficiency for PFOA relative to PFOS, though exhibiting an inverse correlation with elevated PFAS concentrations. Hu et al. [213] reported 29.6 % degradation and 7.7 % defluorination for PFOA via standalone sonolysis, while potassium permanganate supplementation enhanced removal to 84.3 % degradation with 63.1 % defluorination. Field applications revealed significant influence of aquatic matrices on treatment efficacy. Cheng et al. [214] applied sonochemical treatment to landfill-adjacent groundwater containing co-contaminants (organic matter/PFASs), observing 20.5–29.7 % lower PFAS removal efficiencies compared to pure water systems. Primary inhibition stemmed from volatile organic compounds

(VOCs), accounting for reduced PFOA/PFOS degradation rates, whereas soluble natural organic matter (NOM) exhibited negligible impacts on PFAS sonolysis.

Rodriguez-Freire et al. [215] investigated the sonochemical degradation of PFOS under varying acoustic frequencies and initial concentrations. At 500 kHz, PFOS degradation (10–460 μM) followed pseudo-first-order kinetics with rate enhancement proportional to concentration increase. When frequency was elevated to 1 MHz, pseudo-first-order kinetics governed PFOS degradation within 10–100 μM , achieving complete degradation in this range. For concentrations exceeding 100 μM , zero-order kinetics prevailed, rendering degradation rates concentration-independent. Notably, comparable degradation efficiencies emerged at 460 μM between 500 kHz and 1 MHz systems, attributed to reduced cavitation bubble lifetime (1.05 μs vs 2.1 μs) and collapse intensity at higher frequencies. These compressed bubble dynamics diminished radical generation, thereby impairing degradation efficacy. While ultrasonic treatment demonstrates effectiveness across broad PFOS concentrations (10–460 μM), current applications remain confined to laboratory-scale experimentation.

The degradation effects and mechanisms of the above-mentioned oxidation reactions on long/short-chain PFASs are classified and summarized, as shown in Table 5. Within advanced oxidation processes, degradation discrepancies originate from molecular structural responses to radical attacks. Long-chain PFASs undergo preferential $\cdot\text{OH}$ or $\text{SO}_4^{\cdot-}$ targeting at terminal carboxyl/sulfonate groups due to lower C-F bond dissociation energies (105–115 kcal/mol), initiating chain-reaction degradation via sequential decarboxylation/desulfonation. Short-chain homologues, however, exhibit structural compactness and higher perfluorination degrees that elevate C-F bond stability (118–125 kcal/mol) and reduce accessible radical attack sites, resulting in markedly reduced degradation efficiencies under conventional AOPs such as UV/ H_2O_2 .

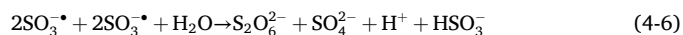
4.2. Advanced reduction degradation

Advanced reduction processes (ARPs) represent an emerging technology for PFASs degradation, utilizing strongly reducing hydrated electrons (e_{aq}^-) and hydrogen atoms ($\text{H}\cdot$) generated via ultraviolet-excited photosensitizers to achieve efficient defluorination while minimizing fluorinated intermediate accumulation. The high electronegativity of fluorine atoms renders C-F bonds particularly susceptible to electron attack, enabling simultaneous cleavage of C-F and C-C bonds [131,240,241], making reductive degradation outperform oxidative approaches. Hydrated electrons are typically produced through UV-activated photosensitizers like sulfite (SO_3^{2-}), iodide (I^-), and hexacyanoferrate ($\text{Fe}(\text{CN})_6^{4-}$), whereas hydrogen atoms predominantly originate from UV/ H_2O_2 or UV/sulfite systems. These $\text{H}\cdot$ radicals initiate PFAS degradation via hydrogen abstraction from C-H bonds.

ARPs demonstrate complete mineralization of diverse PFASs across aqueous matrices, particularly excelling in high-fluorine systems. However, photosensitizers can easily affect the chemical stability of water bodies and pose environmental risks. A large number of studies have shown that the ultraviolet-sulfite method (UV/ SO_3^{2-}) and the ultraviolet-potassium iodide method (UV/KI) have effective degradation effects on various PFASs in water. Although the use of advanced reduction technology to remove PFASs in water has a high degradation efficiency, the reaction was greatly affected by coexisting ions in the system, and large-scale in-situ removal of PFASs was still difficult.

4.2.1. UV sulfite (UV/ SO_3^{2-})

UV SO_3^{2-} was to generate e_{aq}^- and $\text{SO}_3^{\cdot-}$ by UV irradiation of SO_3^{2-} , thereby degrading PFAS. The chain reaction of SO_3^{2-} photoionization to generate active groups was as follows [242] (eqs 4–5–4–8). Under alkaline conditions, SO_3^{2-} will photolyze to produce hydrated electrons and $\text{SO}_3^{\cdot-}$. The hydrated electrons attacked the fluorine atoms on the α -carbon to gradually defluorinate PFOA and degrade to generate short-chain PFAS.



Ren et al. [243] employed UV/sulfite systems for aqueous PFOA degradation (10 $\text{mg}\cdot\text{L}^{-1}$ initial concentration, pH 12), achieving 98 % removal after 24 h. Carbonate and nitrate co-contaminants exhibited inhibitory effects through UV absorption and hydrated electron (e_{aq}^-) scavenging. Song et al. [244] demonstrated near-complete PFOA degradation (88.5 % defluorination) in UV- $\text{SO}_3^{2-}\text{-N}_2$ systems, where elevated sulfite concentrations and alkaline conditions enhanced e_{aq}^- generation. The suppression effect of $\text{NO}_3^-/\text{NO}_2^-$ additives confirmed e_{aq}^- pivotal role in PFOA decomposition. Vacuum ultraviolet (VUV) irradiation further amplified e_{aq}^- quantum yields via water ionization, capitalizing on shorter wavelengths and higher photon energies.

Gu et al. [245] compared PFOS degradation efficiencies between UV254 and VUV185 systems. While UV254 or sulfite alone showed no PFOS removal, VUV185 achieved 46.2 % degradation in 4 h through water-derived radicals (e_{aq}^- , $\text{H}\cdot$). The VUV/ SO_3^{2-} system outperformed UV/ SO_3^{2-} , attaining 97.3 % versus 85.8 % PFOS removal via synergistic mechanisms (Equations 4–9–4–10). These findings underscore VUV capacity to enhance PFAS degradation kinetics in sulfite-mediated advanced reduction processes.



UV/ SO_3^{2-} photogenerated e_{aq}^- also has a good degradation effect on short-chain PFASs substances. Bao et al. [246] demonstrated the superior efficacy of UV254/ SO_3^{2-} systems for short-chain PFAS degradation, achieving complete GenX removal within 2 h (>90 % defluorination after 6 h), a stark contrast to UV/ $\text{S}_2\text{O}_8^{2-}$ systems showing < 5 % GenX degradation under identical conditions. This disparity highlights the limited oxidative contribution of $\cdot\text{OH}/\text{SO}_4^{\cdot-}$ radicals toward short-chain PFASs decomposition. The UV/ SO_3^{2-} system generates both hydrated electrons e_{aq}^- and hydrogen atoms $\text{H}\cdot$ simultaneously, e_{aq}^- dominate short-chain PFASs degradation. Hydrogen atoms $\text{H}\cdot$ can assist decarboxylation, but dissolved oxygen suppresses this contribution. Hydrated electrons e_{aq}^- drive defluorination as the core mechanism, they directly cleave C-F bonds through electron transfer.

Hydrated electrons (e_{aq}^-) were considered to be effective nucleophiles for the decomposition of PFASs, but e_{aq}^- in previous studies was usually limited to anaerobic or highly alkaline environments. Zhai et al. [247] effectively degraded hexafluoropropylene oxide trimer acid (HFPO-TA) (81.92 %, 0.834 h^{-1}) and defluorination rate (48.99 %, 0.312 h^{-1}) by UV/ $\text{SO}_3^{2-}/\text{I}^-$ under neutral and mild conditions. I^- was the main source of e_{aq}^- in the system, and SO_3^{2-} played a role in regenerating I^- and removing oxidative substances. Therefore, UV/ $\text{SO}_3^{2-}/\text{I}^-$ performed better than other systems under mild conditions. Electron paramagnetic resonance (EPR) and quenching experiments determined that e_{aq}^- was the main active component, and there was no signal without UV irradiation. After ultraviolet irradiation, the characteristic peak of DMPO- $\text{H}\cdot$ was detected, and the signal intensity increased with the increased of light excitation time. This indicated that UV/ $\text{SO}_3^{2-}/\text{I}^-$ can efficiently and continuously produce e_{aq}^- . A degradation process was proposed, in which e_{aq}^- first attacked the ether bond (C6-O7) to produce HFPO-DA, TFA, acetic acid and formic acid. The degradation processes of HFPO-DA (short chain) and hexafluoropropylene oxide tetrameric acid (HFPO-TeA) (long chain) were further compared. The defluorination efficiencies of HFPO-DA, HFPO-TA and HFPO-TeA were 64.66 %, 48.79 % and 23.62 %, respectively, and the rate constants were

Table 5

Degradation effects and mechanisms of various oxidation reactions on long/short chain per-and polyfluoroalkyl substance.

Oxidation	Catalyst	PFASs	C-F	Long/ Short chain	C ₀ (mg/L); removal rate	K (min ⁻¹)	Cost	Mechanism	Refs
Fenton	Iron-modified diatomite	PFOA	7	Long chain	10; 83 %	-	1.5 mol/L H ₂ O ₂	O ₂ ^{-•} , ·OH	[216]
Fenton	Carbon/MnO ₂ particles	PFOA	7	Long chain	0.1; 73 %	0.0930	0.03 mol/L H ₂ O ₂	O ₂ ^{-•} , ·OH	[217]
Photo-Fenton	UVC light sources	PFBS	4	Short chain	0.01; 13 %	-	0.6 mM H ₂ O ₂	·OH	[218]
Electro-Fenton	Fe ₃ O ₄ modified reduced graphene oxide aerogel	PFOA	7	Long chain	100; 98.25 %	0.0107	23.4 kWh g-TOC ⁻¹	O ₂ ^{-•} , ·OH	[219]
Electro-Fenton	Cu modified reduced graphene oxide aerogel	PFOA	7	Long chain	100; 98.25 %	0.0096	23.3 kWh g-TOC ⁻¹	O ₂ ^{-•} , ·OH	[219]
Electro-Fenton	Ti/BDD and Ti/IrO ₂ electrodes	GenX	4	Short chain	10 ng/L; 95 %	-	15 mA/cm ² current density	·OH, Electron transfer	[220]
Electro-Fenton	Ni-foam and boron doped diamond	GenX	4	Short chain	18; 92.2 %	0.0175	2.03 kWh g-TOC ⁻¹	·OH, Electron transfer	[221]
Electro-Fenton	Boron-doped diamond (BDD)	PFOA	7	Long chain	5; 97 %	0.0103	2.03 kWh g-TOC ⁻¹	·OH	[222]
Ozonation	Heterogeneous	PFOA	7	Long chain	0.015; 90 %	-	1.29 g/h O ₃	O ₃	[18]
Ozonation	2.2 mg/min ozone	PFPeA	4	Short chain	171 ng/L; 46 %	-	10 mg/L O ₃	O ₃	[223]
Ozonation	2.2 mg/min ozone	PFHxA	5	Short chain	219 ng/L; 21 %	-	173 mg/L O ₃	O ₃	[223]
Ozonation	2.2 mg/min ozone	PFHpA	6	Short chain	134 ng/L; 84 %	-	173 mg/L O ₃	O ₃	[223]
Ozonation	2.2 mg/min ozone	PFBS	4	Short chain	62 ng/L; 15 %	-	10 mg/L O ₃	O ₃	[223]
Photo-electro-ozonation	TiO ₂	PFOA	7	Long chain	10; 99.1 %	-	0.05 kWh g-TOC ⁻¹	·OH, h ⁺	[19]
Persulfate	NaOH-modified activated carbon fiber	PFOA	7	Long chain	100, 93.63 %	0.0468	0.002 mol /L PMS	¹ O ₂ , O ₂ ^{-•} , SO ₄ ^{-•} , ·OH	[224]
Persulfate	N-doped citrate-sludge-derived carbon	PFOA	7	Long chain	2, 99.8 %	0.1088	0.01 mol /L PMS	¹ O ₂ , SO ₄ ^{-•} , ·OH, Electron transfer	[225]
Thermally-persulfate	Heterogeneous	PFOA	7	Long chain	0.2; 93.5 %	0.0013	4398 kWh g-TOC ⁻¹	SO ₄ ^{-•}	[226]
Thermally-persulfate	Carbon Aerogel	PFOA	7	Long chain	100; 85.7 %	0.0056	16.36 kWh g-TOC ⁻¹	SO ₄ ^{-•}	[227]
Thermally-persulfate	Laser	PFBA	3	Short chain	50 mM;	5.4 × 10 ⁵	4.9 ± 0.2 mJ Laser	SO ₄ ^{-•}	[228]
Thermally-persulfate	Laser	TFA	1	Short chain	50 mM;	4.9 × 10 ⁵	4.9 ± 0.2 mJ Laser	SO ₄ ^{-•}	[228]
Photo-persulfate	Heterogeneous	PFBS	4	Short chain	5; 13.1 %	-	100.67 kWh g-TOC ⁻¹	e _{aq} ^{-•}	[229]
Electro- Persulfate	Ti ₄ O ₇	PFOA	7	Long chain	10; 99.9 %	0.1590	0.34 kWh g-TOC ⁻¹	SO ₄ ^{-•} , ·OH, Electron transfer	[230]
Electro- Persulfate	Fe foam	PFOA	7	Long chain	100; 80.2 %	0.023	0.14 kWh g-TOC ⁻¹	SO ₄ ^{-•} , ·OH	[231]
Electron- persulfate	Heterogeneous	PFOS	8	Long chain	10; 65.6 %	-	1957 kWh g-TOC ⁻¹	e _{aq} ^{-•} , SO ₄ ^{-•} , ·OH	[232]
Electron- ultrasonic-persulfate	Ti/SnO ₂ -Sb/Ce-PbO ₂	PFOA	7	Long chain	60; 98.7 %	-	9.5 kWh g-TOC ⁻¹	·OH, Bubble collapse	[233]
Photo	Heterogeneous	PFOA	7	Long chain	1; 100 %	0.0017	150 kWh g-TOC ⁻¹	Bond cleavage	[234]
Photo	Fe(III)-loaded zeolites	PFOS	8	Long chain	20; 99 %	0.0050	1010.53 kWh g-TOC ⁻¹	Electron transfer	[235]
Photo	Heterogeneous	PFOS	8	Long chain	1.4; 97.9 %	-	0.0098 kWh g-TOC ⁻¹	e _{aq} ^{-•} , I ^{-•} , Electron transfer	[236]
Photo	Heterogeneous	PFPeA	4	Short chain	1; 60 %	0.0014	150 kWh g-TOC ⁻¹	Bond cleavage	[234]
Photo	Heterogeneous	PFHxA	5	Short chain	1; 60 %	0.0016	150 kWh g-TOC ⁻¹	Bond cleavage	[234]
Photo-persulfate-iodide	Heterogeneous	PFHxA	5	Short chain	7.5; 90 %	0.3250	623.7 kWh g-TOC ⁻¹	e _{aq} ^{-•} , I ^{-•} , h ⁺	[237]
Photo-persulfate-iodide	Heterogeneous	PFHpA	6	Short chain	101; 90 %	0.2917	529.7 kWh g-TOC ⁻¹	e _{aq} ^{-•} , I ^{-•} , h ⁺	[237]
Photo-electrocatalytic Ozonation	BiOCl /reduced Graphene	PFOA	7	Long chain	10; 95.4 %	72.8	661.2 kWh g-TOC ⁻¹	·OH, h ⁺	[238]
Electron	Boron-doped diamond (BDD)	PFBS	4	Short chain	3; 80 %	0.0003	2197.5 kWh g-TOC ⁻¹	·OH, electron transfer	[205]
Electron	Boron-doped diamond (BDD)	PFHxA	5	Short chain	0.8; 95 %	0.0017	586 kWh g-TOC ⁻¹	·OH, electron transfer	[205]
Electron	Boron-doped diamond (BDD)	PFOA	7	Long chain	1.3; 95 %	0.0018	1300 kWh g-TOC ⁻¹	·OH, electron transfer	[205]
Thermal activation	Heterogeneous	PFOA	7	Long chain	1; 70 %	0.0031	-	Bond cleavage	[234]
Alkaline thermal	Heterogeneous	PFBS	4	Short chain	1.5; 80 %	0.0015	5 mol/L NaOH	Bond cleavage	[211]
Alkaline thermal	Heterogeneous	PFOA	7	Long chain	1.5; 90 %	0.0020	5 mol/L NaOH	Bond cleavage	[211]
Ultrasonic	Heterogeneous	PFOA	7	Long chain	1; 99 %	0.0444	567 kWh g-TOC ⁻¹	bubble collapse	[239]
Ultrasonic	Heterogeneous	PFOS	8	Long chain	1; 90 %	0.0153	1644 kWh g-TOC ⁻¹	bubble collapse	[239]
Ultrasonic	Heterogeneous	GenX	4	Short chain	1; 90 %	0.0501	502 kWh g-TOC ⁻¹	bubble collapse	[239]

0.257 h⁻¹, 0.160 h⁻¹ and 0.050 h⁻¹, respectively. Short-chain HFPOs were easier to defluorinated than long-chain HFPOs.

4.2.2. UV potassium iodide (UV/KI)

In the UV/KI system, I⁻ absorbed UV energy under ultraviolet light and then transitions to an excited state (I•, H₂O^{•+}) (Eq 4-11). This state was unstable and can decay back to I⁻ and H₂O or decompose into intermediate products (I•, e⁻) (Eqs 4-12–4-13). The intermediate state (I•, e⁻) meant that the electron was free near the I atom and eventually dissociated to produce I• and e_{aq}⁻ (Eq 4-14). In the UV/KI system, I• and e_{aq}⁻ were produced in pairs, and I• undergoes a series of reactions in the solution (Eqs 4-15–4-19) [248]. Increasing the concentration of KI can improve the degradation of PFASs. But the degradation of PFASs by the UV/KI system will be inhibited when the concentration increased to above 10 mmol·L⁻¹. This was because as the initial concentration of KI increased, the oxidative I₃⁻ accumulated in the solution (Eqs 7-19) which consumed the amount of e_{aq}⁻. It involved in the reduction degradation and inhibited the degradation of PFASs (Eqs 20-21) [249].



Jiang et al. [250] developed an integrated adsorption-photoreduction system using magnetic modified clay (MMC), achieving near-quantitative adsorption efficiency (≈100 %) for six regulated PFASs. Subsequent 285 nm UV irradiation under optimized conditions (pH 12, 10 mM KI) enabled 66.5 ± 1.1 % total defluorination over 48 h. The MMC adsorbent demonstrated excellent regenerability over five cycles with < 10 % efficiency loss. Liu et al. [237] added iodine (I⁻) to the UV/sulfite system (UV/S) to significantly accelerate the reduction degradation of PFSA, (C_nF_{2n+1}SO₃⁻) and PFCAs (C_nF_{2n+1}COO⁻). Using C₄F₉SO₃⁻ as a probe, the UV/sulfite and iodide system (UV/S+I) was optimized for the degradation of PFASs. In UV/S+I, the kinetics of PFASs decay, defluorination, and transformation products were 3 times faster than in UV/S, but the maximum defluorination rates of the two systems were similar. The relative quantum yield of e_{aq}⁻ produced by I⁻ was higher, and the utilization rate of hydrated electrons (e_{aq}⁻) in UV/S+I and UV/I was twice that in UV/S. At the same time, the rapid scavenging of active iodine by SO₃²⁻ extended the lifetime of e_{aq}⁻ in UV/S+I by eight times compared with that in UV/I. The optimized UV/S+I system has a removal efficiency of more than 99.7 % for most PFASs and PFCAs, and the total defluorination rate was also greater than 90 % in the synthetic solution of concentrated PFASs mixture and NaCl.

Park et al. [251] investigated the decomposition of 6 PFASs with different head groups and carbon chain lengths in the UV/KI system, including PFOA, PFOS, PFHxS, PFHxA, PFBA, and PFBS. They conducted in-depth research on the hydrated electrons generated by

UV-254 nm during iodine photolysis. The cyclic voltammogram (CV) showed that a potential of + 2.0 V (relative to NHE) was required to induce PFC oxidation, while a potential of -1.0 V was required to induce PFC reduction, indicating that PFASs reduction was thermodynamically preferred. Scattering Compared with the generation of hydrated electrons (E°=-2.9 V) by UV (254 nm)/iodine (I⁻) photolysis, PFASs degraded faster during the generation of sulfate radicals (E°=+2.4 V) by UV (254 nm)/persulfate (S₂O₈²⁻) photolysis. The reason was that the scavenging effect of hydrated electrons of photogenerated triiodide (I₃⁻) can reach a steady-state concentration proportional to [PFOS]₀, thereby reducing the efficiency of the UV/iodide system for PFASs degradation. The kinetics of PFASs photoreduction were related to the PFASs head group, perfluorocarbon chain length, initial PFASs concentration, and iodine concentration. The pH has no significant effect on the kinetics of PFASs photoreduction, indicating that hydrated electrons were the main reducing agent and the contribution of H[•] can be ignored.

I⁻ was prone to produce a variety of iodine derivatives including iodoacetic acid and iodoform during water treatment, which have stronger genotoxicity and cytotoxicity than chloro derivatives [236]. Therefore, it was necessary to focus on the application field and the boundary of KI dosage, and monitor the iodine derivatives.

4.3. Degradation pathways of advanced oxidative PFASs

The core mechanism of advanced oxidation processes (AOPs) for PFAS degradation lies in generating strongly oxidative radicals to disrupt PFASs' stable fluorocarbon structures. Current AOPs targeting PFASs and emerging contaminants primarily include Fenton systems, ozonation, persulfate activation, photocatalysis, electrocatalysis, thermal catalysis, and sonocatalysis - all previously discussed. Distinct oxidation systems and radical species induce varied bond cleavage patterns in PFASs, with radical attack positions critically determining degradation pathways.

In Fenton and Fenton-like systems, ferrous ions (Fe²⁺) react with hydrogen peroxide (H₂O₂) to generate hydroxyl radicals ·OH (2.8 V). It can attack the carboxyl carbon of PFOA, triggering a series of reactions that cause the C-F bond to break. There are also Fenton-like reactions by introducing other transition metal ions (such as Co²⁺, Cu²⁺, etc.) or changing the reaction conditions. O₃ itself has a high oxidation potential (2.07 V) and can react directly with PFASs molecules. At the same time, O₃ decomposes in water to produce ·OH. The efficiency of ozone oxidation alone was limited, but combined with other technologies (such as O₃/H₂O₂ system) can significantly improve the degradation ability of PFASs.

Persulfate-based systems activate S₂O₈²⁻ or HSO₅ via thermal, photolytic, or metallic activation to yield SO₄^{•-} radicals (E°=2.5–3.1 V). These sulfate radicals degrade PFASs through electron transfer and addition mechanisms-particularly effective against PFOS by targeting sulfonic acid groups. Photocatalytic systems utilize semiconductors (TiO₂, ZnO, g-C₃N₄) to generate electron-hole pairs under irradiation, producing ·OH through water/OH⁻ oxidation. These AOPs collectively destabilize PFASs via radical-mediated C-F bond cleavage and functional group modification, achieving progressive chain-shortening from long-chain precursors to short-chain intermediates, ultimately mineralizing them into inorganic constituents (F⁻, CO₂, etc.).

Fu et al. [252] engineered iron-doped sludge biochar (ISBC) through EDTA-citric acid leaching and pyrolysis, demonstrating exceptional peroxymonosulfate (PMS) activation for PFOA degradation. The ISBC coral-like porous architecture, characterized by high surface area (312 m²/g) and pore volume (0.58 cm³/g), coupled with homogeneous iron/nitrogen distribution (Fe: 4.7 wt%, N: 3.2 wt%), facilitated interfacial PMS activation. Integrated DFT calculations (Bader charge analysis) with experimental validation revealed ¹O₂ mediated C-F bond cleavage preferentially occurring at the terminal -CF₃ group (activation energy: 1.7 eV), followed by progressive chain-shortening via β-scission

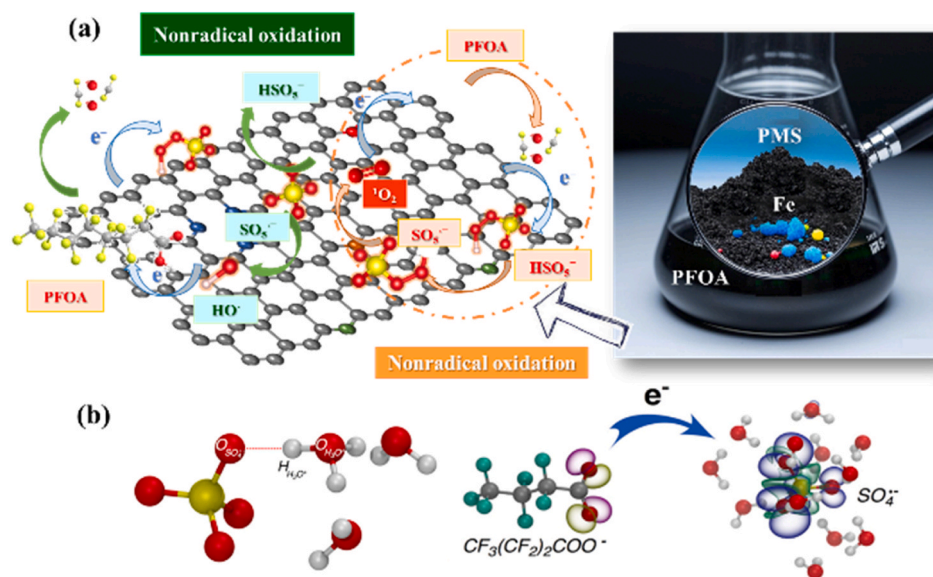
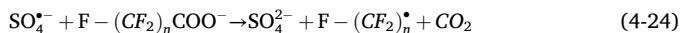


Fig. 3. (a) Mechanism scheme of PFOA removal in ISBC/PMS system; (b) Protonation behavior of sulfate radicals and degradation pathway for short-chain PFASs. Reprinted with permissions from Elsevier. Copyright 2022 Elsevier B.V. All rights reserved and Copyright © 2021, American Chemical Society [228,252].

(Fig. 3a). The non-radical mechanism, governed by surface-confined electron shuttle processes (Equations 4-22–4-23).



Carre-Burritt et al. [228] investigated persulfate degradation mechanisms for short-chain PFCAs (PFBA, TFA). Experimental and computational analyses revealed distinct pathways versus long-chain PFOA degradation. Density functional theory (DFT) calculations on optimized $\text{SO}_4^{\cdot-}(\text{H}_2\text{O})_3$ clusters reveal protonated species exist as H_3O^+ contact pairs or solvent-separated ion pairs with $\text{SO}_4^{\cdot-}$ when 3 water molecules coordinate rather than forming stable covalent HSO_4^- configurations. Fig. 3b details activated persulfate degradation of PFCAs. Single electron transfer (SET) initiates the reaction sequence. Persulfate activation generates $\text{SO}_4^{\cdot-}$ radicals via thermal photolytic or transition metal pathways. This radical exhibits strong oxidation capability with 2.437 V reduction potential. $\text{SO}_4^{\cdot-}$ abstracts electrons from short-chain PFASs carboxylate groups like $\text{CF}_3(\text{CF}_2)_2\text{COO}^-$ inducing decarboxylation. Resultant perfluoroalkyl radicals $\text{F}-(\text{CF}_2)_n\cdot$ undergo sequential β -scission of CF_2 units achieving complete mineralization to CO_2 and F^- (Equations 4-24).



Cho et al. [228] systematically evaluated PFOA degradation across three systems (TiO_2 , VUV, TiO_2/VUV) under varying pH conditions. The hierarchical degradation efficiencies at 6 h were: TiO_2/VUV (pH4, 98.3 % degradation, 52.4 % defluorination) > TiO_2/VUV (pH10) > VUV (pH4) > VUV (pH10) > TiO_2 (pH4) > TiO_2 (pH10), demonstrating optimal performance in acidic TiO_2/VUV systems. Chen et al. [229] engineered a Pb-doped TiO_2/UV system exhibiting 32.5-fold enhanced PFOA degradation versus undoped TiO_2/UV . This enhancement stemmed from bandgap engineering reducing electron-hole recombination (PL intensity decreased 78 %), thereby improving quantum efficiency. As illustrated in Fig. 4, UV-excited Pb- TiO_2 initiates C-C bond cleavage between - C_7F_{15} and - COOH groups via hole-mediated oxidation ($k = 0.142 \text{ min}^{-1}$). The resultant perfluoroalkyl radicals undergo hydrolysis and β -elimination, sequentially generating $\text{C}_6\text{F}_{13}\text{COF} \rightarrow \text{PFHpA} \rightarrow \text{PFHxA} \rightarrow \text{PFPeA} \rightarrow \text{PFBA} \rightarrow \text{PFPrA} \rightarrow \text{TFA}$, ultimately mineralizing to CO_2 and F^- through continuous chain-shortening pathways.

Short-chain PFASs demonstrate weaker adsorption capacity compared to long-chain PFASs. Wen et al. [253] identified non-sequential defluorination during short-chain PFAS degradation. GenX exhibits substantially diminished hydrophobicity relative to PFOA and PFOS, limiting catalyst surface contact and impairing photocatalytic rates. Fig. 4b reveals GenX undergoing fragmentation rather than sequential - CF_2 - unit removal characteristic of long-chain PFASs, directly yielding short-chain products. Each mole of degraded GenX generates two moles of ultrashort-chain PFCAs (C2 TFAA and C3 PFPrA). Initial electrostatic binding with Fe^{3+} forms $[\text{GenX-Fe}]^{2+}$ complexes. Subsequent ligand-metal charge transfer dissociates these complexes into $\text{C}_3\text{F}_7\text{-O-CF}(\text{CF}_3)\text{COO}^\cdot$ radicals, followed by carboxyl group cleavage producing CO_2 and $\text{C}_3\text{F}_7\text{-O-CF}(\text{CF}_3)$. Ether bond cleavage further yields $\text{C}_3\text{F}_7\cdot$ radicals and CF_3CFO . Hydrolytic defluorination converts $\text{C}_3\text{F}_7\cdot$ to PFPrA, while CF_3CFO hydrolyzes to TFAA. Both PFPrA and TFAA display minimal catalyst adsorption owing to extreme hydrophilicity, preventing further degradation and causing aqueous accumulation.

According to HPLC-MS analysis, degradation intermediates including PFHpA, PFHxA, PFPeA, PFBA, and PFPrA were identified [255]. The photocatalytic degradation mechanisms of PFASs involve two distinct pathways: (A) photoredox pathway and (B) β -fragmentation pathway, as illustrated in Fig. 5 [256]. The degradation process comprises ten sequential stages (a-j). Reaction a Photoexcitation, UV irradiation activates TiO_2 to generate electron-hole pairs, initiating PFOA degradation. Reaction b Electron Transfer, TiO_2 accepts electrons from aqueous PFOA ($\text{CF}_3(\text{CF}_2)_6\text{COO}^-$), forming PFOA radicals ($\text{CF}_3(\text{CF}_2)_6\text{COO}^\cdot$). Reaction c Decarboxylation, Initiation: Carboxyl group undergoes Kolbe decarboxylation. Reaction d Radical Interaction, $\text{C}_7\text{F}_{15}\cdot$ radicals combine with $\cdot\text{OH}$ from water oxidation to form perfluoroalcohols ($\text{C}_7\text{F}_{15}\text{OH}$). Reaction e Peroxyl Radical Formation, $\text{C}_7\text{F}_{15}\cdot$ reacts with oxygen to produce peroxyl radicals ($\text{C}_7\text{F}_{15}\text{COO}^\cdot$). Reaction f Radical Coupling, Dimerization of peroxyl radicals generates dioxygen species. Reaction g Precursor Generation, Electron-mediated synthesis of unstable perfluoroalcohol precursors. Reaction h β -Elimination, $\text{C}_7\text{F}_{15}\text{COO}^\cdot$ radical decarboxylates to $\text{C}_7\text{F}_{15}\text{OH}$, followed by HF elimination forming $\text{C}_6\text{F}_{13}\text{COF}$. Reaction i Hydrolysis & Chain Shortening, $\text{C}_6\text{F}_{13}\text{COF}$ hydrolyzes to $\text{C}_6\text{F}_{13}\text{COH}$, progressively degrading to short-chain intermediates (C_5 - C_2 PFCAs) before final mineralization into CO_2 , H^+ , and F^- . Reaction j Monomeric Cleavage, COF_2 elimination via β -scission produces C_{n-1} radicals for subsequent degradation cycles.

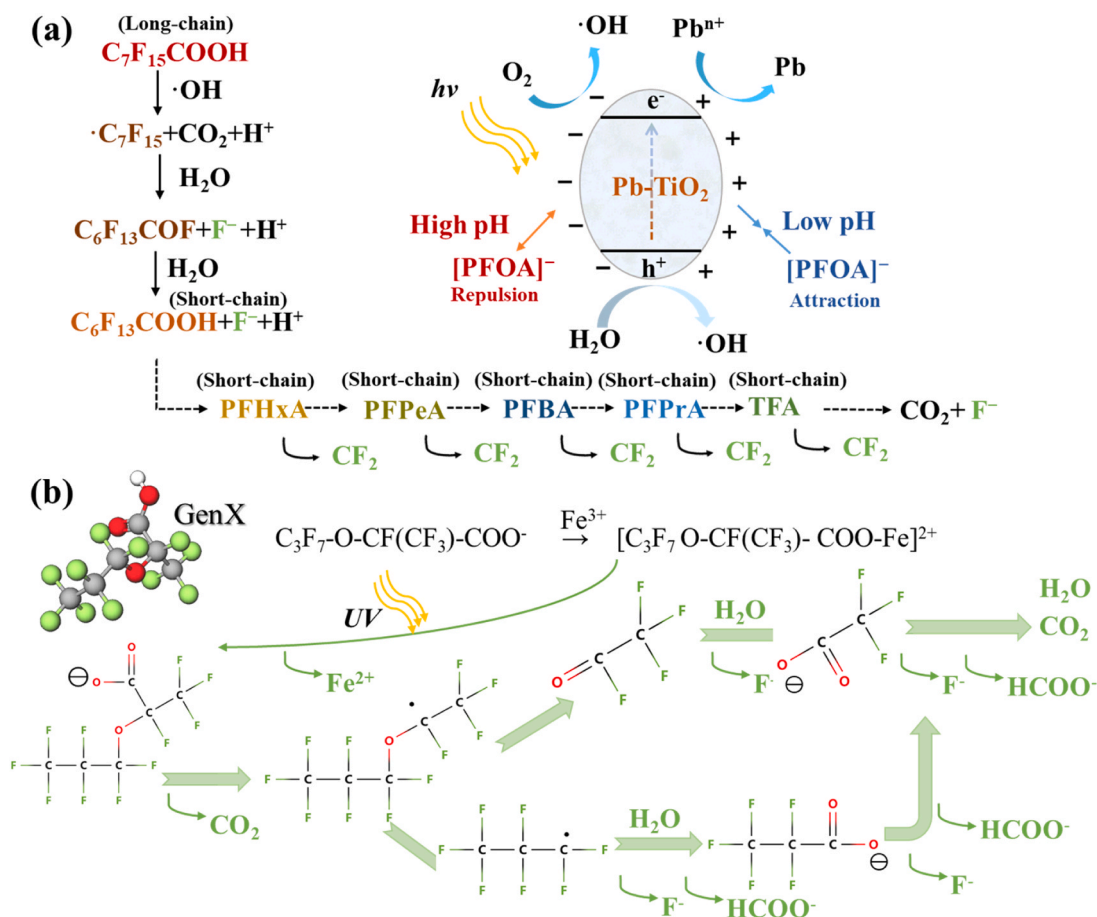


Fig. 4. (a) Photocatalytic pathways of PFOA decomposition; (b) Photocatalytic pathways of GenX decomposition. Reprinted with permission from Elsevier. Copyright 2015 Elsevier B.V. All rights reserved and 2023 The Authors. Published by Elsevier Ltd. [253,254].

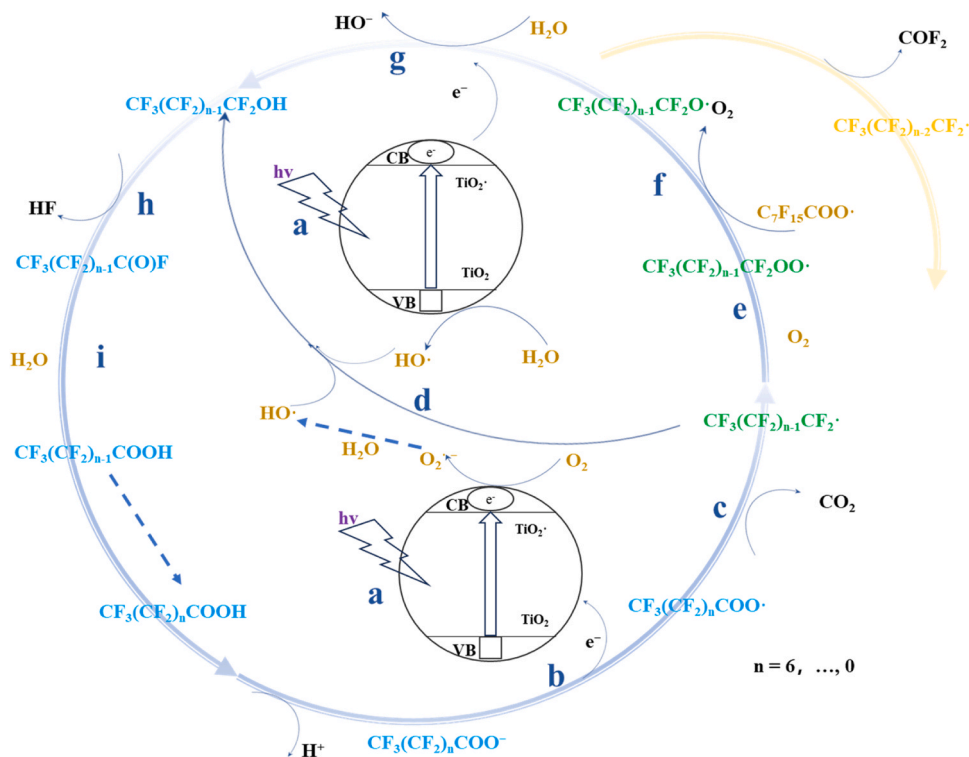
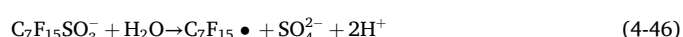
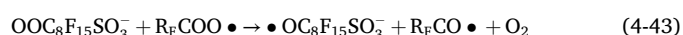
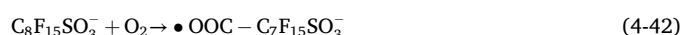
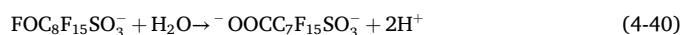
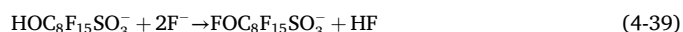
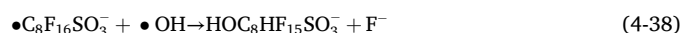
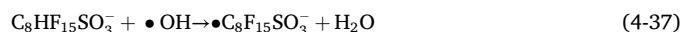
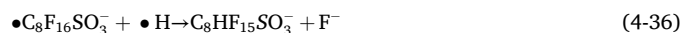
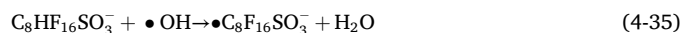
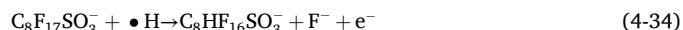
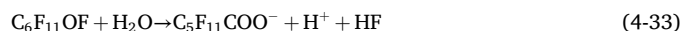
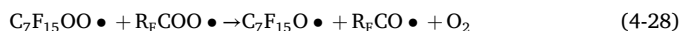


Fig. 5. PFOA degradation mechanism in the presence of TiO_2 photocatalyst: photo-redox pathway (A blue arrows); β -scission pathway (B orange arrows). Reprinted with permission from Elsevier. Copyright 2015 Elsevier B.V. All rights reserved [256].

Based on electrospray ionization mass spectrometry (ESI-MS) analysis, Pierpaoli [20] elucidated the electrochemical anodic degradation pathways of PFOA, involving four principal mechanisms: direct electron transfer, radical-mediated reactions, Kolbe decarboxylation, and hydroxylation processes (Equations 4–25–4–33). The carboxyl group of PFOA undergoes direct electron loss, forming a PFOA radical ($C_7F_{15}COO\cdot$). This unstable radical undergoes Kolbe decarboxylation, generating a $C_7F_{15}\cdot$ species that reacts with molecular oxygen to form perfluoroheptyl peroxy radicals ($C_7F_{15}OO\cdot$). Subsequent reactions with perfluoroalkoxy groups yield $C_7F_{15}O\cdot$ radicals, which decompose into perfluorohexyl radicals ($C_6F_{13}\cdot$) and carbonyl fluoride (COF_2). The COF_2 intermediate hydrolyzes to carbon dioxide (CO_2) and hydrofluoric acid (HF). The shortened perfluoroheptyl chain ($C_6F_{13}\cdot$) undergoes hydroxylation and intramolecular rearrangement, followed by hydrolytic defluorination.

Additionally, Pierpaoli established analogous electrochemical degradation pathways for PFOS anodic decomposition, encompassing radical formation, Kolbe decarboxylation, hydrolytic cleavage, and hydroxylation mechanisms (Equations 4–34–4–46). The comprehensive degradation routes for both PFOA and PFOS are systematically illustrated in Fig. 6 [20]. PFOS undergoes sequential fluoride elimination via radical-mediated pathways, producing $\cdot\text{C}_8\text{F}_{16}\text{SO}_3$ radicals. These radicals react with hydroxyl radicals ($\cdot\text{OH}$) to form intermediate $\text{FOC}_8\text{F}_{15}\text{SO}_3$, which undergoes hydrolysis and Kolbe decarboxylation to yield perfluoroheptyl sulfonate ($\text{C}_7\text{F}_{15}\text{SO}_3$). Alternatively, $\cdot\text{C}_8\text{F}_{16}\text{SO}_3$ reacts with oxygen and perfluoroalkoxy groups to generate $\text{OC}_8\text{F}_{15}\text{SO}_3$, decomposing into $\cdot\text{C}_7\text{F}_{15}\text{SO}_3$ radicals and COF_2 . The COF_2 hydrolyzes to CO_2 and HF , while $\cdot\text{C}_7\text{F}_{15}\text{SO}_3$ undergoes progressive hydrolysis and chain-shortening degradation.



Zeidabadi et al. [257] examined electrocatalytic degradation mechanisms using boron-doped diamond electrochemical systems. Short-chain PFASs such as PFBA and GenX demonstrated fundamental mechanistic distinctions from long-chain PFAS degradation pathways. Fig. 7 delineates the PFBA degradation route where direct electron transfer generates radicals that initiate decarboxylation and carbon-chain cleavage at BDD anodes. This process sequentially yields intermediates including PFPrA and TFA prior to mineralization. The pathway indicates that short-chain PFCA degradation depends on synergistic interactions between direct electron transfer and sulfate radicals. GenX undergoes dual degradation pathways involving carboxylic head oxidation and ether bond cleavage intermediates. Compared to PFBA, the presence of ether bonds produces more intermediates, indicating greater degradation complexity for ether-containing PFAS.

PFBA degradation primarily involves DET at anode surfaces. The PFBA molecule generates the radical $\text{C}_3\text{F}_7\text{COO}\cdot$ through DET, and forms the perfluoroalkyl radical $\text{C}_3\text{F}_7\cdot$ via the Kolbe decarboxylation reaction.

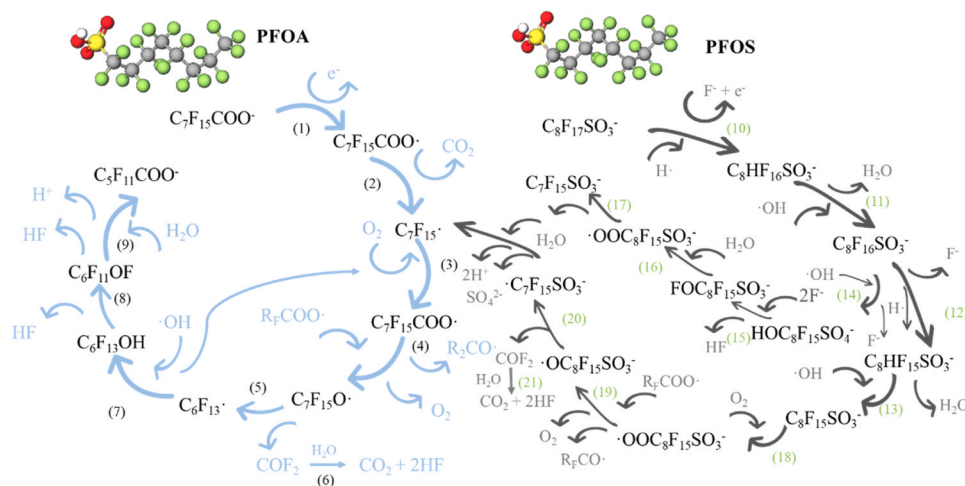


Fig. 6. Degradation reaction pathway for the PFOA and PFOS electrochemical oxidation. Reprinted with permission from Elsevier. Copyright 2020 Elsevier B.V. All rights reserved [20].

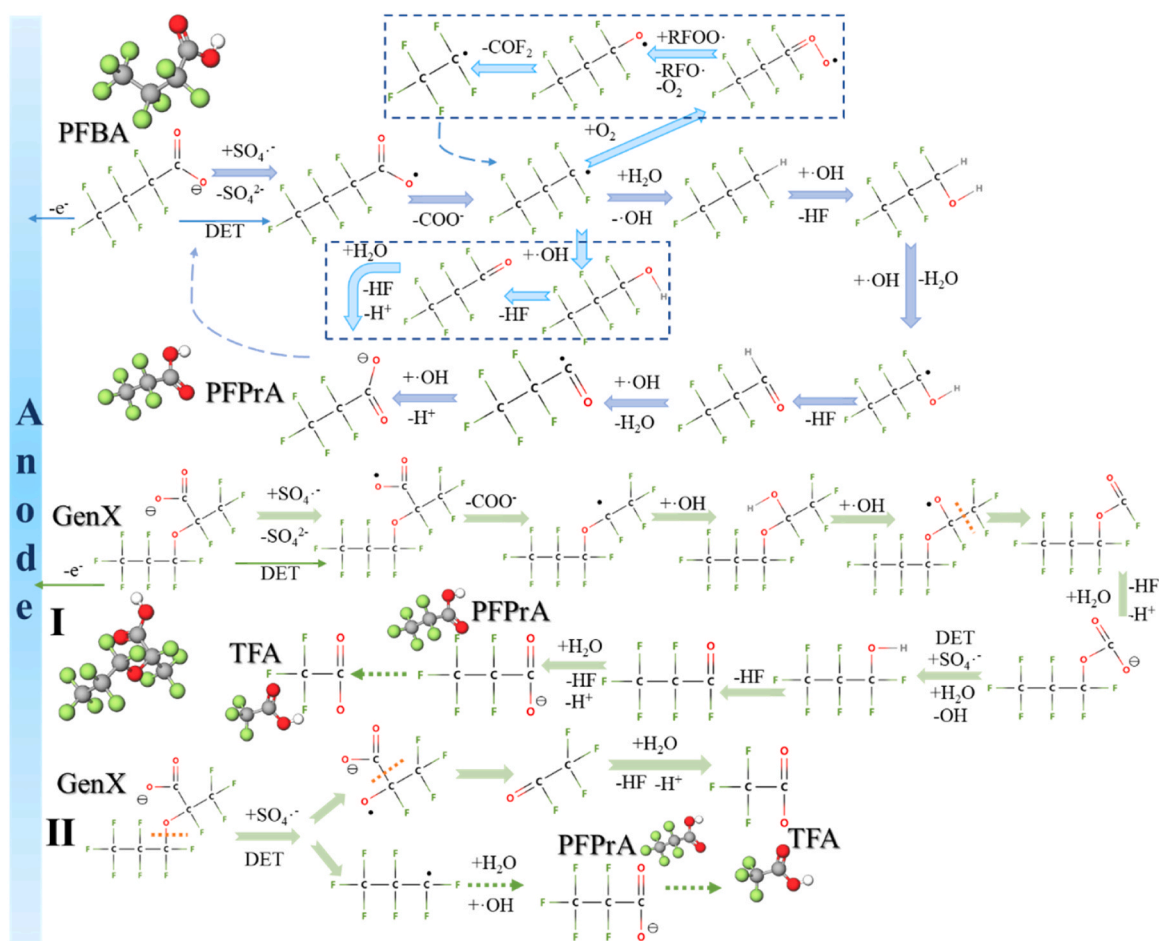


Fig. 7. Degradation reaction pathway for the PFBA and GenX electrochemical oxidation., Reprinted with permission from Elsevier 2024 Elsevier Ltd. All rights are reserved [257].

The unstable free radicals further react with water or oxygen, then progressively cleave carbon chains through CF_2 unzipping to generate short-chain intermediates like PFPrA and TFA, ultimately mineralizing into fluoride ions and CO_2 . During this process, $\text{SO}_4^{\bullet-}$ facilitates oxidation by accelerating free radical intermediate formation, while $\cdot\text{OH}$ contribution remains negligible. GenX degradation proceeds via two pathways. Oxidation at the carboxylic head via DET or $\text{SO}_4^{\bullet-}$ generates alkyl radical $\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\cdot$, which undergoes decarboxylation and hydroxylation to form short-chain intermediates $\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{OH}$ and $\text{C}_3\text{F}_7\text{COO}^\bullet$, subsequently degrading into PFPrA and TFA. Concurrently, the ether linkage with lower bond dissociation energy undergoes radical-induced cleavage, yielding perfluoroalkyl radical $\text{C}_3\text{F}_7\cdot$ and acyl fluoride intermediate $\cdot\text{OCF}(\text{CF}_3)\text{COO}^\bullet$. The former produces short-chain PFCAs via CF_2 unzipping, while the latter decarboxylates into trifluoroacetyl fluoride CF_3COF before hydrolyzing to TFA. $\text{SO}_4^{\bullet-}$ serves as the primary oxidant with negligible $\cdot\text{OH}$ contribution, and ether bond cleavage represents the key step distinguishing GenX from other PFCAs. Compared to long-chain PFOA, short-chain PFAS exhibit weaker adsorption onto anode surfaces due to shorter chain length and higher solubility, resulting in lower degradation efficiency. Within 120 min, degradation efficiencies reach 65.6 % for PFBA, 84.9 % for GenX, and 97.9 % for PFOA, with GenX demonstrating more complex degradation pathways due to its ether linkage[257].

Lei et al. [258] established a dual-frequency ultrasound-activated persulfate oxidation pathway for PFOA degradation, as illustrated in Fig. 8. The integration of dual-frequency ultrasound into the US/PS system significantly enhanced cavitation bubble density, cavitation efficiency, and pyrolysis intensity (Eqs. 4–46 to 5–51) [231].

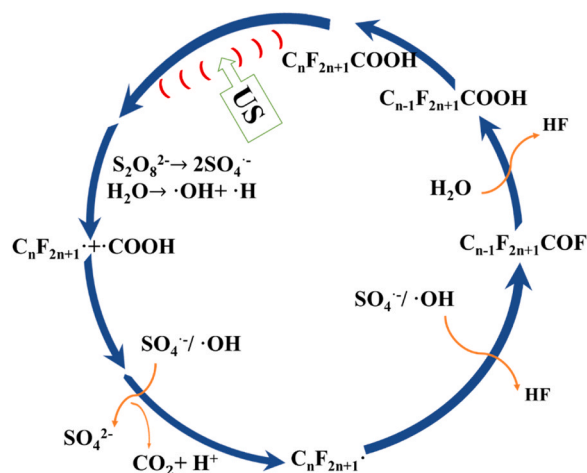
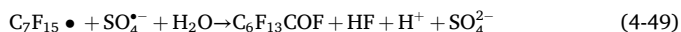


Fig. 8. Degradation pathway of PFOA by dual frequency ultrasound activated persulfate oxidation., Reprinted with permission from Elsevier. Copyright 2020 Elsevier B.V. All rights reserved. [258].

Cavitation-induced pyrolysis under extreme temperatures (4000–10,000 °C) initiated PFOA decarboxylation, generating perfluoroalkyl radicals ($\text{C}_7\text{F}_{15}\cdot$) and carboxyl radicals ($\cdot\text{COOH}$) - identified as the primary rate-limiting step. Subsequent radical interactions involved: (1) $\text{SO}_4^{\bullet-}$ and $\cdot\text{OH}$ attack on $\text{C}_7\text{F}_{15}\cdot$ yielding $\text{C}_6\text{F}_{13}\text{COF}$; (2) Oxidative conversion of $\cdot\text{COOH}$ by these radicals; (3) Hydrolysis of $\text{C}_6\text{F}_{13}\text{COF}$ to $\text{C}_6\text{F}_{13}\text{COOH}$; (4)

Iterative chain-shortening through analogous mechanisms, producing PFHxA, PFHpA, PFPeA, and PFBA intermediates.



4.4. Degradation pathway of advanced reduction PFASs

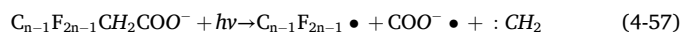
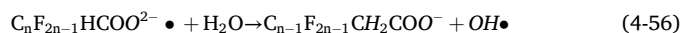
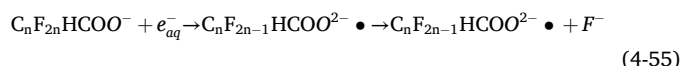
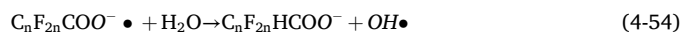
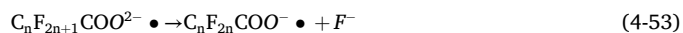
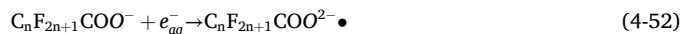
In advanced reduction processes for PFASs degradation, hydrated electrons (e_{aq}^-) play a pivotal role. The degradation efficiency and pathway are governed by three molecular characteristics: perfluorocarbon chain structure, functional group configuration, and C-F bond properties (bond length/energy), coupled with electron distribution patterns. Two primary e_{aq}^- -mediated reduction mechanisms exist: (1) H/F substitution through C-F bond cleavage, and (2) C-C bond cleavage via the DHEH mechanism yielding short-chain PFASs for subsequent degradation.

(1) H/F substitution mechanism

The hydrated electron (e_{aq}^-) selectively targets the α -carbon position in PFASs due to the characteristically low carbon-fluorine bond dissociation energy (BDE) at this molecular site. Bentel et al. [23] employed density functional theory (DFT) to calculate C-F BDEs across various PFASs (Fig. 9), revealing two critical trends. Terminal CF_3 groups exhibit higher C-F BDEs compared to mid-chain CF_2 positions. Perfluorocarbon chain elongation progressively decreases C-F BDEs along the backbone. This BDE gradient explains e_{aq}^- enhanced reactivity with long-chain PFASs: mid-chain CF_2 groups demonstrate stronger e_{aq}^- affinity and higher cleavage susceptibility due to reduced BDEs (averaging 385 kJ/mol vs 412 kJ/mol for terminal CF_3) [23]. Consequently, long-chain PFASs show superior degradation efficiency compared to short-chain analogs under reductive conditions.

Qu et al. [259] detected the degradation intermediate $\text{C}_{n-1}\text{F}_{2n-1}\text{CH}_2\text{COO}^-$ formed by up to two H/F substitutions on α -C during the degradation of PFOA by e_{aq}^- . Therefore, he proposed that H/F substitution may also occurred on other C atoms of long-chain PFASs except

α -C, as shown in Equations 4-52–4-56. $\text{C}_{n-1}\text{F}_{2n-1}\text{CH}_2\text{COO}^-$ was decomposed into $\text{C}_{n-1}\text{F}_{2n-1}\bullet$, $\text{COO}\bullet$ and methyl group ($:\text{CH}_2$) by UV. $\text{C}_{n-1}\text{F}_{2n-1}\bullet$ and $\text{COO}\bullet$ were further recombined into $\text{C}_{n-1}\text{F}_{2n-1}\text{COO}^-$, as shown in Equations 4-57–4-58. After the parent PFASs removed CF_2 , it entered a new degradation cycle. However, H/F substitution cannot completely degrade PFASs. The reduction in the concentration of $\text{C}_{n-1}\text{F}_{2n-1}\bullet$ made it difficult for $\text{C}_{n-1}\text{F}_{2n-1}\bullet$ to recombine with carboxyl groups, thus limiting the reaction.



(2) DHEH process, breaking C-C bond cleavage

The e_{aq}^- mediated degradation of PFASs proceeds through the DHEH mechanism (Decarboxylation-Hydroxylation-Defluorination-Hydrolysis), as detailed in Equations 4-59–4-63. UV/ e_{aq}^- induced C-C cleavage generates perfluoroalkyl radicals ($\text{C}_n\text{F}_{2n+1}\bullet$) and carboxyl radicals ($-\text{COO}\bullet$). These intermediates subsequently undergo hydroxylation and hydrolysis, ultimately forming short-chain PFASs with reduced CF_2 units compared to parent compounds. Through iterative DHEH cycles, complete PFAS mineralization occurs, yielding CO_2 , H_2O , and F^- as terminal products [260]. Competitive interplay exists between the DHEH pathway and H/F substitution mechanisms. Post H/F substitution, the resultant $-\text{CH}_2-$ moiety strengthens the C-C bond linking the fluorocarbon chain to the carboxyl group, thereby impeding the critical decarboxylation step required for DHEH progression.

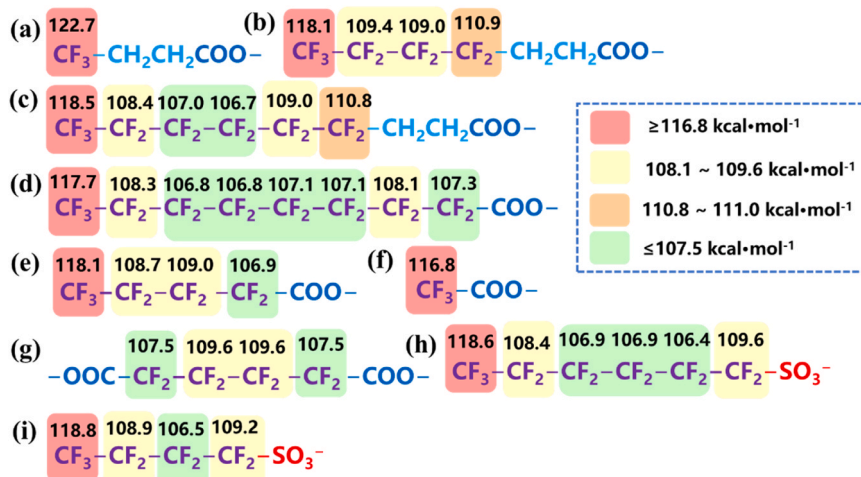
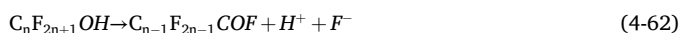


Fig. 9. Degradation and defluorination mechanism for PFCA and BDE of C-F bonds in PFASs (kcal/mol). [23].



Zhai et al. [247] implemented a UV/SO₃²⁻/I⁻ system under neutral conditions, achieving 81.92 % HFPO-TA degradation ($k = 0.834 \text{ h}^{-1}$) with 48.99 % defluorination ($k = 0.312 \text{ h}^{-1}$). Hydrated electrons (e_{aq}^-) were identified as the dominant reactive species, initiating degradation through ether bond (C6-O7) cleavage to yield HFPO-DA, TFA, acetic acid, and formic acid. Subsequent studies revealed chain-length-dependent defluorination patterns, with bond dissociation energies and degradation pathways detailed in Fig. 10. Zhai et al. [261] conducted quantum chemical analyses of HFPO-TA bond dissociation energies (BDEs) for C-F bonds (Fig. 10a). The C8-F bond exhibited the lowest BDE among C-F bonds, rendering it most susceptible to e_{aq}^- mediated H/F substitution. The C5-F bond demonstrated secondary vulnerability to continued H/F exchange. Fig. 10b maps potential H/F substitution sites. The C-F bond at the C8 position exhibits relatively low bond energy, making it the primary target for e_{aq}^- attack. This nucleophilic substitution leads to the formation of a more stable C-H bond through H/F exchange. Notably, the C5 position also demonstrates comparable vulnerability, suggesting a potential sequential H/F substitution process may occur at this adjacent position following the initial reaction at C8. The dissociation energies of the C-C and C-O bonds in HFPO-TA are shown in Fig. 10(c), C-O bonds showed significantly lower

BDEs than C-C bonds, with the ether linkage constituting a structural weak point in HFPO-TA carbon chain [246]. The ether linkages in HFPO-TA introduce structural vulnerabilities within the carbon chain framework. Computational analysis reveals that the C6-O7 position exhibits the lowest bond dissociation energy (258.4 kJ·mol⁻¹) among the C-O bonds, suggesting this site likely represents the most reactive center in the HFPO-TA molecular architecture. This structural predisposition facilitates ether bond cleavage-driven degradation, with proposed pathways illustrated in Fig. 10d-e involving sequential chain-shortening through radical intermediates.

HFPO-TA Degradation Pathway: Initial ether bond cleavage at the C6–O7 site by e_{aq}^- generates $\cdot\text{C}_6\text{F}_{13}\text{O}$ and $\cdot\text{C}_3\text{F}_4\text{O}_3\text{H}$ radicals. The $\cdot\text{C}_6\text{F}_{13}\text{O}$ undergoes hydrolysis to unstable $\text{C}_6\text{F}_{13}\text{O}_2\text{H}$, subsequently eliminating HF to form $\text{C}_6\text{F}_{12}\text{O}_2$ [261]. Progressive hydrolysis and HF elimination convert $\text{C}_6\text{F}_{12}\text{O}_2$ to $\text{C}_6\text{F}_{11}\text{O}_3\text{H}$ (HFPO-DA). Concurrently, $\cdot\text{C}_3\text{F}_4\text{O}_3\text{H}$ undergoes decarboxylation yielding $\cdot\text{C}_2\text{F}_3\text{O}$, which hydrolyzes to $\text{C}_2\text{F}_4\text{O}_2\text{H}$. Subsequent HF elimination produces $\text{C}_2\text{F}_4\text{O}$, ultimately hydrolyzing to CF_3COOH (TFA).

HFPO-DA Degradation Pathway: Ether bond cleavage in HFPO-DA produces $\cdot\text{C}_3\text{F}_7$ and $\cdot\text{C}_3\text{F}_4\text{O}_3\text{H}$ [246]. The $\cdot\text{C}_3\text{F}_7$ radical hydrolyzes to unstable $\text{C}_3\text{F}_7\text{OH}$, undergoing β -HF elimination to form $\text{C}_2\text{F}_5\text{COF}$. Hydrolysis of $\text{C}_2\text{F}_5\text{COF}$ yields $\text{C}_2\text{F}_5\text{COOH}$ (PFA), which undergoes e_{aq}^- mediated cleavage into $\cdot\text{C}_2\text{F}_5$ and $\cdot\text{COOH}$. $\cdot\text{C}_2\text{F}_5$ hydrolyzes to $\text{C}_2\text{F}_5\text{OH}$, eliminating HF to form $\text{C}_2\text{F}_4\text{O}$ ultimately hydrolyzing to TFA. TFA

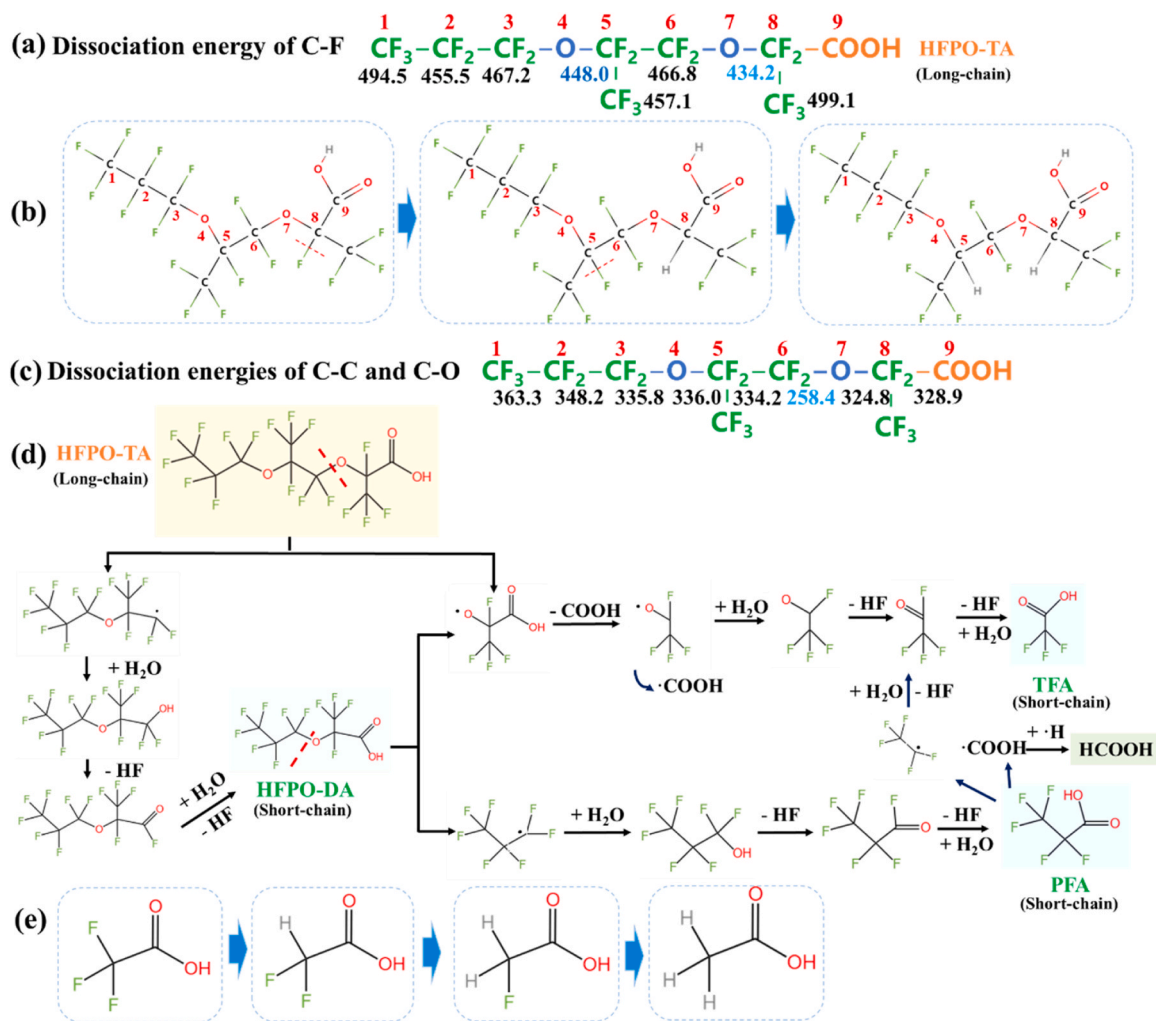


Fig. 10. (a) Bond dissociation energy of C-F bond in HFPO-TA; (b) Possible locations for H/F exchange; (c) Bond dissociation energies of C-C and C-O in HFPO-TA; (d) The degradation pathway of HFPO-TA; (e) The pathway of TFA conversion to CH₃COOH. Reprinted with permission from Elsevier 2024 Elsevier Ltd. All rights are reserved [247].

undergoes sequential e_{aq}^- mediated H/F substitutions (three cycles), culminating in complete conversion to CH_3COOH through cumulative C-F bond replacement [247].

The detection of F^- , TFA, PFA, and HFPO-DA intermediates confirms concurrent cleavage of C-F, C-O, and C-C bonds during HFPO-TA degradation. Early-stage F^- liberation suggests direct H/F substitution occurring at the α -carbon position of HFPO-TA. Fluorine exceptional electronegativity ($\chi=4.0$) and electron-withdrawing capacity enable e_{aq}^- nucleophilic attack on C-F bonds [262], with preferential targeting of the lowest bond dissociation energy (BDE) C-F linkages as demonstrated through computational modeling [261].

The chain-length dependent characteristics of PFASs, as illustrated in Fig. 11, necessitate tailored remediation strategies. For long-chain PFASs integrated GAC adsorption with thermal regeneration, coupled with persulfate-based advanced oxidation processes, achieves efficient mineralization. Short-chain analogues require synergistic functionalized ion-exchange resins and bioelectrochemical treatment to enhance electrostatic interactions and biological defluorination pathways. While nanofiltration/reverse osmosis (NF/RO) systems serve as broad-spectrum barriers, concentrated brine management remains critical. This multi-tiered approach effectively addresses concurrent removal requirements for complex PFAS mixtures in heterogeneous matrices.

Long-chain and short-chain PFASs exhibit distinct treatment characteristics as illustrated in the Fig. 11. Regarding adsorption, long-chain PFASs benefit from robust hydrophobic interactions coupled with electrostatic attraction and hydrogen-bonding-assisted surface enrichment, enabling efficient adsorption despite rate limitations from adsorption site competition. Conversely, short-chain PFASs rely predominantly on electrostatic interactions due to their hydrophilic nature, yet exhibit diffusion-limited weak adsorption where mass transfer and electrostatic binding restrict kinetics. In persulfate-catalyzed oxidation, enriched long-chain PFASs undergo attack by surface-immobilized $SO_4^{\cdot-}$ or $^1O_2$ via non-radical pathways including singlet oxygen oxidation and surface electron transfer, initiating chain defluorination through decarboxylation. In contrast, short-chain PFASs depend on diffusible free $SO_4^{\cdot-}$, a diffusion-controlled process requiring high oxidant dosages while suffering rapid radical quenching. For photocatalytic oxidation, long-chain PFASs adsorb on catalysts like TiO_2 and g- C_3N_4 , utilizing surface holes or free radicals alongside high local reactive species concentrations for direct chain scission and mineralization. Short-chain PFASs however primarily undergo solution-phase degradation by diffusible radicals like $\cdot OH$ and $SO_4^{\cdot-}$, demanding elevated radical concentrations to break stable C-F bonds. During electrochemical oxidation, long-chain PFASs achieve direct electron transfer at anode surfaces while indirect $\cdot OH$ mineralization of intermediates results in limited electrode-surface reactions. Short-chain PFASs rely on indirect oxidation via solution $\cdot OH$, necessitating elevated electrode overpotentials to sustain radical concentrations. In advanced reduction, long-chain PFASs experience direct C-F bond attack by surface-bound e_{aq}^- with hydrogen-assisted defluorination, enhanced by hydrophobic enrichment. Short-chain PFASs also engage e_{aq}^- but face diffusion-limited mass transfer, yielding slow kinetics and constrained reactive species availability. Collectively, these mechanistic divergences in adsorption behavior, oxidation pathways, and reduction efficiencies necessitate tailored PFASs remediation strategies, with future research needing to address short-chain PFASs mass transfer challenges and long-chain PFASs deep mineralization barriers to advance treatment technologies.

5. Field applications and matrix composition impact

5.1. PFASs removal systems in field engineering

PFASs have emerged as a critical concern in global aquatic environmental management owing to their exceptional persistence and bioaccumulative potential. Current engineering solutions primarily target long-chain PFASs, whereas short-chain counterparts demonstrate

substantially lower removal efficiencies due to enhanced aqueous solubility and mobility [263]. Operational PFASs remediation technologies in practical applications encompass coagulation separation, adsorption processes, filtration systems, ion exchange resins, membrane retention, and advanced oxidation methods. Appleman [5] studied the full-scale water treatment systems in the United States, comprising 11 surface water bodies, 6 groundwater reservoirs, 1 hybrid surface/groundwater source, and 2 treated wastewater effluents. Post-treatment monitoring revealed PFASs detection in over 80 % of samples subjected to conventional processes like coagulation/flocculation, filtration and disinfection. Some treated water samples exceeded the Minimum Reporting Levels (MRLs) stipulated in the U.S. Unregulated Contaminant Monitoring Rule 3 (UCMR 3), including instances PFHpA surpassed 10 ng/L, PFOA exceeded 20 ng/L, and PFOS reached over 40 ng/L. But the majority of water treatment facilities maintained PFASs concentrations below the health advisory thresholds established by the U.S. EPA and state regulatory guidelines.

(1) Engineering applications of adsorption and ion exchange system

Activated carbon adsorption remains the most prevalent technology in drinking water treatment facilities. This method demonstrates adsorption capacities of 1.2–3.5 mg/g for long-chain PFASs, whereas its efficiency drops below 30 % for short-chain analogues, primarily owing to their reduced hydrophobicity and elevated desorption potential. To enhance short-chain PFAS removal, engineered systems frequently employ integrated activated carbon-ion exchange resin processes. Appleman's investigation[5] of full-scale granular activated carbon (GAC) systems revealed substantial removal efficacy for long-chain PFCAs and PFSA, achieving concentrations near or below MRLs, with partial removal observed for short-chain PFCAs. Groundwater treatment applications demonstrated effective PFAS removal across most species, though PFBA exhibited breakthrough after approximately two months of operation. Notably, extended operation without GAC replacement/regeneration in certain plants resulted in effluent concentrations exceeding influent levels during secondary sampling.

Ion exchange resins demonstrate distinct advantages in industrial wastewater remediation. Appleman[5] also documented concurrent PFAS removal (46 % PFHpA, 75 % PFOA, 81 % PFBS) during arsenic treatment using Purolite FerriXA33e media in anion ion exchange (AIX) softeners, with superior performance for long-chain PFASs and PFSA compared to PFCAs. While magnetic anion exchange processes effectively reduce total organic carbon, their PFAS removal capacity remains negligible, potentially attributable to continuous regeneration protocols, resin capacity limitations, or operational kinetics. Fang et al. [264] evaluated 75 PFASs (including 63 polyfluorinated compounds) adsorption using 14 commercial ion exchange/non-ionic resins and GAC in AFFF mixtures. Their findings revealed anion exchange resins (AERs) outperformed cation exchange resins (CERs), non-ionic resins (NIRs), and GAC in PFAS adsorption across all charge states. Isotherm analyses indicated macroporous AERs possessed superior adsorption capacities relative to gel-type variants. Selectivity coefficient (K_{ex}) cross-correlations demonstrated that resin-PFAS affinity predominantly depends on AER functional group characteristics and matrix hydrophobicity. PFAS structural parameters significantly influenced adsorption behavior, with enhanced uptake correlating with increased chain length and net negative charge density.

(2) Engineering applications of filtration and coagulation technologies

Conventional filtration media exhibit limited PFAS removal efficacy due to contaminant competition for adsorption sites. While media replacement incurs substantial costs, in situ adsorption capacity regeneration presents a cost-effective alternative. Appleman[5] research on riverbank filtration at a water treatment facility employing 10-day hydraulic retention revealed limited PFOA and PFOS removal efficacy. The system achieved 20 % PFHxA reduction, 19 % PFDA removal, and 68 % N-MeFOSAA elimination, while simultaneously exhibiting concentration increases for PFBA, PFHpA, PFBS, and FOSA.

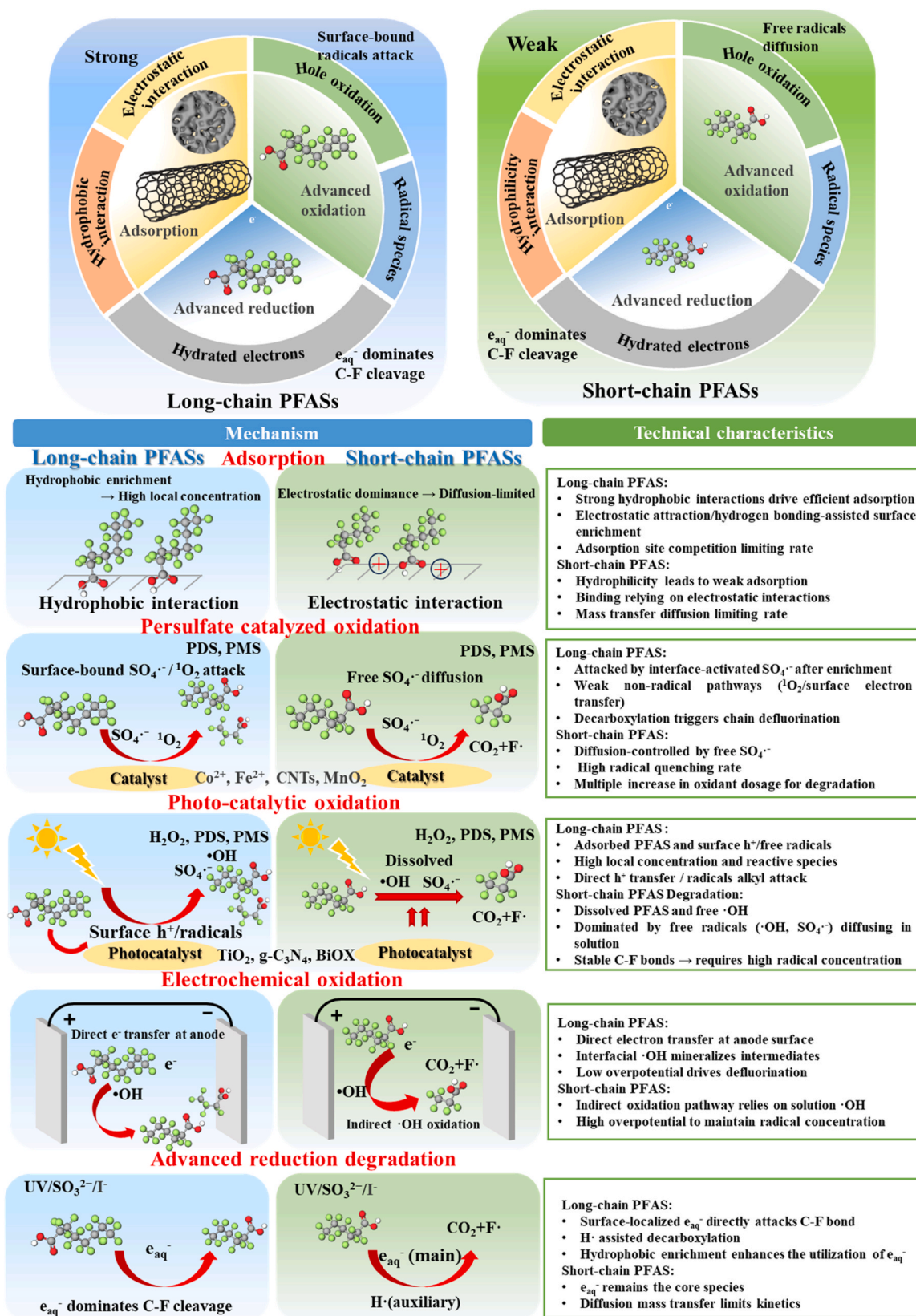


Fig. 11. Reaction mechanism of long/short chain PFASs in the remediation strategies.

Borthakur et al. [265] established that in situ application of cationic polymers like polydiallyl dimethyl ammonium chloride (PDADMAC) effectively regenerates filter media's anionic PFASs removal capacity. PDADMAC efficacy inversely correlated with PFAS chain length, enhancing removal efficiencies by 9.9 fold (87 % PFBA), 1.6 fold (85 % PFHxA), and 0.3 fold (97 % PFOA). This approach particularly improves short-chain PFASs removal – traditionally challenging for carbon-based media – without compromising biofilter hydraulic conductivity. PDADMAC-modified biofilter required 35.3 % greater suspended sediment loading to achieve 50 % conductivity reduction, while simultaneously reducing colloidal release during intermittent flow by stabilizing adsorbed PFASs. The non-degrading nature of PDADMAC enables sustained PFASs removal, demonstrating practical potential for converting conventional biofilters into regenerative systems for storm-water management.

Coagulation processes employing aluminum sulfate or poly-aluminum chloride with sedimentation/dissolved air flotation (DAF) demonstrate minimal PFAA removal efficacy. Appleman [5] observed negligible PFAA reduction through coagulation-sedimentation, with DAF systems achieving only 49 % PFOS and 29 % PFNA removal while remaining ineffective for short-chain PFCAs/PFSAs. Granular media filtration (sand/anthracite) shows limited PFAA removal, occasionally increasing PFOS post-coagulation-filtration. Micro-filtration/ultrafiltration systems generally achieve marginal PFAS removal (24 % PFOS, 44 % PFDoA, 42 % FOSA in select applications), underscoring their limited suitability for PFASs remediation.

(3) Engineering applications of membrane separation technologies

The integrated nanofiltration-reverse osmosis (NF-RO) system has become prevalent in water treatment engineering for cost optimization, where NF membranes preliminarily intercept long-chain PFASs to reduce subsequent RO energy demands. Liu et al. [266] evaluated 26 NF/RO membranes PFASs removal efficiency, confirming their effectiveness for long-chain contaminants. Zhao et al. [267] demonstrated enhanced PFOS rejection (92–99 %) using ESNA-K1 NF membranes in humic acid-inorganic salt coexisting systems, attributable to molecular bridging-induced size exclusion and charge interactions. Comparative studies by Li et al. [176] on tight (NF90) versus loose (NFG) nanofiltration membranes revealed distinct removal mechanisms. NFG performance derived primarily from electrostatic/hydrophobic interactions, whereas NF90 exhibited less than 10 % contribution from both mechanisms. Appleman's investigation [5] of two RO based water reclamation facilities in California employed polyamide Hydranautics ESPA2 membranes alongside Toray and Hydranautics RO membrane systems. Post-treatment analysis revealed all PFAS concentrations below MRLs, with the RO process demonstrating exceptional efficacy including substantial removal of short-chain PFBA. Despite its superior performance, the membrane separation technology presents operational challenges through elevated implementation costs and critical concentrate treatment requirements.

Emerging forward osmosis (FO) technology shows promise for short-chain PFAS remediation through osmotic pressure-driven separation. Choi et al. [268] developed a low-pressure PA-VRO system achieving > 98 % PFOS/PFOA removal, suitable for energy-constrained regions. While FO offers advantages in energy efficiency and fouling resistance for desalination and water reuse, ammonia liberation during draw solution regeneration remains a critical barrier to large-scale implementation.

(4) Engineering applications of oxidation process

Conventional water oxidation treatment processes including ozonation, aerated packed towers, potassium permanganate oxidation, ultraviolet irradiation (80 mJ/cm²), AOPs (e.g., UV/H₂O₂), and chlorine-based disinfection systems exhibit limited PFAS removal efficacy. Appleman's findings [5] revealed 34–35 % PFHxS and PFOS reduction through UV treatment, while demonstrating negligible removal of PFCAs and PFBS, with occasional concentration increases post-treatment. Although laboratory-scale AOPs achieve > 90 % PFASs

mineralization, field applications face significant technical barriers, primarily due to constrained degradation rates and substantial short-chain byproduct generation, rendering their implementation most viable as supplementary to adsorption/membrane systems.

Emerging ozone foam fractionation presents a promising solution for PFASs remediation in landfill leachate. Vo et al.'s comparative study [18] demonstrated > 90 % long-chain PFASs removal through ozone-enhanced interfacial adsorption, achieving optimal performance at 1 L/min ozone flow rate and 43 mg/L dosage with minimized foam generation (4 % wettability). This technology reduced foam production by 2–4 fold compared to conventional air fractionation, significantly lowering waste disposal costs and storage requirements while maintaining treatment efficacy.

(5) Synergistic Treatment System Configuration

PFASs remediation unit integration into existing water treatment infrastructure has become the predominant engineering strategy, often combined with biological treatment systems in wastewater plants for synergistic removal. Li et al. [269] conducted a field-scale evaluation of advanced water treatment (AWT) processes using secondary effluent samples from a full-scale water reclamation facility (WRF). Analysis of samples collected from April to October 2020 identified PFCAs as dominant contaminants, with PFPeA showing the highest mean concentration, while PFSAs remained significantly lower. Total PFASs concentrations peaked in September 2020, reflecting seasonal emission patterns linked to AFFF and pesticide applications.

The coagulation-flocculation-clarification-filtration train demonstrated negligible PFAS reduction, with ozonation unexpectedly increasing PFBS and PFBA levels. Biological activated carbon (BAC) filtration effectively removed long-chain compounds like PFOS and PFHxS, but elevated short-chain PFAS concentrations post-treatment. GAC emerged as the most effective technology, eliminating all PFSAs below detection limits and substantially reducing most PFCAs, though short-chain residuals persisted. Ultraviolet treatment showed no efficacy against short-chain PFCAs including PFBA, PFPeA, and PFHxA. These findings confirm GAC effectiveness in potable water reuse systems while underscoring persistent challenges with short-chain PFAS management and the critical need for customized treatment solutions.

Current engineering applications of PFASs removal technologies face multiple critical bottlenecks. The inferior removal efficiency for short-chain PFASs necessitates targeted development of molecularly imprinted adsorbents. Safe concentrate disposal requires enhanced technical-economic viability through membrane-electrochemical hybrid systems enabling in situ treatment. Furthermore, comprehensive ecological risk assessments must address potential hazards from PFAS degradation byproducts.

5.2. Effect of environmental matrix composition on defluorination

Phosphates demonstrate potential to enhance plant tolerance to PFOS while significantly inhibiting its uptake, indicating that phosphate amendment in PFOS-contaminated soils could serve as an effective strategy for either reducing PFOS accumulation in edible crops or enhancing PFOS uptake during phytoremediation applications [270]. However, phosphate solutions exhibit inhibitory effects on PFAS adsorption through multiple mechanisms. The presence of phosphate alters adsorbent surface characteristics by reducing zeta potential and competes in the surface adsorption processes, particularly diminishing adsorption capacity for specific fluorinated compounds containing terminal sulfonate groups [271]. Empirical shows that phosphate pre-treatment prior to air stripping reduces PFAS adsorption capacity on ion-exchange media by 15 %-25 % [272]. Concurrently, phosphate, ammonium, and bicarbonate ions demonstrate radical scavenging effects that impair hydroxyl radical activity, thereby limiting PFOA defluorination efficiency [273]. This occurs as phosphate and ammonium undergo oxidation to form free radicals that occupy electrode sites, ultimately disrupting PFAS removal mechanisms and altering PFOA

oxidation kinetics from first-order patterns. Furthermore, stable complex formation between PFAS molecules containing Scorpion type macrocyclic ligands with anthracene-functionalized tails and anions such as phosphate and benzoate introduces additional challenges for PFOA oxidation processes [274]. Notably, under solvent-free mechanochemical conditions, PFAS reacts with potassium phosphate to achieve mineralization, recovering fluorine as KF and K_2PO_3F . Recent Nature studies reveal that mechanical grinding of PTFE with $K_4P_2O_7$ enables fluorine recovery, though with inferior efficiency compared to systems using K_2HPO_4 or generic phosphate additives [275].

In electrochemical oxidation of PFAS, elevated chloride concentrations promote chlorate formation. However, high chlorate concentrations suppress its conversion to perchlorate, allowing accumulated oxidizing chlorate to subsequently enhance PFAS degradation rates [276]. In photochemical systems, while chloride ions attenuate light energy through absorption, their UV-activated transformation into reactive chlorine species ($\cdot Cl/Cl_2^{\cdot -}$) critically facilitates PFOA degradation via decarboxylation-hydroxylation-elimination-hydrolysis pathways [277]. Metz [277] studied the techniques for combining ultraviolet (UV) and chlorine to degrade perfluorooctanoic acid (PFOA) in water. Compared with UV photolysis and chlorine treatment alone, UV/Chlorine treatment can significantly promote the degradation and de-fluorination of PFOA. Free radical scavenging experiments indicated that $Cl\cdot$ and $Cl_2^{\cdot -}$ played a key role in the degradation of PFOA, and the possible degradation mechanism is electron abstraction leading to decarboxylation-hydroxylation-elimination-hydrolysis (DHEH) pathway. This mechanistic advantage arises from the higher reactivity of $\cdot Cl$ (sharing halogen similarity with fluorine) compared to $\cdot OH$ in interacting with perfluorinated compounds [278]. Recent findings reveal chloride's concentration-dependent dual role in UV/VUV/sulfite processes: at lower concentrations (1–10 mM), it accelerates PFAS degradation by mediating aqueous electron ($e_{aq}^{\cdot -}$) transfer, whereas higher concentrations (20–500 mM) impair degradation efficiency through radical scavenging by chlorine species [279].

6. Conclusion

This review systematically elucidates the regional distribution and transformation dynamics of PFASs, while comprehensively analyzing recent advancements and mechanistic underpinnings of adsorption technologies and advanced oxidation/reduction processes for PFASs remediation. Particular emphasis is placed on the environmental interplay between long- and short-chain PFASs variants.

The principal conclusions are summarized as follows:

- (1) Structural Determinants of Environmental Behavior. PFASs exhibit unique amphiphilic characteristics (polar/non-polar, hydrophilic/hydrophobic duality). Enhanced aqueous solubility of short-chain PFASs confers greater environmental persistence and mobility compared to long-chain analogs. Their bioaccumulative potential and biomagnification capacity pose significant cross-trophic risks to ecosystem integrity and human health.
- (2) Toxicokinetic Profiles. Long-chain PFASs demonstrate prolonged bioaccumulation in mammalian blood compartments, whereas short-chain variants exhibit reduced half-lives but comparable toxicological endpoints. Chronic exposure to both classes induces analogous adverse health impacts through bioaccumulative pathways.
- (3) Physicochemical Treatment Efficacy. Adsorption, ion exchange, and membrane filtration demonstrate effective PFASs removal capabilities, operating across broad concentration ranges with established field implementation histories. However, short-chain PFASs exhibit significantly lower removal efficiencies compared to long-chain homologues. Long-chain PFASs are preferentially eliminated through synergistic mechanisms including electrostatic interactions, hydrogen bonding, and van der Waals forces,

with hydrophobic effects playing a dominant role. Conversely, short-chain PFASs' diminished hydrophobicity limits their capacity to traverse the solid-liquid interface, substantially compromising removal effectiveness.

- (4) Degradation Technology Limitations. Thermal and ultrasonic decomposition enable complete PFASs mineralization, though constrained by prohibitively high operational costs. Photocatalytic, electrochemical, and persulfate-based oxidation systems effectively degrade long-chain PFASs, with hydrated electron ($e_{aq}^{\cdot -}$) mediated advanced reduction technologies showing particular promise. Critical limitations persist as long-chain degradation generates structurally analogous short-chain intermediates. These short-chain derivatives exhibit greater molecular stability than parental compounds, with trace-level PFASs demonstrating exceptional resistance to complete mineralization through existing degradation pathways.

This review underscores the urgent need for developing cost-effective, environmentally benign remediation strategies addressing full-spectrum PFASs contamination. Future innovations must reconcile water matrix complexities (ionic composition, coexisting contaminants) and differential behaviors of mixed-chain PFASs, particularly optimizing technologies for short-chain PFASs elimination while preventing long-chain degradation byproduct formation.

CRediT authorship contribution statement

Kai Zhang: Writing – original draft, Software, Methodology, Data curation, Conceptualization. **Cong Li:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition. **Yulin Bian:** Writing – original draft, Formal analysis, Data curation. **Siyi Gu:** Software, Investigation, Data curation. **Jingzhen Su:** Investigation, Data curation. **Jieming Yuan:** Writing – review & editing, Investigation. **Hyunook Kim:** Writing – review & editing, Supervision, Resources, Conceptualization.

Declaration of Competing Interest

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

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Data availability

Data will be made available on request.

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