Remediation of Per- and Polyfluoroalkyl Substances (PFAS)-Contaminated Environments: Emerging Nanomaterials, Electrochemical, and Biological Strategies

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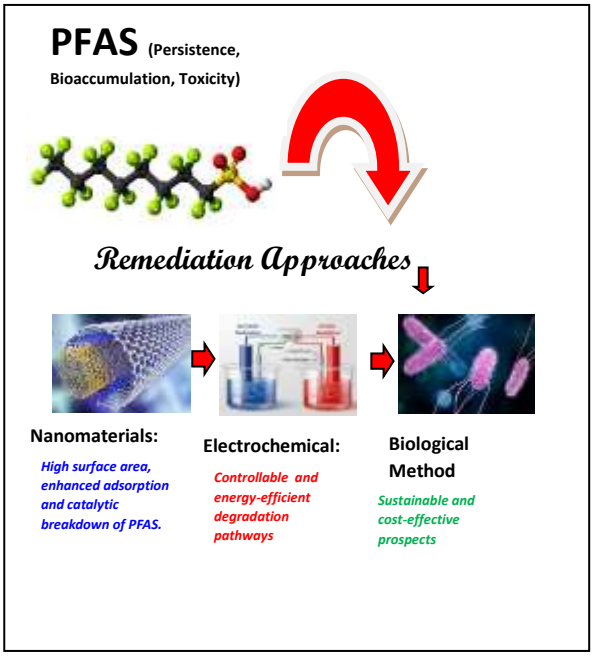
Abstract
Per- and polyfluoroalkyl substances (PFAS) are a large class of synthetic chemicals widely used for their hydrophobic and lipophobic properties in industrial and consumer products. However, their extreme persistence, bioaccumulation, and toxicity have led to significant environmental and human health concerns. Conventional treatment methods are often inadequate for PFAS removal due to the stability of the carbon-fluorine bond. In recent years, innovative approaches have emerged, particularly those employing advanced nanomaterials, electrochemical oxidation, and biological degradation techniques. Nanomaterial-based remediation leverages high surface area and tailored surface functionalities for enhanced adsorption and catalytic breakdown of PFAS. Electrochemical methods offer controllable and energy-efficient degradation pathways, capable of mineralizing PFAS into less harmful by-products. Meanwhile, biological strategies, though still developing, present sustainable and cost-effective prospects through microbial adaptation and enzymatic degradation mechanisms. Despite these advancements, key challenges remain, including incomplete defluorination, by-product formation, scalability, and economic feasibility. Future research should focus on integrating these methods into hybrid systems, optimizing materials design, and understanding degradation mechanisms at the molecular level to achieve effective and sustainable PFAS remediation.

Keywords: *Per- and Polyfluoroalkyl Substances, nanomaterials, electrochemical oxidation, biodegradation, PFAS remediation technologies, environmental sustainability*

Graphical abstract



1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are a large class of synthetic organofluorine compounds distinguished by their strong carbon-fluorine bonds, which contribute to exceptional chemical stability and environmental persistence [1]. Common PFAS such as PFOA, PFOS, and emerging alternatives like GenX have been used extensively since the 1940s in firefighting foams, non-stick cookware, waterproof textiles, lubricants, and various industrial processes. Their resistance to heat, water, and oils has made them commercially valuable but has also earned them the designation "forever chemicals." Due to their high stability, PFAS resist hydrolysis, photolysis, and biodegradation, resulting in widespread contamination of water, soils, sediments, and biota, including detection in remote environments. Growing toxicological evidence links PFAS exposure to endocrine disruption, immune suppression, hepatic toxicity, developmental effects, and certain cancers [2]. Human exposure occurs primarily through contaminated drinking water, food, indoor dust, and food packaging. In response, regulatory agencies such as the U.S. EPA and the European Union have introduced stringent limits and restrictions on PFAS production and use, and several compounds have been listed under the Stockholm Convention. Despite increased regulatory attention, PFAS remediation remains a major challenge due to the exceptional strength of the C-F bond. Conventional treatment technologies, including activated carbon, ion exchange resins, and membrane filtration, can remove PFAS from water but do not degrade them. Thermal incineration and advanced oxidation/reduction processes often demand extreme conditions and still show limited effectiveness or risk generating toxic by-products [3]. These limitations have intensified efforts to develop more efficient and sustainable destruction technologies. Recent research has focused on nanomaterial-based systems, electrochemical degradation, and emerging biological approaches for PFAS treatment. Nanomaterials offer tailored surface chemistry and catalytic properties for enhanced adsorption and degradation. Electrochemical methods provide a

promising route for direct mineralization of PFAS without external chemical inputs. Biological strategies, including microbial and enzymatic pathways, are being explored as environmentally benign alternatives for breaking down PFAS or transforming them into less persistent intermediates. Integrating these approaches into hybrid systems may offer improved efficiency and scalability. This review highlights recent advancements in PFAS remediation, evaluates the mechanisms and performance of emerging technologies, and identifies knowledge gaps and future research priorities aimed at developing sustainable and effective solutions for PFAS-contaminated environments.

2. Overview of PFAS Chemistry and Environmental Behaviour

Per- and polyfluoroalkyl substances (PFAS) possess exceptionally stable carbon-fluorine bonds, giving them strong thermal, chemical, and environmental persistence. Their mobility in water, resistance to degradation, and tendency to bioaccumulate make PFAS widespread contaminants with complex environmental behaviour.

2.1. Molecular Structure and Physicochemical Properties

Per- and polyfluoroalkyl substances (PFAS) represent a large and diverse class of synthetic organofluoride compounds characterized by the presence of multiple carbon-fluorine (C-F) bonds [4]. Their unique molecular architecture imparts exceptional chemical stability, surface activity, and resistance to thermal, biological, and photolytic degradation. The general structure of PFAS can be represented as R–(CF_2) n–CF_3, where *R* denotes a functional head group such as carboxylate (COOH), sulfonate (SO_3H), or phosphate. This amphiphilic configuration, consisting of a hydrophobic perfluoroalkyl tail and a hydrophilic functional head, dictates both their environmental fate and their complex interactions with biotic and abiotic matrices.

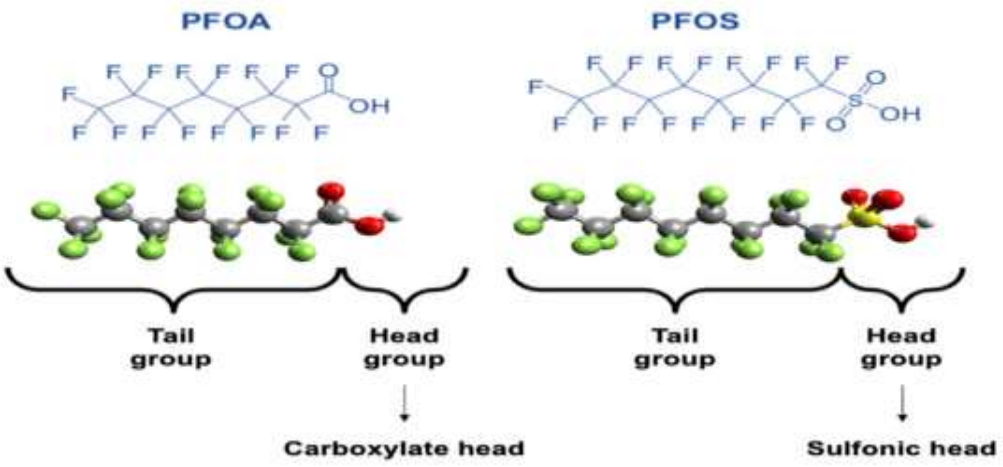


Figure 1: **PFOA and PFOS Chemical Structures [5]**

Carbon- Florine (C-F) Bond Characteristics

The C–F bond is among the strongest in organic chemistry, possessing a bond dissociation energy of approximately 485 kJ·mol^{-1} [4]. This exceptional strength arises from the high electronegativity of fluorine and the short bond length (1.35 Å), resulting in a highly polarized but covalent bond that resists cleavage under typical environmental conditions. Moreover, the extensive substitution of hydrogen with fluorine atoms shields the carbon skeleton from

nucleophilic, oxidative, and reductive attack, thereby enhancing molecular inertness [4]. The perfluoroalkyl chain exhibits low polarizability and high thermal stability, properties that collectively explain the extraordinary persistence of PFAS in both natural and engineered systems.

Figure 2:PFAS Carbon-Florine (C-F) Bond Structure Illustration [6]

Hydrophobic-Hydrophilic Duality

PFAS molecules display a distinctive hydrophobic-hydrophilic duality arising from their bifunctional nature [7]. The per fluorinated carbon chain is strongly lipophobic and hydrophobic due to the dense electron cloud around the C-F bonds, while the terminal polar group confers hydrophilicity and surface activity. This duality enables PFAS to act as surfactants, preferentially orienting at air, water and solid-liquid interfaces. The chain length and functional group strongly influence their partitioning behavior, long-chain PFAS (e.g., PFOS, PFOA) tend to adsorb to organic matter and sediments, whereas short-chain analogues exhibit greater aqueous solubility and mobility.

Implications for Environmental Persistence and Mobility

The chemical inertness and amphiphilic character of PFAS confer a suite of environmentally significant behaviors. Their persistence results primarily from the recalcitrance of the C-F bond, rendering them resistant to hydrolysis, photolysis, and microbial degradation [8]. Consequently, PFAS are often termed "forever chemicals," accumulating in diverse environmental compartments including groundwater, surface water, sediments, and biota. Mobility patterns vary with molecular structure: short-chain PFAS (e.g., perfluoro butanoic acid, PFBA) exhibit higher solubility and lower sorption to soil particles, facilitating their long-range transport through aqueous pathways. In contrast, long-chain PFAS show stronger adsorption to organic carbon and proteins, leading to bioaccumulation and trophic magnification. Additionally, precursor compounds, polyfluorinated species that can degrade to perfluoroalkyl acids (PFAAs), further complicate environmental dynamics by acting as secondary sources of contamination.

2.2. Environmental Distribution and Transport

The environmental distribution and transport of contaminants determine their persistence, ecological risks, and potential for human exposure. Understanding the behavior of pollutants across various environmental compartments, soil, groundwater, and surface water, is crucial for assessing their environmental fate and designing appropriate mitigation strategies [9].

Behavior in Soil, Groundwater, and Surface Water

Once released into the environment, contaminants interact dynamically with abiotic and biotic components. In soil**,** their behavior is influenced by several physicochemical parameters such as pH, organic matter content, redox potential, cation exchange capacity, and clay mineralogy.

Hydrophobic compounds tend to adsorb strongly to soil organic carbon, reducing their mobility but enhancing their persistence. Conversely, hydrophilic substances or those existing as ionic species may exhibit high solubility, promoting vertical leaching and groundwater contamination [10]. In groundwater systems**,** contaminant transport is governed by advection, dispersion, and sorption processes. Persistent organic pollutants (POPs), pesticides, and heavy metals can migrate considerable distances through porous media, especially in regions with high rainfall and permeable soils. The absence of sunlight and limited microbial activity in subsurface environments further slows degradation, leading to long-term contamination of aquifers. In surface waters**,** pollutants are distributed between dissolved, colloidal, and particulate phases. Hydrophobic chemicals such as polycyclic aromatic hydrocarbons (PAHs) and chlorinated Organics preferentially associate with suspended sediments, whereas metals may form complexes with dissolved organic ligands. Processes such as sedimentation, resuspension, volatilization, and photolysis significantly affect their environmental half-lives. Seasonal variations in flow, temperature, and sediment load also influence concentration dynamics within rivers, estuaries, and coastal waters [11].

Bioaccumulation and Biomagnification Tendencies

The tendency of a contaminant to accumulate in biological tissues is a key determinant of its ecological impact [12]. Bioaccumulation refers to the uptake and retention of substances by organisms from water, sediment, and food sources, while biomagnification describes the progressive increase in concentration along trophic levels within a food web [12]. Lipophilic compounds such as organochlorine pesticides, polychlorinated biphenyls (PCBs), and certain heavy metals (e.g., mercury and cadmium) exhibit high bioaccumulation potential due to their poor metabolic degradation and strong affinity for lipid-rich tissues. Once incorporated into biota, these compounds can reach toxic concentrations even when environmental levels appear low. Biomagnification further amplifies this effect in higher trophic organisms, including predatory fish, birds, and mammals, ultimately posing risks to human health through dietary exposure [12]. For instance, methyl mercury formed in aquatic systems bioaccumulates in plankton and biomagnifies through successive trophic transfers, reaching hazardous levels in piscivorous fish. The extent of bioaccumulation and biomagnification depends on factors such as the chemical's octanol-water partition coefficient (Kow), biotransformation rate, and organismal metabolic capacity. Ecological conditions, such as food web complexity, temperature, and habitat type, also influence accumulation dynamics. Persistent contaminants with high Kow values (>5) and low metabolic degradation rates are most prone to trophic transfer and long-term ecological harm [12].

3. Analytical and Monitoring Techniques

Accurate detection and quantification of per- and polyfluoroalkyl substances (PFAS) in environmental matrices are essential for understanding their occurrence, distribution, and potential health risks [13]. Due to their strong carbon-fluorine (C-F) bonds, PFAS exhibit exceptional chemical stability, thermal resistance, and hydrophobic-lipophobic characteristics, which complicate their analysis. Hence, robust analytical methodologies combining effective sample preparation, sensitive detection, and reliable quantification are required for precise environmental monitoring.

Sample Preparation and Pre-concentration

Environmental PFAS analysis begins with appropriate sample pretreatment, as their concentrations are typically at trace to ultra-trace levels (ng L^{-1} or pg L^{-1} range). Common matrices include surface water, groundwater, soil, sediment, and biota. Solid-phase extraction (SPE) remains the most widely used pre-concentration technique due to its efficiency in isolating PFAS from complex matrices while minimizing matrix interference [14]. SPE cartridges containing weak anion exchange (WAX) or hydrophilic-lipophilic balanced (HLB) sorbents are often employed. Alternative extraction methods such as QuEChERS**,** dispersive liquid-liquid micro-extraction (DLLME)**,** and ultrasound-assisted extraction (UAE) have been developed for faster and solvent-saving procedures. Given the widespread background contamination by fluoropolymer lab ware and PTFE materials, strict contamination control protocols, such as the use of polypropylene containers and PFAS-free solvents, are critical throughout sampling and analytical processes.

Common Detection and Quantification Techniques

(a) Atomic Absorption Spectroscopy (AAS)

Although Atomic Absorption Spectroscopy (AAS) is not commonly used for direct PFAS determination due to the absence of metal elements in PFAS molecules, it can serve as a complementary technique in studies involving PFAS-associated metals or co-pollutants. AAS effectively quantifies metal ions that may interact with PFAS through adsorption, complexation, or co-transport mechanisms in soil and water systems. For PFAS-metal interactions or remediation research involving metal-modified adsorbents, AAS provides accurate elemental analysis and serves as a quality control tool [15].

(b) Gas Chromatography–Mass Spectrometry (GC–MS)

GC-MS has historically been used for analyzing volatile and thermally stable PFAS precursors such as fluorotelomer alcohols (FTOHs), per fluorinated sulfonamides (FOSAs), and sulfonamidoethanols (FOSEs). However, because most PFAS are non-volatile and thermally stable, chemical derivatization (e.g., methylation or sialylation) is often required prior to GC analysis to enhance volatility and chromatographic performance. When coupled with electron ionization (EI) or chemical ionization (CI) mass spectrometry, GC-MS provides reliable qualitative and quantitative data for volatile PFAS congeners at low detection limits (typically in the ng L^{-1} range). Recent advancements in two-dimensional GC (GC x GC-MS**)** have further improved resolution and selectivity, enabling comprehensive PFAS fingerprinting in complex environmental samples [16].

(c) Liquid Chromatography–Tandem Mass Spectrometry (LC–MS/MS)

LC–MS/MS is the current gold standard for PFAS analysis in environmental and biological matrices. The technique offers superior sensitivity, specificity, and quantification capability for ionic and non-volatile PFAS without requiring derivatization [13]. In this approach, high-performance liquid chromatography (HPLC) or ultra-performance liquid chromatography (UPLC) is combined with tandem mass spectrometry operated typically in negative electrospray ionization (ESI) mode. The use of multiple reaction monitoring (MRM) transitions allows for selective quantification of individual PFAS congeners with detection limits as low as 0.1 ng L^{-1}. Recent methodological innovations include high-resolution mass spectrometry (HRMS) platforms such as quadrupole time-of-flight (QTOF)and Orbitrap systems, which enable non-

target screening and identification of novel PFAS analogues and transformation products. Moreover, the integration of LC–MS/MS with suspect and non-target workflows enhances monitoring of emerging PFAS beyond the conventional suite (e.g., PFOS, PFOA, PFHxS, PFNA).

Quality Assurance and Data Validation

Quality assurance and control (QA/QC) are vital components of PFAS analytical workflows. This includes the use of isotope-labeled internal standards for quantification, method blanks to assess background contamination, field and trip blanks to ensure sample integrity, and matrix spikes for recovery assessment. Data validation follows regulatory guidelines such as those of the U.S. EPA**,** ISO 25101:2019, and ASTM D7979, ensuring reproducibility and inter-laboratory comparability.

Emerging and Complementary Monitoring Tools

Advances in passive sampling techniques (e.g., Polar Organic Chemical Integrative Samplers-POCIS) and sensor-based monitoring are expanding PFAS detection capabilities in situ. These technologies provide time-integrated measurements and reduce sampling bias from short-term fluctuations. Furthermore, machine-learning-assisted spectral deconvolution and data-driven chemometric models are increasingly applied for PFAS source apportionment and transformation pathway analysis [13].

4. Nanomaterial-Based Remediation Approaches

The recalcitrant nature of per- and polyfluoroalkyl substances (PFAS) presents a formidable challenge to conventional water and soil treatment technologies [17]. Their exceptional thermal stability, resistance to hydrolysis and oxidation, and strong carbon-fluorine (C-F) bonds render them persistent in environmental compartments. In recent years, nanotechnology-based remediation has emerged as a promising alternative due to the unique physicochemical properties of nanomaterials, such as high surface area-to-volume ratios, tunable surface chemistry, and enhanced catalytic reactivity. These attributes enable nanoscale materials to interact more effectively with PFAS molecules, either through adsorption, catalysis, photodegradation, or reductive transformation processes [17].

4.1. Types of Nanomaterials

The design and application of nanomaterials for per- and polyfluoroalkyl substances (PFAS) remediation have attracted increasing scientific interest due to their tunable surface properties, high specific surface areas, and the ability to tailor chemical functionalities [18]. Nanomaterials can be broadly categorized into three classes based on composition and structural characteristics: carbon-based nanomaterials**,** metal and metal oxide nanoparticles**,** and nanocomposites orhybridsystems**.** Each class presents unique mechanisms of PFAS removal, including adsorption, catalysis, reduction, and photodegradation, depending on the physicochemical properties of the nanomaterial and the target PFAS species [18, 25, 26, 27].

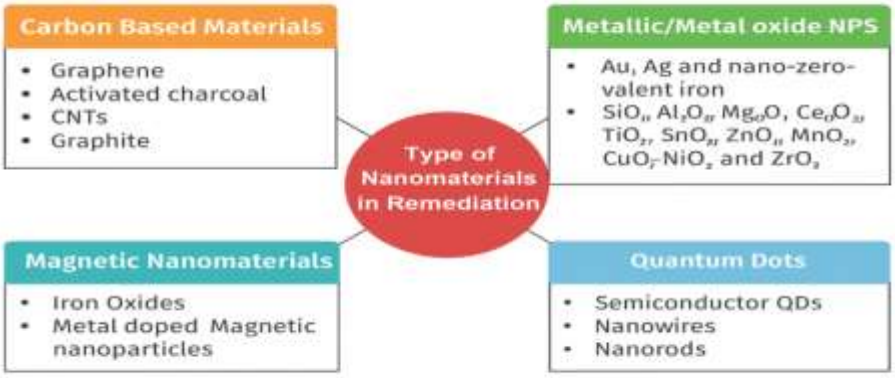


Figure 3: Types of Nanomaterials for PFAS Remediation [19].

Carbon-Based Nanomaterials

Carbon-based nanomaterials such as graphene**,** carbon nanotubes (CNTs), andactivatedcarbon nanoparticles have emerged as effective sorbents for PFAS due to their high surface area, hydrophobic domains, and tunable surface functionalities. Graphene and Graphene Oxide (GO): Graphene, a two-dimensional sheet of sp^2-hybridized carbon atoms, and its oxidized derivative, GO, exhibit exceptional adsorption capacities toward PFAS due to π–π interactions, van der Waals forces, and electrostatic attractions between functional groups (-OH, -COOH) and PFAS molecules. GO's oxygenated groups enhance dispersibility and create sites for hydrogen bonding and electrostatic interactions, thereby improving affinity for anionic PFAS such as perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS). Additionally, reduced graphene oxide (rGO) can act as a photocatalytic support, improving charge separation when combined with semiconductors like TiO_2 for photo-assisted PFAS degradation [17, 25, 26].

Carbon Nanotubes (CNTs): Both single-walled (SWCNTs) and multi-walled (MWCNTs) carbon nanotubes exhibit strong hydrophobic and electrostatic interactions with PFAS due to their hollow cylindrical morphology and tunable surface charge [19]. Functionalization with amine, carboxyl, or metal oxide groups further enhances PFAS uptake by promoting electrostatic attractions and hydrogen bonding. Studies have shown that amine-functionalized MWCNTs can remove >90% of PFOA under optimized conditions, outperforming many conventional sorbents [18].

Activated Carbon Nanoparticles: Nanoscale activated carbon (nAC) materials exhibit high surface roughness, microporosity, and strong affinity for long-chain PFAS via hydrophobic partitioning. The nanoscale form enhances mass transfer and adsorption kinetics compared to bulk activated carbon. Modification of activated carbon with iron or aluminum oxides has been reported to improve affinity toward both long- and short-chain PFAS, addressing the key limitation of traditional sorbents that preferentially remove long-chain PFAS [18, 26, 27].

Metal and Metal Oxide Nanoparticles

Metal and metal oxide nanoparticles have been extensively explored in PFAS remediation due to their redox reactivity, catalytic properties, and surface hydroxyl functionalities. Commonly

investigated examples include iron oxide (Fe_3O_4), titanium dioxide (TiO_2), zinc oxide (ZnO),andaluminum oxide (Al_2O_3)nanoparticles[18, 17].

Iron-Based Nanoparticles (Fe_3O_4, nZVI): Magnetite (Fe_3O_4) and nanoscale zero-valent iron (nZVI) are among the most widely used nanomaterials in PFAS treatment. Their large surface area, magnetic separability, and catalytic activity under reductive conditions enable PFAS adsorption and, in some cases, defluorination. Fe_3O_4 nanoparticles can adsorb PFAS via electrostatic interactions between positively charged surface sites and anionic PFAS head groups. Furthermore, when integrated with UV or persulfate systems, Fe_3O_4 can catalyze sulfate radical formation, enabling oxidative degradation of PFAS. nZVI, especially when modified with bimetallic coatings (e.g., Pd, Ni), can enhance reductive defluorination of shorter-chain PFAS under optimized conditions [18, 26].

Titanium Dioxide (TiO_2):TiO_2 nanoparticles, particularly in their anatase phase, are effective photocatalysts capable of generating reactive oxygen species (ROS) such as hydroxyl radicals and superoxide anions under UV or visible light. These ROS can attack C–F bonds, initiating PFAS degradation. Surface modification of TiO_2 with carbonaceous materials or dopants (e.g., N, F, or Fe) improves visible-light absorption and enhances photocatalytic efficiency. Moreover, TiO_2 can serve as a support material for coupling with other nanomaterials, such as graphene or Fe_3O_4, forming hybrid systems that integrate adsorption and photodegradation functionalities[17, 18].

Zinc Oxide (ZnO) and Aluminum Oxide (Al_2O_3): ZnO nanoparticles exhibit photocatalytic and adsorptive behavior similar to TiO_2, though they are more susceptible to dissolution in acidic conditions. Al_2O_3 nanoparticles, on the other hand, provide abundant surface hydroxyl groups and high surface charge, enhancing PFAS sorption via electrostatic interactions. However, the weak reactivity of Al_2O_3 toward C-F bond cleavage limits its use primarily to adsorption-based removal systems [19, 25, 27].

Nanocomposites and Hybrid Systems

Nanocomposites and hybrid systems integrate the properties of two or more materials to achieve synergistic effects in PFAS removal. Typical combinations include magnetite-clay composites, biochar-supported nanoparticles,andcarbon-metal oxide hybrids. These systems are designed to enhance surface reactivity, stability, and reusability while minimizing potential environmental risks [18].

Magnetite-Clay and Magnetite-Carbon Hybrids: Incorporating Fe_3O_4 nanoparticles into clay minerals (e.g., montmorillonite, bentonite) or carbon matrices (e.g., biochar, activated carbon) yields composites with high adsorption capacity and easy magnetic recovery. The clay or carbon substrate enhances dispersion and provides additional adsorption sites, while the magnetic phase facilitates separation and potential catalytic activity. For instance, Fe_3O_4-montmorillonite composites have demonstrated strong PFOS sorption through combined electrostatic and hydrophobic interactions, as well as reusability over multiple cycles [18, 27].

Biochar-Supported Catalysts: Biochar serves as an environmentally friendly and low-cost support for metal nanoparticles (Fe, TiO_2, or ZnO). Its porous carbon matrix enhances adsorption

and stabilizes nanoparticles against aggregation. Biochar-supported Fe_3O_4 and TiO_2 nanocomposites exhibit dual adsorption-photocatalytic functions, enabling both concentration and degradation of PFAS under light irradiation. Surface oxygenated groups and persistent free radicals within biochar can also participate in PFAS transformation processes [18, 26].

Carbon–Metal Oxide Hybrids: Hybrid materials such as rGO-TiO_2, CNT-Fe_3O_4, or grapheme-ZnO integrate the high adsorption capacity of carbonaceous nanomaterials with the catalytic or magnetic properties of metal oxides. These systems exhibit superior PFAS removal efficiencies compared to single-component materials. For example, rGO–TiO_2 composites have demonstrated enhanced photodegradation of PFOA due to improved electron transfer and reduced charge recombination. Similarly, CNT-Fe_3O_4 hybrids combine strong PFAS sorption with facile magnetic separation [17, 18, 19].

4.2. Mechanistic Insights

Understanding the mechanisms governing PFAS-nanomaterial interactions is crucial for optimizing removal efficiency and ensuring long-term environmental safety [20]. PFAS remediation using nanomaterials occurs mainly through sorption and catalytic degradation. Sorption enables the initial capture of PFAS on nanomaterial surfaces, while catalytic degradation drives their chemical transformation and potential mineralization. Mechanistic insights clarify how nanomaterial properties and reaction conditions shape PFAS behavior and transformation pathways.

Sorption Kinetics and Surface Chemistry

Sorption kinetics describe the rate and mechanism by which PFAS molecules interact with and become immobilized on the surface of nanomaterials [21]. This kinetics are controlled by factors such as surface charge, hydrophobicity, pore structure, and the presence of functional groups capable of electrostatic or hydrogen-bonding interactions.

(a) Kinetic Models and Rate-Limiting Steps

PFAS sorption on nanomaterials is commonly described using kinetic models such as pseudo-first-order, pseudo-second-order, and intraparticle diffusion models. The pseudo-first-order model reflects physisorption dominated by weak van der Waals or hydrophobic interactions, while the pseudo-second-order model represents chemisorption involving stronger forces like hydrogen bonding and electrostatic attraction. The intraparticle diffusion model highlights the role of pore diffusion, especially in porous materials such as activated carbon and biochar. Sorption typically progresses through rapid surface adsorption, slower diffusion into pores, and eventual equilibrium. The rate-limiting step is strongly influenced by PFAS chain length and hydrophobicity, with longer-chain PFAS adsorbing more readily [22, 25].

(b) Role of Surface Chemistry

The surface chemistry of nanomaterials strongly influences their affinity and selectivity toward different PFAS, requiring a balance between hydrophobic attraction and electrostatic interactions. Positively charged surfaces, such as protonated Fe_3O_4 or Al_2O_3 below their pHpzc, enhance adsorption by attracting the anionic PFAS head groups. Carbon-based materials like graphene, CNTs, and biochar rely primarily on hydrophobic interactions through van der Waals forces and π–π stacking with PFAS tails. Surface functionalization, including amine groups or

metal doping, further strengthens mechanisms such as hydrogen bonding and ligand exchange, improving the removal of even challenging short-chain PFAS [23].

(c) Thermodynamic Considerations

Thermodynamic analyses, through parameters such as $\Delta G°$, $\Delta H°$, and $\Delta S°$, provide insights into the spontaneity and nature of PFAS sorption. Most PFAS adsorption processes on nanomaterials are spontaneous ($\Delta G° < 0$) and endothermic ($\Delta H° > 0$), indicating that increased temperature enhances sorption due to improved molecular mobility and pore accessibility. Positive entropy changes ($\Delta S° > 0$) typically reflect the displacement of water molecules at the solid-liquid interface during PFAS binding, suggesting a hydrophobic partitioning mechanism.

Catalytic Degradation Pathways and By-Product Analysis

While sorption immobilizes PFAS, catalytic degradation aims to destructively break the strong C-F bonds (bond dissociation energy 485 kJ mol^{-1}) that confer their persistence. Nanomaterial-enabled catalytic systems, such as photocatalysis, reductive catalysis, and advanced oxidation/reduction processes, facilitate PFAS mineralization through generation of reactive species capable of initiating defluorination [24].

(a)Photocatalytic Pathways

In photocatalytic systems such as TiO_2, ZnO, and Fe_3O_4 composites, light exposure generates electron-hole pairs that form reactive oxygen species responsible for PFAS degradation. PFAS molecules first adsorb onto the catalyst surface, where ROS attack the head groups and initiate carbon-fluorine bond cleavage, producing shorter-chain intermediates and fluoride ions [24]. The overall efficiency depends on factors like bandgap energy, surface charge, and the suppression of electron-hole recombination. Dopants such as Fe, N, or Ag enhance visible-light activity and charge separation, significantly improving PFAS mineralization.

(b) Reductive and Catalytic Hydrogenation Mechanisms

Reductive pathways for PFAS degradation, often catalyzed by nanoscale zero-valent iron, bimetallic nanoparticles, or carbon-supported metals, involve electron transfer to break C-F bonds. During this process, electrons generated at the metal surface reduce PFAS molecules, producing defluorinated hydrocarbons and fluoride ions, as seen in Pd/Fe-catalyzed hydro defluorination of PFOA [24]. This approach is especially effective under anaerobic conditions and can be integrated with adsorption for enhanced PFAS removal and transformation.

(c) Advanced Oxidation and Reduction Processes (AOPs/ARPs)

Nanomaterials enhance advanced oxidation and reduction processes by catalyzing oxidants or reductants, such as persulfate and hydrogen peroxide, to generate reactive radicals that attack PFAS molecules. Transition metal oxides like Fe_3O_4, MnO_2, and Co_3O_4 enable radical generation and, when combined with adsorption, can synergistically degrade PFAS, though oxidation alone often targets only the headgroup. Emerging approaches, including nanomaterial-assisted photoelectrocatalysis and plasma-catalysis, show promise for near-complete PFAS mineralization with lower energy input [24].

(d) By-Product Formation and Toxicological Considerations

A crucial aspect of catalytic PFAS degradation involves the identification and control of transformation products. Analytical tools such as liquid chromatography-tandem mass spectrometry (LC-MS/MS) and fluoride ion-selective electrodes are used to monitor degradation intermediates and quantify released fluoride [24]. Common intermediates include shorter-chain perfluoro carboxylic acids (PFCAs)**,** per fluoroalkenes, and fluorinated alcohols**,** which may exhibit varying degrees of toxicity and mobility. While these products confirm progressive defluorination, their transient accumulation underscores the importance of optimizing reaction conditions to favour complete mineralization rather than partial degradation. Comprehensive mass balance analysis, tracking carbon and fluorine, has become a standard criterion in evaluating the effectiveness and environmental safety of nanomaterial-based PFAS remediation systems.

Advantages and Limitations of Nanomaterial-Based PFAS Remediation:

The key advantages and limitations of these nanomaterial-based PFAS remediation strategies are summarized in Table 1.

Table 1: Advantages and Limitations of Nanomaterial-Based PFAS Remediation

Advantages	Limitations	Citations
High surface area and hierarchical porosity enable rapid PFAS uptake and adsorption of both long- and short-chain PFAS.	Potential toxicity, persistence, and formation of secondary pollutants pose ecological risks.	Li *et al.,* 2022
Tunable surface reactivity via functionalization and doping enhances adsorption and catalytic degradation.	Poor regeneration over multiple cycles and high synthesis costs limit practical application.	Gao *et al.,* 2021
Dual functionality allows simultaneous adsorption and catalytic degradation, improving defluorination efficiency.	Catalytic processes may generate partially defluorinated intermediates that remain environmentally persistent.	Sharma & Kumar., 2020
Magnetic or photocatalytic recovery improves reusability and reduces operational costs.	Scaling up to field conditions is challenging, with integration into existing treatment systems difficult.	Li *et al.,* 2022
Maintains high performance under diverse environmental conditions, including varying pH, ionic strength, and co-contaminants.	Limited selectivity for short-chain PFAS may require additional modifications or hybrid approaches.	Gao *et al.,* 2021

5. Electrochemical Remediation Techniques

Electrochemical remediation uses applied electrical currents to break down PFAS through advanced oxidation, reduction, or radical-driven pathways that can cleave the strong C-F bonds. These techniques offer high removal efficiency and controllability, making them a promising approach for treating PFAS-contaminated water.

5.1. Principles and Mechanisms

Electrochemical remediation uses electrical energy to drive redox reactions within a cell consisting of an anode, cathode, and electrolyte, generating reactive intermediates that degrade PFAS either directly or indirectly [28, 29]. PFAS degradation can occur via direct oxidation, indirect oxidation, or electrochemical reduction, depending on electrode material, applied potential, and electrolyte chemistry. This approach offers advantages over conventional methods, including in-situ generation of reactive species, minimal chemical additives, controllable conditions, and potential for complete mineralization. The effectiveness of electrochemical PFAS treatment relies on optimizing electrode properties, electrolyte composition, and operational parameters to efficiently break the strong C-F bonds [29].

Direct Electrochemical Oxidation

Direct oxidation involves PFAS molecules transferring electrons directly at the anode surface, leading to cleavage of functional groups or C-F bonds without intermediate species. PFAS adsorption on non-active anodes like boron-doped diamond (BDD), SnO_2, or PbO_2 facilitates electron transfer and generates highly reactive hydroxyl radicals at high potentials. Degradation typically proceeds via sequential decarboxylation for PFCAs or desulfonation for PFSAs, producing shorter-chain intermediates and fluoride ions. BDD electrodes are especially effective due to their high oxygen evolution over-potential, which enhances reactive species generation and energy efficiency, enabling near-complete mineralization of PFAS [28].

Indirect Electrochemical Oxidation

In indirect oxidation, PFAS degradation occurs via reactive oxidants or radicals generated from water or electrolytes, rather than direct electron transfer. Species such as hydroxyl radicals, sulfate radicals, peroxydisulfate, and active chlorine oxidize PFAS non-selectively in solution or at the electrode interface. Key mechanisms include anodic water oxidation, persulfate activation, and chlorine-mediated oxidation, all of which break C-F and C-C bonds in PFAS molecules. This approach is effective for treating dilute PFAS-contaminated water, but care must be taken to avoid forming chlorinated by-products and other secondary pollutants [28].

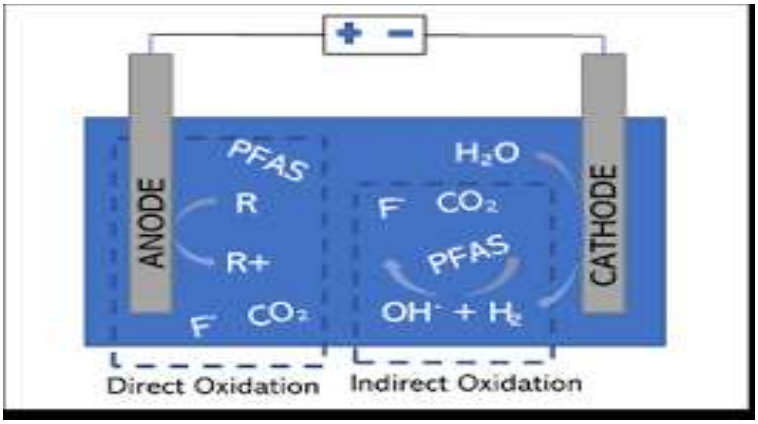


Figure 4: Mechanisms of Electrochemical Oxidation [28].

Electrochemical Reduction Processes

Electro reductive processes are emerging as effective complements to oxidative PFAS remediation, particularly for breaking strong C-F bonds under reducing conditions [30].

Reduction occurs at the cathode, either through direct electron transfer to PFAS or via reducing agents like hydrated electrons and hydrogen radicals from water. Mechanisms include stepwise defluorination by hydrogen radicals and catalytic hydro defluorination on metal-coated cathodes such as Pd, Ni, or Fe. Combining cathodic reduction with anodic oxidation in dual-cell systems further enhances degradation, enabling near-complete PFAS mineralization.

Role of Electrodes and Electrolytes

Electrode material critically influences PFAS electrochemical degradation, determining efficiency, selectivity, and stability [31]. Non-active electrodes like BDD generate weakly adsorbed hydroxyl radicals for direct oxidation, while active electrodes such as Pt and IrO_2 favor selective but partial oxidation. Cathodes like stainless steel, graphite, and bimetallic catalysts enable reductive processes, and surface modifications enhance PFAS adsorption and reduce fouling. Electrolyte type, pH, ionic strength, and temperature further affect reactive species generation, mass transfer, and degradation efficiency, making careful material and electrolyte selection essential for optimal PFAS removal [31].

Integrated Electrochemical Systems and Synergistic Effects

Recent research has focused on hybrid electrochemical systems that combine anodic oxidation with cathodic reduction or integrate electrochemical treatment with advanced oxidation processes to improve PFAS degradation [32]. Examples include electro-peroxide systems for in situ ozone generation, photo electrocatalytic setups using light and bias for enhanced charge separation, and electro-Fenton or electro-persulfate systems that produce reactive radicals. These integrated approaches achieve higher mineralization efficiency and better control over by-products. They also reduce energy consumption compared to conventional standalone electrochemical methods.

Reaction Products and Mineralization Efficiency

During electrochemical degradation, PFAS molecules undergo stepwise defluorination, producing shorter-chain perfluoro carboxylic acids**,** fluoride ions**,** and CO_2 as major end-products. The extent of defluorination, often expressed as fluoride release ratio (F^-/F_total), is a key performance indicator. High-efficiency systems, particularly those employing BDD or Ti_4O_7 anodes, can achieve >90% defluorination under optimized conditions. However, partial oxidation can lead to persistent intermediates, necessitating careful monitoring through LC-MS/MSandion chromatography. Ensuring full mineralization while minimizing energy consumption and secondary pollution remains an active research frontier [32].

5.2. Emerging Electrochemical Systems

Electrochemical systems are emerging as sustainable technologies for degrading persistent pollutants like PFAS through electron transfer at the electrode, solution interface. They generate reactive intermediates that break down recalcitrant compounds under mild conditions. Advanced hybrid systems integrating electrochemical, photochemical, catalytic, and plasma processes further enhance degradation efficiency and mineralization, making these systems promising for next-generation contaminant remediation [32, 29].

Electrochemical Oxidation (EO)

Electrochemical oxidation (EO) degrades PFAS by generating powerful oxidizing species at high-oxygen over-potential anodes such as BDD, Ti_4O_7, PbO_2, and SnO_2, enabling the breakdown of strong carbon-fluorine bonds. BDD electrodes in particular demonstrate superior stability and oxidative strength, achieving near-complete mineralization of both short- and long-chain PFAS. EO performance depends heavily on operational parameters including current density, pH, electrode potential, and electrolyte composition, all of which must be optimized to maximize efficiency and limit unwanted byproducts [28]. Although advances such as doped nanostructured electrodes and hybrid EO-catalytic systems have improved degradation efficiency, challenges like high energy demand and electrode fouling still hinder large-scale application.

Electro-Fenton and Photoelectrochemical Methods

Electro-Fenton (EF) and photoelectrochemical (PEC) processes generate reactive radicals through electrochemical and light-driven pathways, enabling efficient degradation of PFAS and other persistent pollutants [33]. EF relies on in situ production of hydrogen peroxide and its reaction with Fe^{2+} to form hydroxyl radicals, while photo-assisted variants further enhance radical regeneration and energy efficiency. PEC systems use semiconductor photoanodes and often incorporate nanomaterials to improve charge separation, light absorption, and overall degradation kinetics. Although both methods offer high efficiency and low chemical demand, their performance depends on factors such as pH, solution chemistry, and iron cycling, and complete PFAS mineralization still requires long treatment times, prompting ongoing research into improved catalysts and photoelectrodes

Plasma-Assisted and Coupled Electrochemical Systems

Plasma-assisted electrochemical systems combine plasma discharge with electrochemical processes to generate diverse reactive species that significantly enhance pollutant degradation, including PFAS [34]. By integrating plasma-induced radicals with electrochemical oxidation, these hybrid systems achieve accelerated mineralization, improved mass transfer, and greater energy efficiency. Recent innovations, such as nanostructured catalysts and optimized dielectric materials, have further boosted reactivity and system performance. Although challenges remain in reactor design, scalability, and energy optimization, ongoing advances in materials and power control are rapidly positioning plasma-electrochemical hybrids as leading next-generation remediation technologies.

5.3. Reactor Designs and Electrode Materials

The efficiency and sustainability of electrochemical PFAS degradation depend heavily on reactor design, which controls mass transport and current distribution, and on electrode materials, which determine redox activity and stability [35]. Modern systems emphasize modular, energy-efficient reactors alongside advanced electrodes engineered through nano structuring, doping, and surface modification to improve catalytic performance. Together, these design elements govern the overall effectiveness of electrochemical technologies in degrading PFAS and other persistent pollutants.

Boron-doped diamond (BDD) electrodes: Boron-doped diamond (BDD) electrodes are highly effective in electrochemical oxidation due to their wide potential window, strong hydroxyl radical generation, and exceptional chemical stability, enabling efficient PFAS mineralization. Their sp^3 carbon matrix doped with boron provides high conductivity and durability, allowing operation at high current densities and achieving up to 90–100% degradation of long-chain PFAS [36]. Although their hydrophobic surface enhances PFAS adsorption and oxidation, large-scale use is constrained by high fabrication costs and the energy-intensive CVD process. Current research focuses on developing cheaper deposition methods, composite BDD structures, and hybrid systems that integrate photocatalytic or plasma-assisted modules to further improve performance.

Tin oxide (SnO_2)-based electrodes: particularly Ti/SnO_2–Sb and Ti/SnO_2–Ru variants, have emerged as alternative anode materials offering a balance between performance and cost. SnO_2 exhibits a high overpotential for oxygen evolution and strong catalytic activity toward the generation of hydroxyl radicals, although it is less stable than BDD under long-term operation. Doping SnO_2 with antimony (Sb) or other transition metals improves conductivity, mechanical stability, and corrosion resistance [37]. The Ti/SnO_2 architecture, typically comprising a titanium substrate coated with doped SnO_2 films, promotes efficient electron transfer and allows facile regeneration of the active surface. Such electrodes are particularly attractive for industrial-scale applications due to their scalability, moderate cost, and tunable surface chemistry. However, degradation pathways using Ti/SnO_2 often result in partial mineralization and formation of intermediates, necessitating coupling with other processes such as Fenton oxidation or photocatalysis to achieve complete PFAS breakdown.

Carbon-based electrode: Including graphite, glassy carbon, carbon felt, graphene, and carbon nanotubes (CNTs), constitute another important class of electrode material for electrochemical degradation. These materials offer high electrical conductivity, large surface area, and chemical versatility [38]. The incorporation of functional groups (-OH, -COOH, -C=O) or heteroatoms (N, B, S) into the carbon lattice enhances their catalytic activity and affinity toward fluorinated species. Moreover, nanostructured carbon materials can serve as both electrodes and supports for active catalysts such as metal oxides or nanoparticles, leading to hybrid electrodes with improved charge transfer and stability. Carbon-based cathodes are particularly valuable in electro-Fenton systems, where they facilitate in situ generation of hydrogen peroxide from oxygen reduction, thereby supporting radical-based degradation of PFAS and other persistent organics. Nevertheless, carbon materials may undergo gradual surface oxidation or structural degradation during prolonged anodic operation, limiting their lifespan. Research continues to focus on developing doped or composite carbon electrodes, such as graphene oxide/TiO_2 or CNT/BDD

hybrids, to combine the mechanical robustness of diamond-like carbon with the high reactivity and conductivity of nanostructured carbons. These advancements are critical to achieving scalable, cost-effective, and energy-efficient electrode systems for real-world remediation applications.

Operational Parameters (Current Density, Voltage, pH)

The efficiency of electrochemical PFAS degradation strongly depends on operational parameters such as current density, applied voltage, and solution pH, which collectively influence radical generation, electron transfer, and energy consumption [39]. Optimal current density and voltage are required to maximize hydroxyl radical formation while avoiding parasitic reactions like oxygen evolution and excessive energy use. Solution pH affects both PFAS speciation and radical stability, with acidic conditions generally favoring oxidation, although BDD electrodes maintain high performance across wider pH ranges. Modern optimization tools and renewable power integration are increasingly used to identify ideal operating windows and improve the sustainability of electrochemical remediation systems.

5.4. Performance Evaluation and Limitations

The performance of electrochemical systems for PFAS degradation is governed by a complex interplay between electrode materials, reactor configurations, operational parameters, and solution chemistry [40]. While these systems have demonstrated remarkable potential for the treatment of persistent organic pollutants, a critical evaluation of their efficiency, energy requirements, by-product formation, and scalability is essential for determining their viability in large-scale environmental remediation. Comprehensive assessment of these parameters not only provides insights into the mechanistic pathways of PFAS degradation but also identifies the technological bottlenecks that must be overcome before industrial implementation.

Degradation Efficiency

Degradation efficiency is the key metric for assessing electrochemical PFAS treatment, with systems using BDD, Ti/SnO_2, or Ti/PbO_2 anodes achieving high removal through direct electron transfer and radical-mediated C-F bond cleavage [41]. Long-chain PFAS often degrade more efficiently due to stronger adsorption on electrode surfaces, whereas short-chain PFAS are more resistant because of their higher solubility. Real wastewater constituents such as chloride, sulfate, and natural organic matter can hinder degradation by scavenging radicals or forming less reactive oxidants. To address these challenges, advanced reactor designs and hybrid systems that integrate photocatalysis, plasma, or Fenton-based processes are being developed to enhance mass transfer, radical generation, and overall mineralization efficiency.

Energy Consumption

Energy demand is a major limitation for large-scale electrochemical PFAS treatment, as energy consumption depends on factors such as current density, electrode potential, reactor geometry, and mass transport. Although higher current densities enhance radical production, they also increase ohmic losses and oxygen evolution, reducing overall efficiency, with BDD-based systems typically requiring 50–250 kWh/m^3 [42]. Strategies to lower energy use include optimizing current efficiency, integrating hybrid processes such as photo electrocatalysis or electro-Fenton, and incorporating renewable energy sources. Continued improvements in

electrode design, reactor engineering, and intelligent operational control are essential to achieving both high degradation efficiency and reduced energy consumption.

By-Products

Electrochemical PFAS degradation can generate partially defluorinated intermediates and halogenated by-products, some of which may be as persistent or mobile as the parent compounds [43]. These species, such as short-chain perfluoro carboxylates or chlorinated oxidants, arise through stepwise oxidation or radical reactions, especially in systems containing chloride. Because such by-products may pose environmental or health risks, detailed pathway analysis and toxicity evaluation using advanced analytical techniques are essential. Recent approaches, including coupling electrochemical oxidation with adsorption or biofiltration and incorporating selective nano catalysts, aim to minimize intermediate formation and promote complete mineralization.

Scalability Issues

Scaling electrochemical PFAS treatment from the laboratory to real-world applications is hindered by high costs, energy demands, electrode stability issues, and the complexity of actual wastewater matrices [44]. Advanced electrodes like BDD offer excellent performance but remain expensive to produce, prompting research into lower-cost alternatives and more durable reactor designs. New reactor configurations, such as continuous-flow, modular, membrane-integrated, and 3D systems, are being developed to improve mass transfer, surface area, and operational efficiency while addressing fouling and maintenance challenges. Achieving practical large-scale implementation will require advances in materials, smart reactor control, renewable energy integration, and sustained collaboration across scientific and engineering disciplines.

6. Biological Remediation Strategies

Per- and polyfluoroalkyl substances (PFAS) are highly persistent synthetic chemicals that resist conventional degradation due to their strong carbon-fluorine bonds. Biological remediation offers a sustainable alternative by leveraging microbial, enzymatic, and plant-based processes to transform or immobilize these contaminants. Recent studies have identified specialized bacteria and engineered enzymes capable of initiating PFAS defluorination under controlled conditions. Although still emerging, biological strategies show promising potential for eco-friendly PFAS cleanup in contaminated soils and water systems.

6.1. Microbial Degradation of PFAS

Aerobic vs. Anaerobic Pathways

PFAS biodegradation can occur under both aerobic and anaerobic conditions, with distinct mechanisms and limitations [45]. Aerobic degradation involves the use of oxygen-dependent enzymatic systems, such as oxygenase's, which can catalyze partial defluorination of certain short-chain PFAS, often resulting in shorter perfluoroalkyl acids or fluorinated intermediates. This pathway is generally faster but may not achieve complete mineralization due to the chemical stability of the carbon–fluorine bonds. In contrast, anaerobic degradation occurs in oxygen-limited environments, often mediated by reductive defluorination reactions. Certain anaerobic bacteria can cleave carbon–fluorine bonds through electron transfer processes, leading to stepwise dehalogenation and formation of less fluorinated compounds. Anaerobic pathways

are typically slower than aerobic processes but have shown promise in environments such as sediments and sludge, where oxygen availability is limited.

Identified PFAS-Degrading Microorganisms

Research has identified several microbial taxa with PFAS transformation capabilities [46]. Notable aerobic PFAS degraders include *Pseudomonas* species and *Ralstoniametallidurans*, which exhibit partial defluorination of specific short-chain PFAS. Anaerobic PFAS transformation has been observed in *Desulfitobacterium* species and certain strains of *Clostridium*, capable of reductive defluorination under sulfate-reducing conditions. Additionally, mixed microbial consortia from activated sludge and contaminated soils have shown enhanced PFAS degradation, suggesting synergistic interactions that facilitate defluorination. Continued exploration of microbial diversity and metabolic pathways is critical for developing effective bioremediation strategies for PFAS-contaminated sites.

6.2. Enzymatic Degradation

Enzymatic degradation offers a highly specific and environmentally compatible approach for the remediation of per- and polyfluoroalkyl substances (PFAS), targeting the exceptionally stable carbon-fluorine bonds that resist conventional chemical breakdown [47].

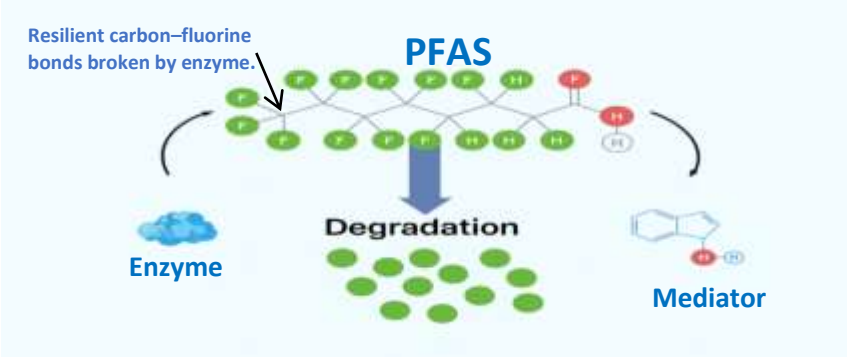


Figure 5: A Typical Degradation of PFAS via Enzyme [47]

Role of Oxidoreductases and Defluorinases

Key enzymes implicated in PFAS transformation include oxidoreductases and defluorinases[48,49]. Oxidoreductases, such as peroxidases, laccases, and cytochrome P450 monooxygenases, facilitate partial defluorination by generating reactive radicals that can cleave C-F bonds or modify PFAS functional groups, enhancing susceptibility to further microbial degradation. Defluorinases, on the other hand, catalyze the direct hydrolytic or reductive cleavage of C-F bonds, producing less fluorinated and potentially more biodegradable intermediates. Although naturally occurring enzymes demonstrate limited efficiency against long-chain PFAS, they provide critical mechanistic insights for designing effective biocatalytic systems [50].

Enzyme Engineering for Enhanced Degradation

To overcome inherent limitations in catalytic efficiency and substrate specificity, enzyme engineering has emerged as a promising strategy [51]. Approaches such as directed evolution, site-directed mutagenesis, and computational protein design have been employed to generate enzyme variants with improved stability, activity, and affinity toward a broader range of PFAS

compounds [52]. Engineered oxidoreductases and defluorinated show enhanced defluorination rates and tolerance to environmental conditions, enabling their potential application in bioreactors, immobilized enzyme systems, or integrated treatment processes. Advances in enzyme engineering thus hold significant promise for developing scalable and selective PFAS remediation technologies [53].

6.3. Phytoremediation and Bioaugmentation

Biological strategies for PFAS remediation increasingly explore the synergistic potential of plants and microorganisms [53]. Phytoremediation**,** the use of plants to remove, stabilize, or transform contaminants, offers a sustainable and environmentally compatible approach to PFAS mitigation.

Plant-Based Uptake and Rhizosphere Interactions

Certain plants, particularly hyperaccumulators, can uptake PFAS from contaminated soils and water, sequestering them in roots, stems, or leaves [48]. The rhizosphere, the narrow region of soil influenced by root exudates, plays a critical role in enhancing PFAS transformation [49]. Root exudates can stimulate microbial activity and co-metabolic processes, facilitating partial defluorination or degradation of PFAS compounds [50]. Additionally, the interaction between plant roots and rhizosphere microbiota can improve PFAS bioavailability, thereby increasing the efficiency of uptake and transformation [51].

Use of Genetically Modified Organisms (GMOs) for Improved Performance

To overcome the slow and limited natural biodegradation of PFAS, bioaugmentation strategies employing genetically modified microorganisms have been developed [52]. Engineered microbes expressing enhanced PFAS-degrading enzymes, such as oxidoreductases or defluorinases, can accelerate defluorination and increase the spectrum of degradable PFAS compounds [53]. Integrating GMOs into the rhizosphere or in plant-microbe consortia has shown improved degradation performance, providing a promising approach for field-scale remediation. However, regulatory and ecological considerations must be addressed before wide deployment [49].

6.4. Limitations and Future Prospects

Despite significant advances in biological remediation of PFAS, several limitations constrain its widespread application [50]. The low degradation rate of both microbial and enzymatic processes, particularly for long-chain PFAS, remains a major bottleneck, often requiring prolonged treatment times to achieve meaningful reductions [51]. Furthermore, the high substrate specificity of most PFAS-degrading enzymes and microorganisms limits their effectiveness across the diverse chemical structures and functional groups present in environmental PFAS mixtures [52]. Field-scale applicability is also challenging due to environmental variability, such as pH, temperature, soil composition, and the presence of co-contaminants, which can inhibit biological activity and reduce overall efficiency. Future prospects lie in the integration of advanced biotechnological approaches, including enzyme engineering, synthetic biology, and genetically modified microbial consortia, to enhance degradation kinetics and broaden substrate range. Combining microbial, enzymatic, and phytoremediation strategies in hybrid systems may offer synergistic benefits, improving efficiency and adaptability under field conditions [49]. Additionally, continued research on rhizosphere interactions, microbial ecology, and real-world pilot studies is critical to bridge

laboratory findings with practical environmental applications. Addressing these challenges will be essential for translating biological PFAS remediation from controlled studies to scalable, sustainable, and effective field solutions [51].

7. Integrated and Hybrid Remediation Approaches

Integrated and hybrid remediation approaches combine physical, chemical, and biological methods to overcome the limitations of single-technique treatments for PFAS. By coupling complementary processes, these systems enhance PFAS removal efficiency, reduce treatment time, and improve overall environmental sustainability.

7.1. Nano-Bio Systems

The integration of nanotechnology with biological remediation, commonly referred to asnano-bio systems**,** represents a promising frontier in the treatment of persistent environmental contaminants such as per- and polyfluoroalkyl substances (PFAS) [54]. These hybrid strategies leverage the unique physicochemical properties of nanomaterials to enhance microbial activity, improve contaminant bioavailability, and accelerate degradation processes that are otherwise slow or inefficient in conventional bioremediation [54].

Use of Nano catalysts to Stimulate Microbial Degradation

Nano catalysts, including metal-based nanoparticles (e.gFe_3O_4, TiO_2, ZnO) and carbon-based nanomaterials (e.g graphene oxide, carbon nanotubes), have been employed to facilitate PFAS degradation by acting as reactive sites or electron donors/acceptors that stimulate microbial metabolism [55]. These nano catalysts can generate reactive oxygen species (ROS) or other radical species that partially oxidize PFAS molecules, making them more susceptible to microbial attack [55]. Moreover, nano catalysts can serve as electron shuttles in microbial redox reactions, enhancing the efficiency of enzymatic processes, such as those catalyzed by oxidoreductases and defluorinases. By reducing activation energy barriers and promoting localized reactions, nano catalysts effectively accelerate biodegradation kinetics [55].

Synergistic Effects and Enhanced Bioavailability

The integration of nanoparticles with microbial systems also improves the bioavailability ofPFAS**,** which are often strongly adsorbed to soil or sediment matrices due to their hydrophobic and surfactant-like properties. Nanomaterials can alter sorption dynamics, desorb bound PFAS, or create microenvironments that increase substrate accessibility to degrading microbes [56]. Furthermore, synergistic interactions between nano catalysts and microbial consortia can enhance defluorination efficiency. For example, nanomaterials can reduce toxicity of certain PFAS intermediates to microbes, while microbial metabolism can regenerate active sites on nano catalysts, creating a positive feedback loop. Despite these advantages, challenges remain, including potential nanomaterial toxicity, aggregation, environmental persistence, and cost considerations for large-scale deployment [56]. Future research should focus on designing biocompatible and environmentally safe nanomaterials**,** optimizing nano-bio ratios, and elucidating mechanistic pathways to maximize degradation while minimizing secondary environmental risks. Ultimately, nano–bio hybrid systems represent a cutting-edge approach capable of bridging the gap between laboratory-scale PFAS remediation and practical, field-scale applications [54].

7.2. Electrochemical-Biological Systems

The combination of electrochemical and biological processes, referred to as electrochemical-biological systems (EBS), has emerged as a highly promising hybrid strategy for the remediation of per- and polyfluoroalkyl substances (PFAS) [57]. By integrating the oxidative power of electrochemical reactions with the selectivity and sustainability of microbial degradation, EBS can overcome the limitations associated with standalone biological or electrochemical approaches. These systems leverage synergistic mechanisms to enhance degradation kinetics, achieve higher mineralization rates, and reduce the formation of recalcitrant intermediates [58].

Sequential or Coupled Treatment Systems

Electrochemical–biological systems can operate as sequential or coupled treatment processes, depending on site-specific requirements and contaminant profiles [58]. In sequential systems, electrochemical oxidation is applied as a pre-treatment step to partially degrade PFAS, generating shorter-chain intermediates or functionalized molecules that are more amenable to microbial assimilation [59]. This pretreatment reduces the recalcitrance of long-chain PFAS, enabling downstream biological processes to achieve greater defluorination efficiency. In coupled systems, electrochemical cells are integrated with bioreactors, allowing simultaneous microbial and electrochemical activity [59]. In such configurations, the applied potential can stimulate microbial metabolism by enhancing electron transfer processes, while microbes assist in regenerating reactive surfaces on electrodes, creating a synergistic environment for continuous PFAS transformation.

Energy Efficiency and Degradation Completeness

One of the critical advantages of EBS lies in its energy efficiency relative to conventional electrochemical systems [60]. By coupling microbial metabolism with electrochemical reactions, EBS can achieve significant PFAS degradation at lower applied voltages, reducing operational costs and minimizing energy consumption [60]. Moreover, the combination of oxidative electrochemical processes and enzymatic or microbial degradation enhances the completeness of PFASmineralization, reducing the accumulation of potentially toxic intermediates such as perfluoroalkyl acids or shorter-chain analogs. Optimization of electrode materials, reactor configurations, and microbial consortia is essential to maximize degradation efficiency while maintaining system stability and sustainability [61]. Despite these advantages, challenges remain in scaling EBS to field applications, including electrode fouling, mass transfer limitations, and the need for robust microbial communities that tolerate electrochemical conditions. Future research should focus on advanced electrode designs, low-energy operation strategies, and the integration of omics-based microbial monitoring to enable reliable, large-scale PFAS remediation. The development of electrochemical–biological hybrid systems therefore represents a transformative approach capable of bridging laboratory innovation with practical environmental applications [61].

7.3. Combined Treatment Optimization

The persistent and recalcitrant nature of per- and polyfluoroalkyl substances (PFAS) in the environment has necessitated the development of treatment strategies that go beyond conventional single-method approaches [57]. Combined treatment optimization, often referred to as hybrid treatment, integrates multiple remediation technologies to enhance PFAS

mineralization and removal efficiency, addressing the limitations inherent in individual treatment methods [58].

Hybrid Systems for PFAS Mineralization

Hybrid treatment systems aim to couple complementary physical, chemical, and biological processes to achieve more complete PFAS degradation [59]. Such systems are designed to leverage the strengths of each component method while mitigating their respective weaknesses. For instance, adsorption-based techniques, such as granular activated carbon (GAC) or ion-exchange resins, are highly effective for PFAS concentration removal but do not destroy the compounds. Coupling adsorption with advanced oxidation processes (AOPs), electrochemical oxidation, or photocatalytic degradation allows the sequestered PFAS molecules to undergo mineralization into innocuous end-products, such as fluoride ions, carbon dioxide, and water [60]. Recent research has demonstrated that integrating electrochemical oxidation with photocatalysis can significantly accelerate the breakdown of both short- and long-chain PFAS. Similarly, combining biological treatment, such as anaerobic or aerobic microbial degradation, with advanced oxidation provides a synergistic effect, wherein partial breakdown products generated by one process become more amenable to degradation in the subsequent step. The optimization of operational parameters, including pH, temperature, redox potential, and residence time, is critical to achieving high mineralization efficiency while minimizing energy consumption and secondary pollution [61].

Case Studies and Pilot-Scale Applications

Several pilot-scale studies have validated the efficacy of combined PFAS treatment systems in real-world settings [59]. In one study, a hybrid system coupling GAC adsorption with UV-activated persulfate oxidation achieved over 90% mineralization of perfluorooctanoic acid (PFOA) in contaminated groundwater, demonstrating both scalability and operational feasibility. Another pilot-scale application integrated foam fractionation with electrochemical treatment to concentrate and degrade PFAS from industrial effluents, effectively reducing PFAS concentrations to below regulatory thresholds. Moreover, full-scale implementations have begun to emerge in industrial and municipal water treatment facilities, highlighting the practical applicability of hybrid systems. These installations often employ a sequential treatment train, where physical removal methods are followed by chemical or biological oxidation [61]. Performance monitoring in these systems indicates that hybrid treatment not only improves overall PFAS removal efficiency but also addresses a broader spectrum of PFAS chain lengths and functional groups. Despite these advances, challenges remain in optimizing hybrid systems for cost-effectiveness, energy efficiency, and environmental sustainability. Future research is focused on integrating machine learning and process modeling to predict optimal treatment combinations, designing modular systems for adaptable deployment, and developing new catalysts and microbial consortia specifically targeted at recalcitrant PFAS compounds [61].

8. Comparative Evaluation and Challenges

Comparative evaluation of PFAS remediation assesses the efficiency, cost, and environmental impact of chemical, biological, and electrochemical methods. Despite advances, challenges remain due to PFAS persistence, complex mixtures, and potential formation of toxic byproducts during treatment.

8.1. Comparative Performance Summary

PFAS remediation methods, including adsorption, advanced oxidation, electrochemical, biological, and hybrid systems, differ in efficiency, cost, scalability, and environmental impact [62]. Adsorption techniques like GAC and ion-exchange resins are effective for long-chain PFAS but do not achieve mineralization and require energy-intensive regeneration. Advanced oxidation and electrochemical methods can mineralize PFAS but face high energy demands and sensitivity to water matrix composition, while biological treatments are sustainable but slow and often incomplete for highly fluorinated compounds. Hybrid approaches combining multiple technologies offer improved efficiency and mineralization potential, though they involve higher complexity and capital costs, making strategy selection context-dependent [62].

Knowledge Gaps

Despite advancements in PFAS remediation, critical knowledge gaps persist that impede the development of fully optimized treatment strategies [63]. Mechanistic understanding of PFAS degradation, particularly for short-chain and branched compounds, remains incomplete, with limited insights into reaction kinetics, transformation pathways, and the influence of water chemistry. Additionally, the identification and characterization of degradation intermediates are essential, as partial breakdown products may exhibit comparable or greater toxicity than parent compounds, raising concerns regarding secondary pollution [63]. Toxicological studies addressing both intermediates and end-products remain sparse, highlighting the need for comprehensive risk assessments. Addressing these knowledge gaps is essential for improving process design, ensuring environmental safety, and informing regulatory frameworks [63].

Regulatory and Socioeconomic Considerations

Global management of PFAS is increasingly influenced by regulatory frameworks that set permissible limits for various PFAS compounds in water, soil, and food matrices [64]. Policies differ significantly across regions, with stringent standards in North America and Europe, while developing countries often face limited regulatory enforcement due to infrastructure, technical capacity, and financial constraints. These disparities impact the adoption of PFAS remediation technologies, as high-cost and technically demanding solutions may not be feasible in low-resource settings [64]. Socio-economic considerations, including community awareness, stakeholder engagement, and cost-sharing mechanisms, play a crucial role in technology implementation. Integrated strategies that combine regulatory compliance, affordable treatment solutions, and public education are necessary to achieve effective PFAS management, particularly in regions where resources and technical expertise are limited [64].

9. Future Perspectives

The persistent and complex nature of per- and polyfluoroalkyl substances (PFAS) continues to challenge conventional remediation strategies, prompting the need for innovative, efficient, and sustainable approaches [70]. Emerging technologies, coupled with interdisciplinary integration, are likely to define the next generation of PFAS treatment methods. Future perspectives focus on technological innovation, sustainability, and policy-driven solutions that enhance remediation efficacy while minimizing environmental and socioeconomic impacts.

Integration of Machine Learning and AI for Process Optimization

The application of machine learning (ML) and artificial intelligence (AI) in environmental remediation offers transformative potential for PFAS treatment [65]. These computational tools enable predictive modeling of treatment performance, real-time process optimization, and decision-making support in complex multi-parameter systems. For example, AI algorithms can predict adsorption capacities of novel materials, optimize reaction conditions in advanced oxidation processes, and forecast PFAS degradation kinetics under varying water chemistries [66]. Integration of AI with sensor-based monitoring systems facilitates adaptive management of pilot and full-scale treatment plants, enhancing efficiency, reducing operational costs, and minimizing energy consumption. Furthermore, data-driven approaches can identify optimal hybrid system configurations, accelerating the translation of laboratory-scale findings into practical applications.

Green Synthesis of Nanomaterials and Sustainable Electrode Design

Nanomaterials and advanced electrochemical systems have demonstrated remarkable potential for PFAS degradation, yet their conventional synthesis often relies on toxic reagents and energy-intensive processes [67]. The green synthesis of nanomaterials using plant extracts, biodegradable polymers, or microbial templates offers a sustainable alternative, reducing environmental footprints while retaining high catalytic activity. In parallel, the development of sustainable electrode materials, including recyclable, low-cost, and corrosion-resistant electrodes, is critical for electrochemical PFAS remediation. Research efforts are increasingly focused on designing electrodes that maximize reactive surface area, minimize energy consumption, and resist fouling, thereby improving the long-term feasibility and economic viability of electrochemical processes.

Advances in Synthetic Biology for PFAS-Degrading Enzymes

Synthetic biology presents a promising frontier in the development of biologically based PFAS remediation strategies. Engineering microorganisms or enzymes capable of selectively degrading highly fluorinated compounds can address the limitations of conventional biological treatments [68]. Progress in protein engineering, directed evolution, and metabolic pathway design enables the creation of robust PFAS-degrading enzymes with enhanced specificity, stability, and turnover rates. Coupling these biocatalysts with hybrid or integrated treatment systems may allow for complete mineralization of PFAS in environmentally relevant conditions. Moreover, the deployment of microbial consortia with complementary degradation capabilities could further expand the spectrum of treatable PFAS compounds, including emerging short-chain and branched species.

Policy-Driven and Circular-Economy-Oriented Remediation Strategies

Technological advancements must be complemented by forward-looking policy and governance frameworks that incentivize sustainable PFAS management [69]. Policy-driven strategies, including regulatory standards, funding mechanisms, and public-private partnerships, can accelerate the adoption of innovative remediation technologies while ensuring environmental protection. The integration of circular-economy principles into PFAS treatment emphasizes resource recovery, recycling, and reuse of by-products, transforming waste management from a disposal-oriented paradigm to one that maximizes environmental and economic value. For instance, spent adsorbents and catalytic materials can be regenerated, repurposed, or valorized,

reducing the environmental burden and cost associated with treatment processes. Holistic strategies that combine scientific innovation with regulatory support and circular-economy principles will be critical for achieving sustainable, globally relevant PFAS mitigation. The future of PFAS remediation lies in the convergence of advanced computational tools, green chemistry, synthetic biology, and policy-driven sustainability frameworks. By leveraging these interdisciplinary approaches, it is possible to develop next-generation treatment strategies that are not only effective and scalable but also environmentally responsible and socially equitable [69].

10. Conclusion

The remediation of PFAS-contaminated environments has witnessed significant advances through the development and application of nanomaterials, electrochemical systems, and biological strategies. Nanomaterials offer high adsorption capacities and catalytic potential, enabling efficient removal and partial degradation of persistent PFAS compounds. Electrochemical approaches, including anodic oxidation and hybrid electrode systems, demonstrate considerable promise for direct PFAS mineralization, while biological strategies, particularly microbial and enzymatic degradation, provide environmentally sustainable pathways for long-term remediation. Despite these advancements, no single method offers a universal solution, highlighting the necessity for integrated treatment approaches that combine complementary technologies. Hybrid systems, optimized through careful process design, can balance efficiency, cost, scalability, and environmental impact, enhancing overall remediation performance. Moreover, the incorporation of emerging tools such as machine learning, green nanomaterials, synthetic biology, and circular-economy-oriented strategies is poised to further improve process sustainability, reduce operational costs, and minimize ecological risks. The collective progress in nanomaterial, electrochemical, and biological strategies underscores a transformative potential for PFAS remediation. Future efforts must focus on integrated, cost-effective, and environmentally responsible solutions that are adaptable to diverse contaminated sites, regulatory frameworks, and socioeconomic contexts, ultimately enabling sustainable management of PFAS-contaminated environments worldwide.

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