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Environmental Significance Statement:

Per- and polyfluoroalkyl substances (PFAS) are synthetic chemicals widely used in industrial and consumer products due to their thermal and chemical stability. However, their resistance to environmental degradation, bioaccumulative behavior, and links to serious health effects have raised global concern. Traditional removal methods, such as adsorption and filtration, are limited by their inability to destroy PFAS, risking secondary pollution. Fenton-based advanced oxidation processes offer a promising pathway toward PFAS mineralization under mild conditions. This review provides a comprehensive analysis of the mechanisms, effectiveness, and technological progress of Fenton-based PFAS degradation. By highlighting current limitations and future directions, it aims to guide the development of practical, scalable, and sustainable remediation strategies for PFAS-contaminated environments, contributing to global efforts in safeguarding ecological and human health.



Degradation of per- and polyfluoroalkyl substances (PFAS) by Fenton reactions

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Abstract

Per- and polyfluoroalkyl substances (PFAS) are persistent organic pollutants with widespread environmental and health threats due to their chemical stability and bioaccumulative potential. The Fenton-based degradation of PFAS demonstrates several advantages, including mild reaction conditions, operational simplicity, and cost-effectiveness, while simultaneously facing challenges such as inefficient cleavage of carbon-fluorine (C–F) bonds and low mineralization. This review comprehensively summarizes the degradation of PFAS using Fenton-based reactions, focusing on mechanisms, efficiencies, and technological advancements. Firstly, the reasons for PFAS prevalence in human society, their pathways into biological systems, the associated health risks, as well as their global distribution and contamination status are elucidated. Secondly, the current major PFAS degradation approaches are summarized, highlighting the principal advantages of Fenton-based degradation. Thirdly, a comprehensive overview of recent advancements in Fenton-based PFAS degradation technologies are reviewed, including chemical-Fenton, electro-Fenton, photo-Fenton, and photo-electro-Fenton processes. Finally, the future research directions are discussed, focusing on catalyst design optimization, structure-activity relationship, and feasibility assessment for large-scale applications. This review provides a critical foundation for advancing sustainable PFAS remediation technologies.

Keywords: PFAS degradation; Advanced oxidation processes; Fenton reaction; Degradation mechanisms; Large-scale application



1. Introduction

Per- and polyfluoroalkyl substances (PFAS) comprise a class of over 6,500 distinct anthropogenic fluorinated organic compounds,^{1,2} characterized by fully or partially fluorinated alkyl chains, terminated with polar acidic moieties such as carboxylates, sulfonates, or phosphonates.³ Based on the carbon-chain length, PFAS are generally classified into long-chain and short-chain types.⁴ Long-chain PFAS, such as perfluorononanoic acid (PFNA) and perfluoropentanoic acid (PP), with more than eight carbon atoms, exhibit distinct physicochemical properties compared to short-chain PFAS (such as perfluorobutanesulfonic acid (PFBS), perfluorohexanoic acid (PFHxA), and perfluorohexanesulfonic acid (PFHxS), with four to seven carbon atoms). These differences are especially evident in aqueous solubility and hydrophilicity, which can be quantified by solubility measurements and octanol-water partition coefficients.^{5,6} For example, short-chain PFAS contain fewer fluorine atoms and lack the pronounced “molecular-brush” architecture of long-chain counterparts,^{1,2} thus having stronger water solubility and affinity for aqueous phases.⁵ Beyond chain length, the inherent stability of PFAS stems from their abundant C–F bonds.⁷ The high electronegativity of F atoms induces strong electron localization, thereby giving the C–F bonds extremely high polarity and bond energy (~110 kcal/mol).⁸ The thermally and chemically robust C–F bonds endows PFAS with outstanding stability, unique lubricating and frictional characteristics, driving their extensive industrial applications since the 1940s, such as refrigerants, polymer-processing aids, pharmaceutical syntheses, adhesives, insecticides, and flame retardants.^{9,10}



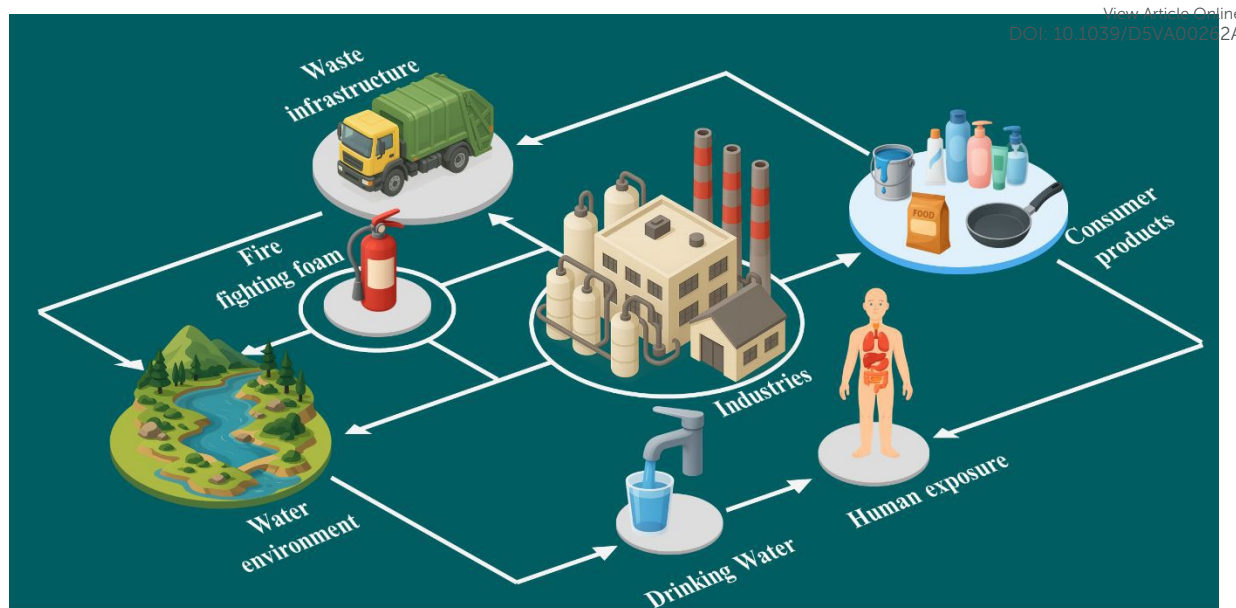


Figure 1. Migration process of PFAS in the environment.

PFAS were first detected in human serum in the 1960s,¹¹ which prompted studies on their environmental and biological risks. Their bioaccumulative potential is well established, with pronounced biomagnification in aquatic food webs.¹² Primary producers (e.g., phytoplankton) capture PFAS and introduce it into ecosystem. For aquatic vertebrates (e.g., cyprinus carpio, danio rerio), they directly absorb PFAS through gills, establishing trophic transfer pathways.¹³ In particular, the perfluoroalkyl phosphinic acids (PFPIAs) upregulate lipid transport genes (e.g., *cd36*, *fabp1*), leading to hepatic steatosis. The disruption of β -oxidation and phospholipid metabolism induces reactive oxygen species (ROS), activates NF- κ B, elevates pro-inflammatory cytokines (tnf- α , il-1 β , il-6), suppresses il-10,¹⁴⁻¹⁷ and triggers inflammation. The perfluorooctane sulfonates (PFOS) analogues bind transthyretin, disturbing thyroid homeostasis.¹⁸ In plants, PFAS are root-absorbed and transported to their above-ground parts. In wheat, fulvic and humic acids (HA) promote uptake of 6:2 Cl-PFAES via H⁺-



ATPase and Ca^{2+} -dependent pathways.^{19,20} In arabidopsis, PFAS-induced ROS causes lipid peroxidation and structural damage.²¹⁻²⁶ Structure-specific effects include PFOA-mediated cation disruption,²² PFOS-induced amino acid dysregulation,²³ and 8:2 FTSA conversion impacting lipid metabolism.²⁶ In mammals, PFAS induce neuro-, hepato-, and reproductive toxicity, and worsen gut inflammation.^{27,28} Dermal exposure models confirm systemic accumulation via CD36-mediated uptake, particularly in liver/kidneys.²⁹⁻³¹ Bioaccumulation is structure- and species-dependent, warranting further mechanistic research.

Due to the bioaccumulative potential and ecotoxicity of PFAS, their environmental contamination has become a pressing concern. Regulatory frameworks demonstrate increasing recognition of PFAS risks. In 2016, the U.S. Environmental Protection Agency (EPA) established health advisory levels at 0.070 $\mu\text{g/L}$ for PFOS. Recent revisions have drastically reduced these thresholds to 0.004 ng/L for PFOA and 0.02 ng/L for PFOS.³² The EU Water Framework Directive proposes a cumulative limit of 0.1 $\mu\text{g/L}$ for 20 prioritized PFAS compounds.³³ However, measured concentrations of PFAS in drinking water and groundwater worldwide often far exceed these thresholds (Figure 2).

Drinking water surveys reveal widespread contamination, with most urban supplies containing >100 ng/L PFAS globally.³⁴⁻⁴¹ South Korea exhibits the highest concentrations (644.6 ng/L) of the untreated drinking water (Figure 2a),³⁸ attributing to dense clustering of chemical plants, electronics manufacturers, and textile facilities discharging PFAS-laden effluents. Conversely, Kampala, the capital of Uganda, shows



minimal contamination (5.3 ng/L) (Figure 2a),⁴¹ potentially due to water sourcing from Murchison Bay where lake dilution mitigates PFAS levels.

The groundwater system is more severely polluted, with the concentrations of PFAS in it being 25 to 500 times higher than drinking water.⁴²⁻⁴⁹ Extreme contamination occurs near Swedish airports (51,000 ng/L) (Figure 2b),⁴⁷ exceeding EU standards by 510 times, stemming from unregulated release of PFAS-containing firefighting foam over several decades. A recent investigation in Shandong Province of China—home to one of Asia's largest fluorochemical industrial parks—identified severe PFAS discharge into nearby streams.^{50,51} Although the affected waterways are relatively small, the industrial park's emissions—totaling 8.4 t of HFPOs (hexafluoropropylene oxides)—represent 85% of all HFPOs discharge into rivers across China.⁵² In contrast, North China Plain aquifers show relatively low PFAS levels (13.4 ng/L) (Figure 2b),⁴² correlating with limited industrial activity in the region. Recent reports indicate that PFAS concentrations in industrial wastewater treatment plants span a wide range, from 310 to 4920 ng/L in influents and from 246 to 27100 ng/L in effluents, reflecting variations over several orders of magnitude.⁵³ The overall PFAS levels observed in these facilities are comparable to those recently reported in Korea for domestic wastewater (>1000 ng/L) and industrial wastewater (>5000 ng/L),⁵⁴ as well as in fluorochemical wastewater treatment plants in France (25260 ng/L).⁵⁵ These cases highlight that industrial wastewater discharge as the primary PFAS entry route into ecosystems. The extreme environmental persistence of PFAS facilitates progressive accumulation, posing severe ecological threats. Consequently, extensive researches



now focus on developing effective PFAS degradation technologies and remediation strategies.

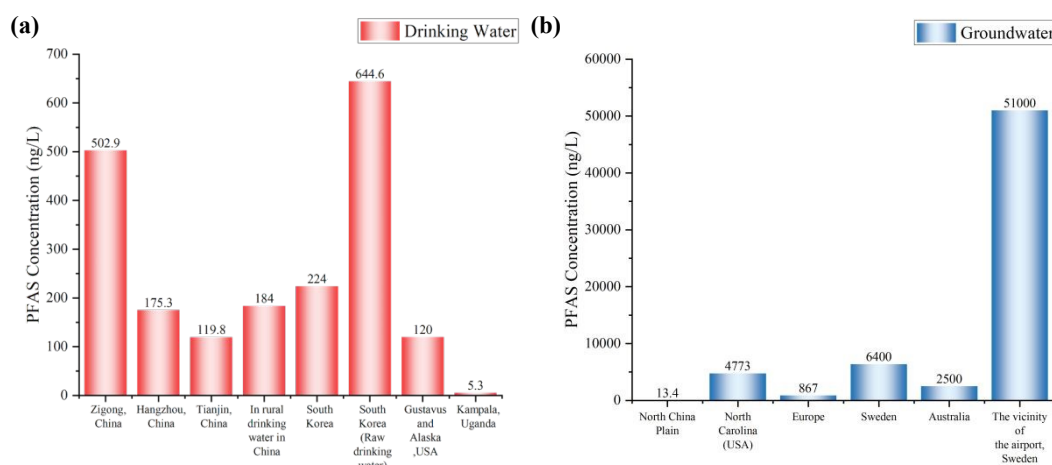


Figure 2. The concentration of PFAS in different water. (a) drinking water, and (b) groundwater.

2. Prevailing PFAS Degradation Strategies

A wide variety of purification methods for PFAS have been developed to date, including biodegradation approaches,^{56,57} physical adsorption,^{58,59} and chemical degradation (oxidation and reduction processes).⁶⁰⁻⁶³ However, physical adsorption, being a non-destructive process, may generate secondary waste such as spent adsorbents, which pose a risk of re-releasing PFAS into the environment. In contrast, biodegradation and chemical degradation aim at the permanent removal of PFAS. Nevertheless, biodegradation is often incomplete, slow, and highly dependent on specific environmental conditions.⁶⁴ More importantly, it is difficult to break the extremely strong C–F bonds of PFAS molecules. Among the chemical degradation methods, advanced oxidation processes (AOPs), first introduced by Glaze in 1987, are



characterized by the generation of highly reactive radical species as oxidants, and are regarded as promising technologies with strong potential for the complete mineralization of PFAS.^{65,66} Among AOPs, the Fenton reaction is one of the most classical and widely studied techniques. The Fenton reaction was first discovered in 1894 by the French scientist Henry.J. Fenton, who observed that tartaric acid could be deactivated and oxidized in a ferrous ion (Fe^{2+})/ hydrogen peroxide (H_2O_2) system at pH 2–3.⁶⁷ The key advantages of the Fenton process include its high oxidative performance and operational simplicity under ambient temperature and atmospheric pressure.^{68,69} Moreover, its toxicity is relatively low because H_2O_2 ultimately decomposes into environmentally benign species such as water (H_2O) and oxygen (O_2).⁷⁰ Mechanistically, utilizing Fe^{2+} as a catalyst, it enables the continuous and stable decomposition of H_2O_2 to generate hydroxyl radicals ($\bullet\text{OH}$) (shown in Eq (1) and Eq (2)). These highly reactive hydroxyl radicals subsequently attack organic pollutants present in water, initiating a cascade of oxidation reactions that ultimately mineralize the contaminants into carbon dioxide (CO_2) and H_2O , thereby achieving water purification.^{71,72}



For the complete mineralization of PFAS, the degradation pathway begins with the initial activation of the molecule to generate perfluoroalkyl radicals ($\bullet\text{C}_n\text{F}_{2n+1}$).



These radicals then react with $\bullet\text{OH}$ to form unstable perfluoroalcohol intermediates, which readily undergo elimination reactions to release hydrogen fluoride (HF). The resulting acyl fluoride intermediates are highly prone to hydrolysis, leading to the formation of shorter-chain perfluorocarboxylic acids.⁷³ Through successive cycles of similar reactions, PFOA can eventually be mineralized into CO_2 and HF (Figure 3).^{74,75} The ability of the Fenton system to continuously supply hydroxyl radicals makes it a promising approach for driving the deep oxidative degradation and potential mineralization of PFAS.

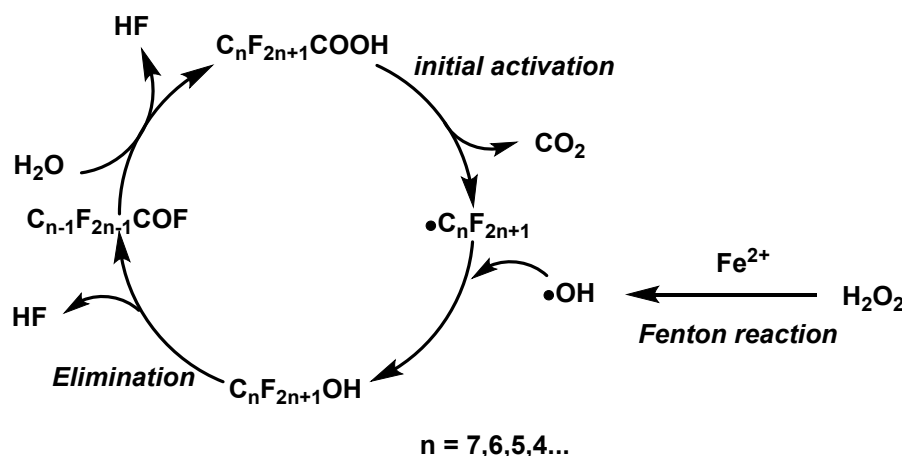


Figure 3. Reaction mechanism for degradation of PFOA via the Fenton process. Upon completion of each reaction cycle, the value of n decreases by one, initiating the subsequent cycle.

However, the Fenton reaction also exhibits certain limitations. When treating wastewater, its efficiency is influenced by factors such as pH and iron ion concentration of wastewater. Neither low nor high pH values enable effective treatment of organic pollutants. The optimal treatment efficiency is achieved within a pH range of 2.0–



4.0.^{76,77} Unfortunately, most organic wastewaters do not naturally fall within this pH range. The substantial amounts of chemical reagents are often required to adjust the pH prior to treatment, which increases the overall cost of wastewater remediation. Furthermore, while Equations (1) and (2) form the basis for the catalytic cycle of the Fenton reaction, the rate of reaction (1) is approximately 6,000 times faster than that of reaction (2),⁷⁸ which severely hampers the regeneration of Fe^{2+} from Fe^{3+} and leads to the accumulation of Fe^{3+} in the system. When the pH values above 3, Fe^{3+} tends to precipitate as hydroxide complexes—commonly referred to as iron sludge.⁷⁹ This sludge is difficult to separate and recover, resulting in substantial loss of catalytic iron species, reduced process efficiency, and the risk of secondary environmental pollution. To overcome these limitations, various strategies have been developed to enhance the Fenton reaction. Depending on the enhancement method, these approaches can be categorized into chemical-Fenton,⁸⁰⁻⁸⁷ electro-Fenton,⁸⁸⁻⁹³ UV/visible/solar light-assisted Fenton (photo-Fenton),⁹⁴⁻¹⁰¹ and solar photo-electro-Fenton (SPEF) systems.¹⁰²⁻¹⁰⁷ Moreover, these technologies can be integrated in a synergistic or coupled manner to minimize or even eliminate the limitations associated with individual processes.

Herein, we focus on the research progress in utilizing Fenton reaction systems for PFAS degradation (Figure 4). Through a systematic discussion of various Fenton systems, this review extensively elucidates degradation pathways, degradation efficiency, the redox potentials of different radical species, byproduct formation, and toxicity assessment. The primary objectives of this review are as follows: (1) to summarize the pathways and mechanisms of different Fenton reaction system; (2) to



summarize the degradation efficiencies of various radicals involved in PFAS removal under Fenton reaction conditions; (3) to systematically compare factors influencing PFAS degradation efficiency; (4) to summarize byproduct formation across different Fenton reaction systems and critically analyze their associated toxicity; and (5) to outline future research prospects. This review aims to establish a theoretical foundation for PFAS removal in practical applications.

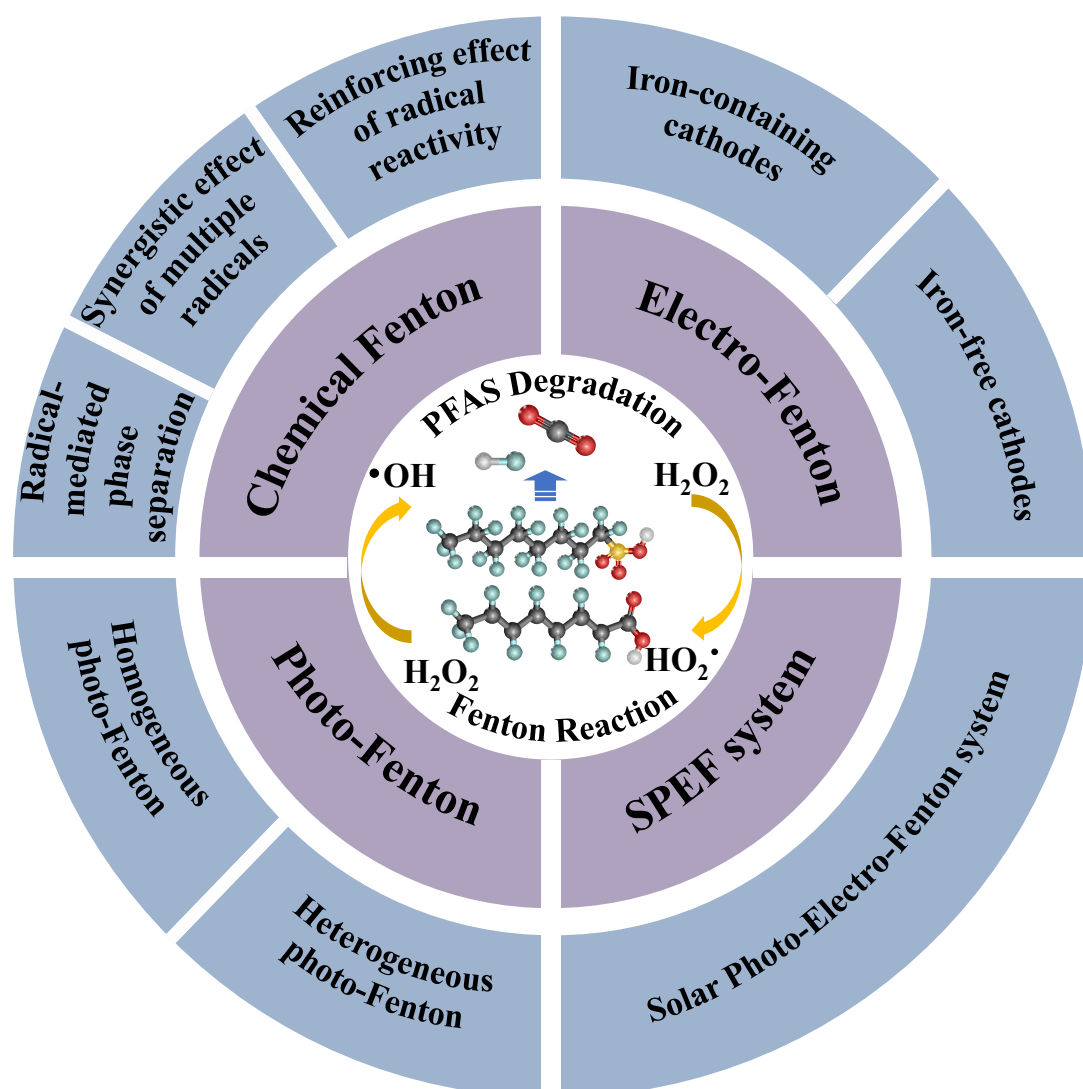


Figure 4. Summary diagram of the contents in this review.



3. Degradation of PFAS via Fenton reactions

3.1 Chemical-Fenton reaction system

Although the classical chemical Fenton reaction provides a stable and efficient source of $\bullet\text{OH}$, these radicals alone have proven inadequate for the effective degradation of PFAS. For instance, in the case of PFOA, studies have demonstrated that even under high concentrations of H_2O_2 , the degradation efficiency is significantly low. Even with the addition of Fe^{2+} and H_2O_2 , negligible degradation of PFOA and PFOS was observed, indicating the limited oxidative capacity of conventional $\bullet\text{OH}$ -based systems in attacking the highly stable C–F bonds.^{108,109} In response, considerable efforts have been made to expand and modify chemical Fenton systems, employing diverse strategies to enhance the degradation efficiency of PFAS, such as synergistic effect of multiple radicals, reinforcing effect of radical reactivity, and radical-mediated phase separation (Figure 5).



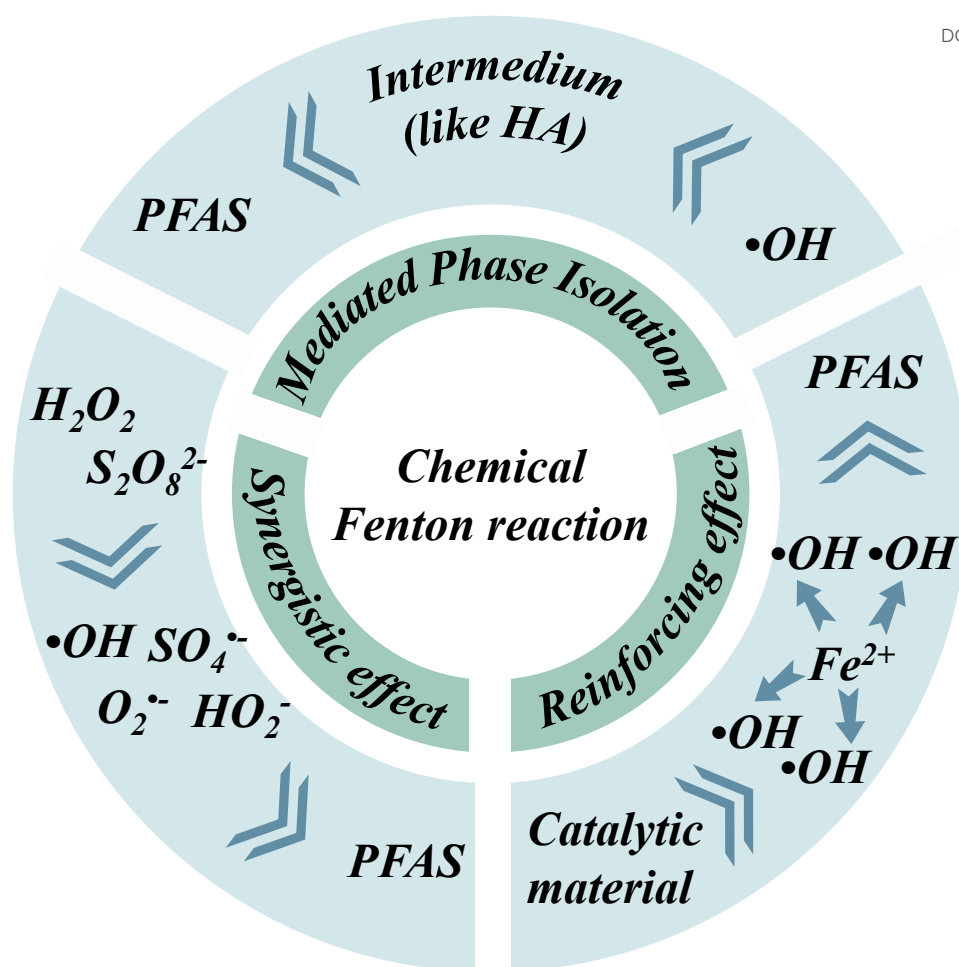


Figure 5. Progress in chemical Fenton reaction system toward PFAS remediation.

3.1.1 Synergistic effect of multiple radicals

To enhance the PFAS degradation ability of chemical Fenton reaction system, the potential of multi-radical synergistic degradation was evaluated, Lo et al. developed a chemical Fenton reaction system employing zero-valent iron (ZVI) to activate persulfate (PS) and $\bullet\text{OH}$ for the decomposition of perfluorooctanoic acid (PFOA).⁸⁰ In this system, PS acts as a sulfate radicals ($\text{SO}_4^{\bullet-}$) precursor, while ZVI serves as a catalyst to lower the activation energy required for the generation of $\text{SO}_4^{\bullet-}$ (shown in Eq (3) to Eq (6)). At the optimal temperature, the degradation rate of PFOA increased from 10% (using $\bullet\text{OH}$ alone) to 68% with the combined action of $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ (Figure 6a),



while the defluorination efficiency improved from 19% to 23% (Figure 6b) within 2 hours, indicating a significant synergistic effect between $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ radicals in promoting PFOA degradation. Notably, $\text{SO}_4^{\bullet-}$ has a higher redox potential of up to 2.6 V, exceeding that of $\bullet\text{OH}$ (2.3 V). Moreover, $\text{SO}_4^{\bullet-}$ demonstrate superior performance in initiating the degradation of PFOA by facilitating the formation of perfluoroalkyl radicals (Figure 6c).

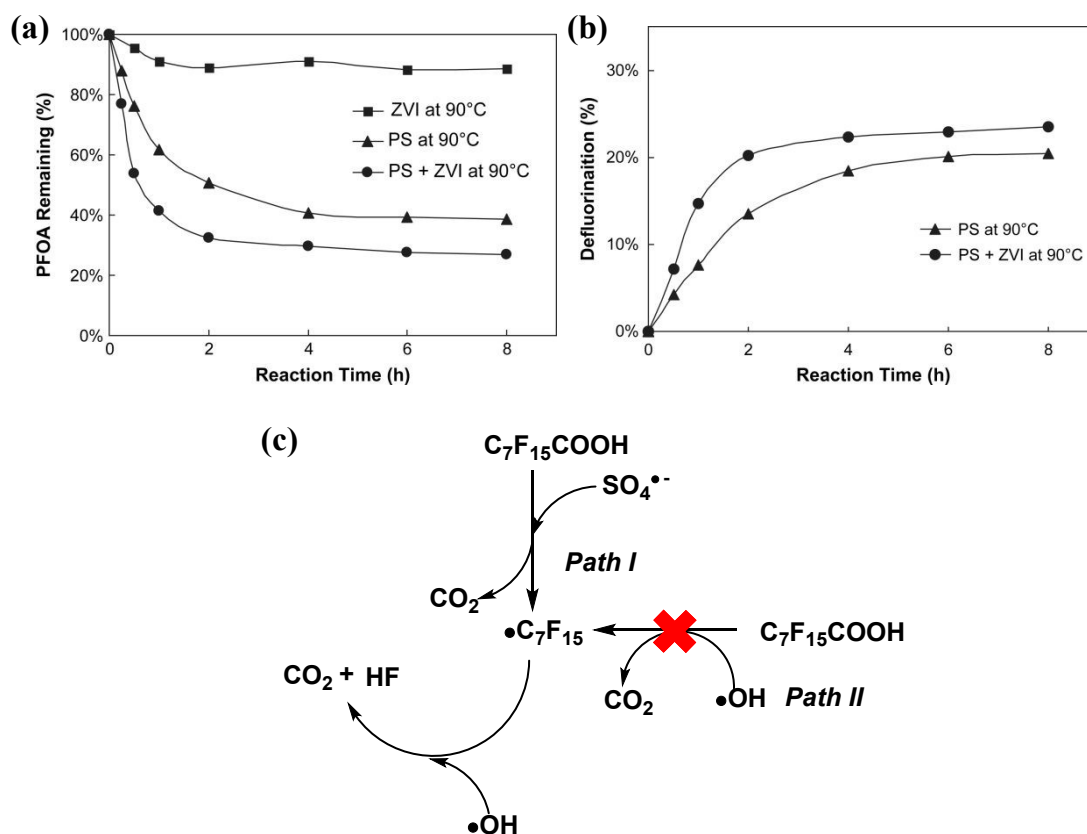


Figure 6. (a) Comparison the decomposition of PFOA in presence of persulfate (PS) at

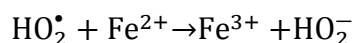


90 °C with or without ZVI. (b) The defluorination of PFOA with persulfate at 90 °C.⁸⁰

(c) The proposed synergistic mechanism of the $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ for PFAS degradation.

In order to further expand the reactive species involved in multi-radical coupling, Watts et al. developed a $\bullet\text{OH}$ /superoxide ($\text{O}_2^{\bullet-}$)/ hydroperoxide anion ($\text{HO}_2^{\bullet}$)-based multi-radical system, enabling a stable and efficient chemical Fenton process for the degradation of PFOA.⁸¹ Through catalyzed hydrogen peroxide (H_2O_2) propagation (CHP) reactions, H_2O_2 can be continuously decomposed to generate $\text{O}_2^{\bullet-}$ and $\text{HO}_2^{\bullet}$ (shown in Eq (7) to Eq (9)). The $\text{O}_2^{\bullet-}$ contributes to maintaining the continuity of the Fenton process by reducing Fe^{3+} to Fe^{2+} , while $\text{HO}_2^{\bullet}$ is generally regarded as a strong nucleophile, capable of attacking electron-deficient carbon atoms in PFOA, particularly those adjacent to the carboxyl group (e.g., the α -carbon). This process facilitate C–F bond cleavage and thus promote both degradation and defluorination (Figure 7a).¹¹⁰ The concentrations of H_2O_2 affect the types and concentrations of free radicals. The synergistic effect of multiple radicals ($\bullet\text{OH}$, $\text{O}_2^{\bullet-}$, and $\text{HO}_2^{\bullet}$) was supported by the optimal degradation efficiency exceeding 80% (Figure 7b). One mol of PFOA molecules contains 15 mol F atoms, at a 1 M H_2O_2 concentration, the ratio of F^- ions to PFOA molecules is approximately 15, indicating complete defluorination mineralization performance (Figure 7c).





(9)

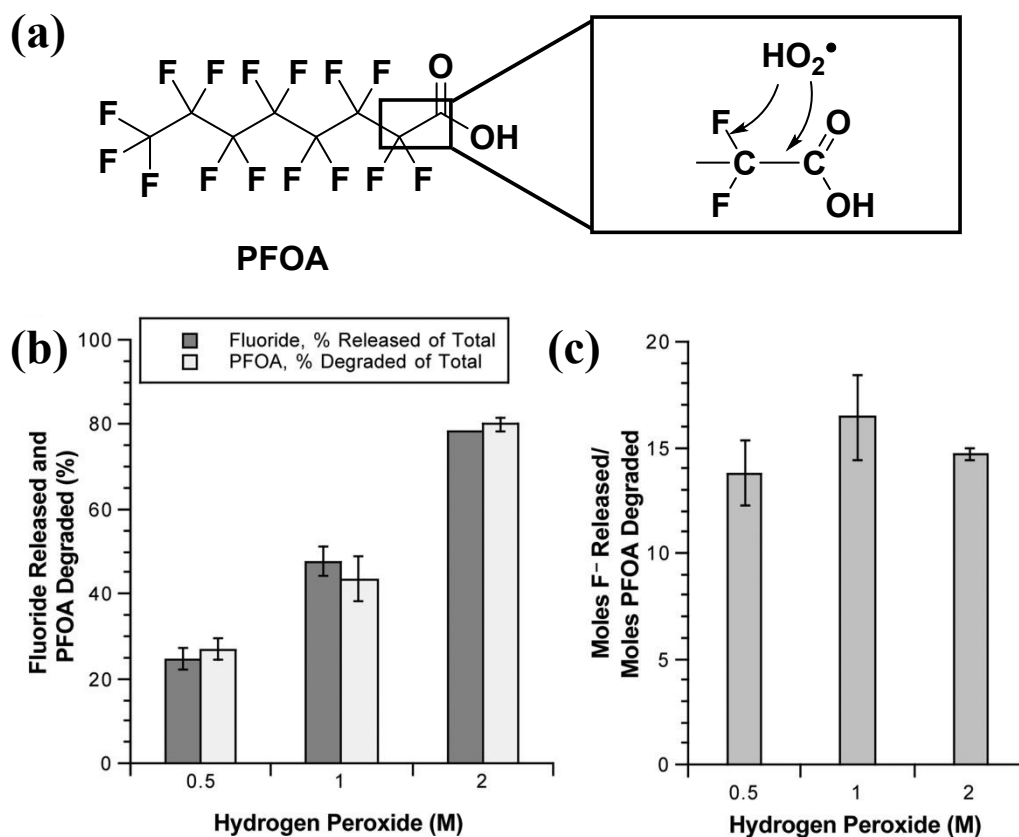
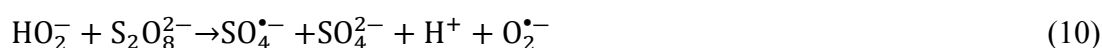


Figure 7. (a) A schematic diagram of HO₂[•] radical attacking electron-deficient carbon atoms in PFOA. (b) The defluorination and degradation efficiency of PFOA under the different concentrations of hydrogen peroxide. (c) The ratio of moles of fluoride released to moles of PFOA degraded under different concentrations of hydrogen peroxide.⁸¹

In addition, the combination of SO₄^{•-}, •OH, and O₂^{•-} radicals has also proven effective. Choi et al. developed an iron-modified diatomite (MD) catalyst capable of efficiently generating SO₄^{•-}, •OH, and O₂^{•-}, thereby promoting PFOA degradation through synergistic radical interactions.⁸² The key advantage of the MD catalyst lies in



its naturally abundant and low-cost material, as a stable and easily separable support for iron loading. At the same time, its high surface area is conducive to the generation of free radicals and the adsorption of pollutants. This system utilizes the catalytic ability of Fe^{2+} to activate H_2O_2 and PS, and can continuously and stably generate $\bullet\text{OH}$, $\text{O}_2^{\bullet-}$ and $\text{SO}_4^{\bullet-}$ (shown in Eq(1), Eq(10) and Eq(11)). In conventional dual-radical systems such as $\bullet\text{OH}/\text{SO}_4^{\bullet-}$, the cleavage of highly inert C–F bonds in PFOA remains limited. However, the introduction of $\text{O}_2^{\bullet-}$ induces an additional reductive and nucleophilic pathway targeting electron-deficient α -carbon atoms adjacent to the carboxyl group, thereby enhancing C–F bond cleavage (Figure 8a). Moreover, the combination of $\text{SO}_4^{\bullet-}$ (a strong oxidant 2.6 V) and $\text{O}_2^{\bullet-}$ (a moderate reductant -0.33 V) provides a more diverse redox environment for $\text{Fe}^{2+}/\text{Fe}^{3+}$ that improves the overall degradation efficiency. As experiment demonstrated, MD was capable of catalyzing both the Fenton reaction with H_2O_2 and the CHP reaction, achieving a moderate PFOA degradation efficiency of 60% (Figure 8b). When PS was further introduced into the reaction system, the synergistic effect of $\text{SO}_4^{\bullet-}$, $\bullet\text{OH}$, and $\text{O}_2^{\bullet-}$ radicals enhanced the degradation efficiency to 69% (Figure 8c), highlighting the effectiveness of multi-radical cooperation.



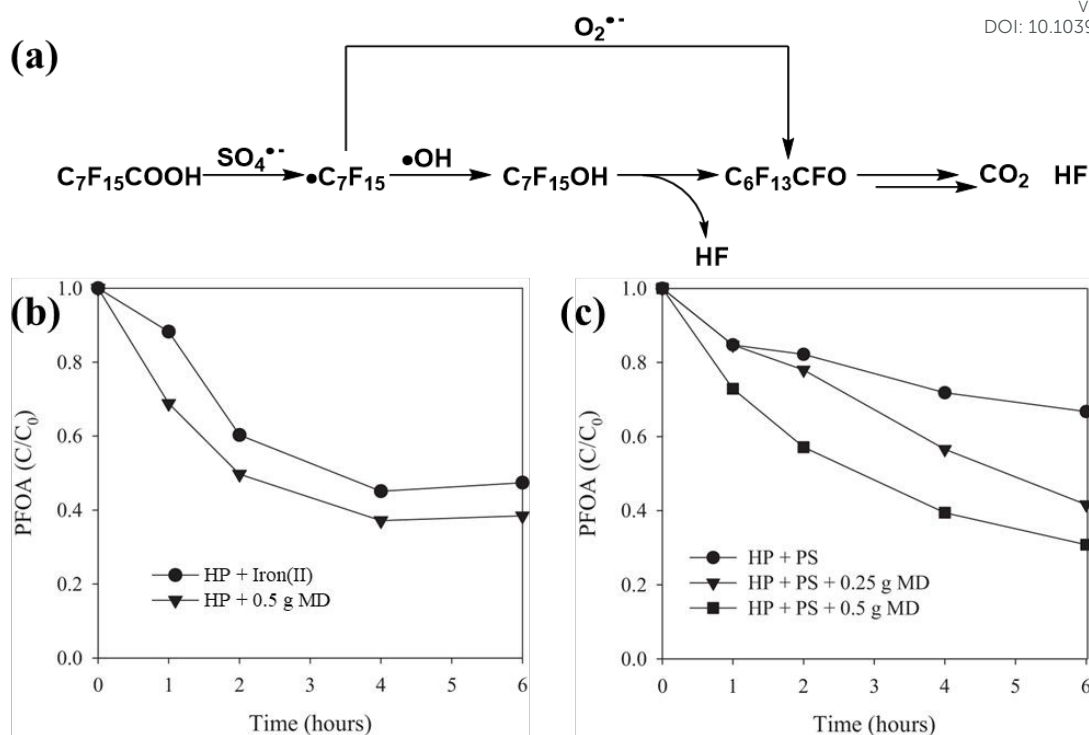


Figure 8. (a) The PFOA degradation mechanism of $\bullet\text{OH}$, $\text{O}_2^{\bullet-}$ and $\text{SO}_4^{\bullet-}$ radicals. (b) Decomposition of PFOA by catalyzed hydrogen peroxide propagation (CHP) reactions in the presence of dissolved Fe ions and in the presence of MD containing Fe species. (c) Decomposition of PFOA by different HP-activated PS systems.⁸² HP: hydrogen peroxide, H_2O_2 ; PS: persulfate, $\text{S}_2\text{O}_8^{2-}$.

In summary, the development of multi-radical synergistic degradation strategies within Fenton-based systems has shown significant promise for improving PFAS treatment efficiency. The combined action of various reactive species—such as $\bullet\text{OH}$, $\text{SO}_4^{\bullet-}$, $\text{O}_2^{\bullet-}$, and $\text{HO}_2^{\bullet}$ —can substantially enhance the degradation process. This improvement is primarily attributed to: (1) the stronger oxidative potential of $\text{SO}_4^{\bullet-}$, which can overcome the limitations of $\bullet\text{OH}$ in initiating the activation of PFAS molecules; (2) the presence of a multi-radical environment that increases the probability



and efficiency of radical attacks on PFAS compared to systems dominated by a single radical species. However, multi-radical Fenton systems also face several limitations. The complexity of the reaction environment, which makes it difficult to clearly elucidate the underlying mechanisms and pathways of radical synergy. In addition, the overall degradation efficiency remains insufficient to meet the demands of rapid and effective PFAS removal. Therefore, efforts are being made to develop strategies aimed at further enhancing the radical reactivity.

3.1.2 Reinforcing effect of radical reactivity

To enhance the activity of reactive radicals, researchers have focused on material structural design with high specific surface areas, whose unique architectures provide several key advantages: (1) increased number of exposed Fe active sites, particularly on surfaces and within micropores; (2) limited diffusion pathways of PFAS molecules, enhancing the contact between contaminants and catalytic sites; and (3) confined microenvironments promoted the local accumulation and prolonged lifetime of reactive radicals.

Wang et al. fabricated a composite material by anchoring Pb-doped BiFeO₃ (Pb-BFO) nanoparticles onto reduced graphene oxide (rGO) nanosheets,⁸³ forming a layered architecture. The Pb-BFO nanoparticles were firmly immobilized on the rGO surface, which effectively inhibited nanoparticle agglomeration and preserved high surface reactivity. Moreover, the formation of nanoscale interlayer gaps between rGO sheets facilitated rapid electron transfer, thereby enabling the localized enrichment of •OH



within the confined interlayer space and the oxidative interaction between $\bullet\text{OH}$ and PFAS molecules (Figure 9a and 9b). Additionally, Pb doping improved the intrinsic charge transport properties of BFO, while the oxygen-containing functional groups (e.g., carboxyl and hydroxyl groups) of rGO were capable of activating H_2O_2 to produce $\bullet\text{OH}$ radicals, collectively contributing to the improved catalytic efficiency of the composite system (Figure 9c). This approach achieved over 95% degradation efficiency of PFOA within 5 minutes, with nearly half of the PFOA undergoing complete mineralization (Figure 9d). These results underscore the feasibility of employing porous materials to promote chemical Fenton-based degradation of PFAS.

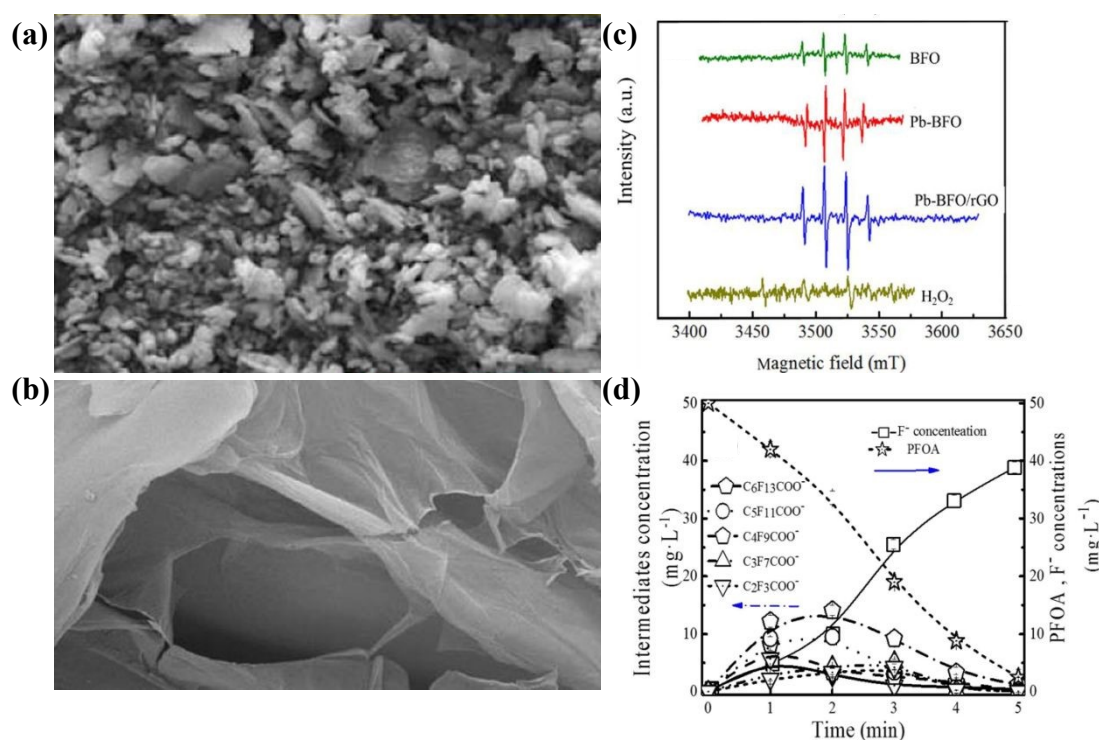


Figure 9. SEM images of Pb-BFO/rGO (a) and GO (b) composite. (c) The EPR spectra of different catalyst suspensions. (d) Evolution of the F concentration and degradation byproducts as a function of degradation time with Pb-BFO/rGO system.⁸³



For the purpose of further understanding the influence of material structure on the efficiency of chemical Fenton degradation of PFAS, Shi et al. extended the structure of conventional two-dimensional reduced graphene oxide (rGO) into a three-dimensional graphene-based framework (OG),⁸⁴ in which the abundant C–O–C bridging structures were found to significantly enhance the Fenton reaction by promoting the generation efficiency of $\bullet\text{OH}$ (Figure 10a). Notably, the OG material was derived from recycled biomass waste, aligning with the principles of green chemistry and offering promising advantages in terms of environmental sustainability and economic viability. Density functional theory (DFT) calculations indicated that the C–O–C bridging structure of OG was key to electron transport. Electrons from the C–F bonds in PFOA could transfer to the OG surface via these bridges (Figure 10b), with the F atom's HOMO contribution increasing significantly from 0.95% to 15.46% (Figure 10c). Moreover, the spatial confinement effect of OG reduced the activation energy for H_2O_2 decomposition (1.10 eV for OG vs. 1.60 eV for 2D graphene).

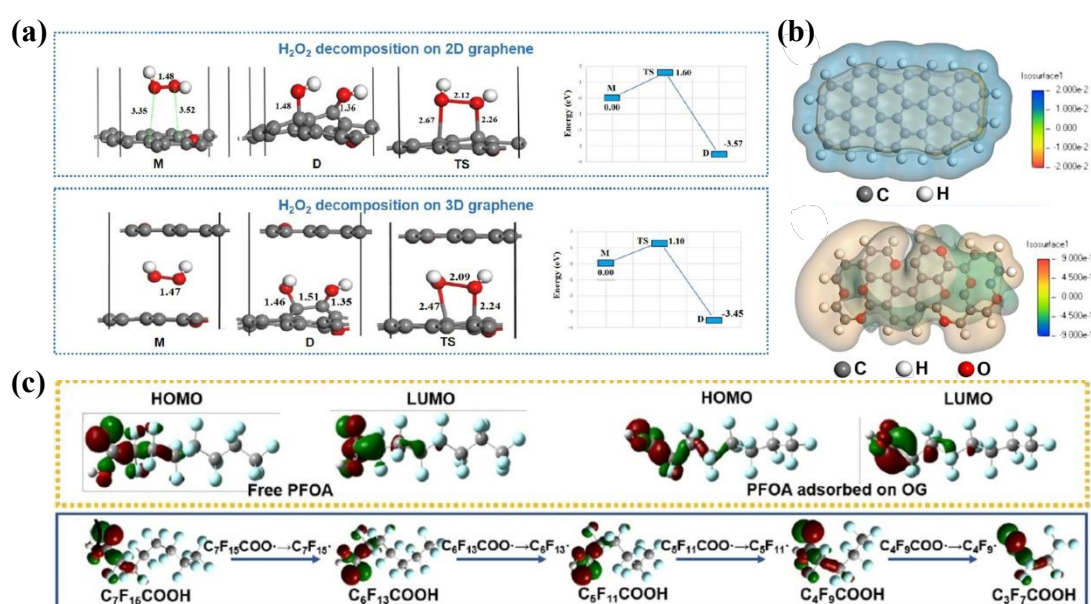


Figure 10. (a) Energy profiles of H_2O_2 decomposition on 2D and 3D graphene. (b)



Comparison of the electrostatic potential distributions of porous graphene and modified graphene. (c) HOMO and LUMO energies of free PFOA, PFOA adsorbed on OG and PFOA intermediates during degradation.⁸⁴

Similar to the above strategy, Zhuang et al. synthesized a Fe/S co-doped carbon aerogel (PGFe),⁸⁵ in which sulfur doping played a crucial role in facilitating covalent bonding between iron and carbon, thereby enhancing the electronic conductivity of the material and accelerating the Fenton reaction by creating a more stable environment for •OH generation. Additionally, the incorporation of polyvinyl alcohol during the carbonization process promoted the formation of a highly porous structure, effectively increasing the specific surface area and exposing a greater number of active sites. Charge and electrophilicity analyses identified C7, C8, terminal F23, and electron-rich O24 atoms in the PFAS molecule as the most susceptible to •OH attack (Figure 11a), providing a theoretical basis for predicting bond cleavage pathways (Figure 11b). This study provides a solid theoretical foundation for understanding the PFOA degradation process. The PFAS degradation efficiency via PGFe modified chemical Fenton-based reactions improved from 15% to 22% (Figure 11c).



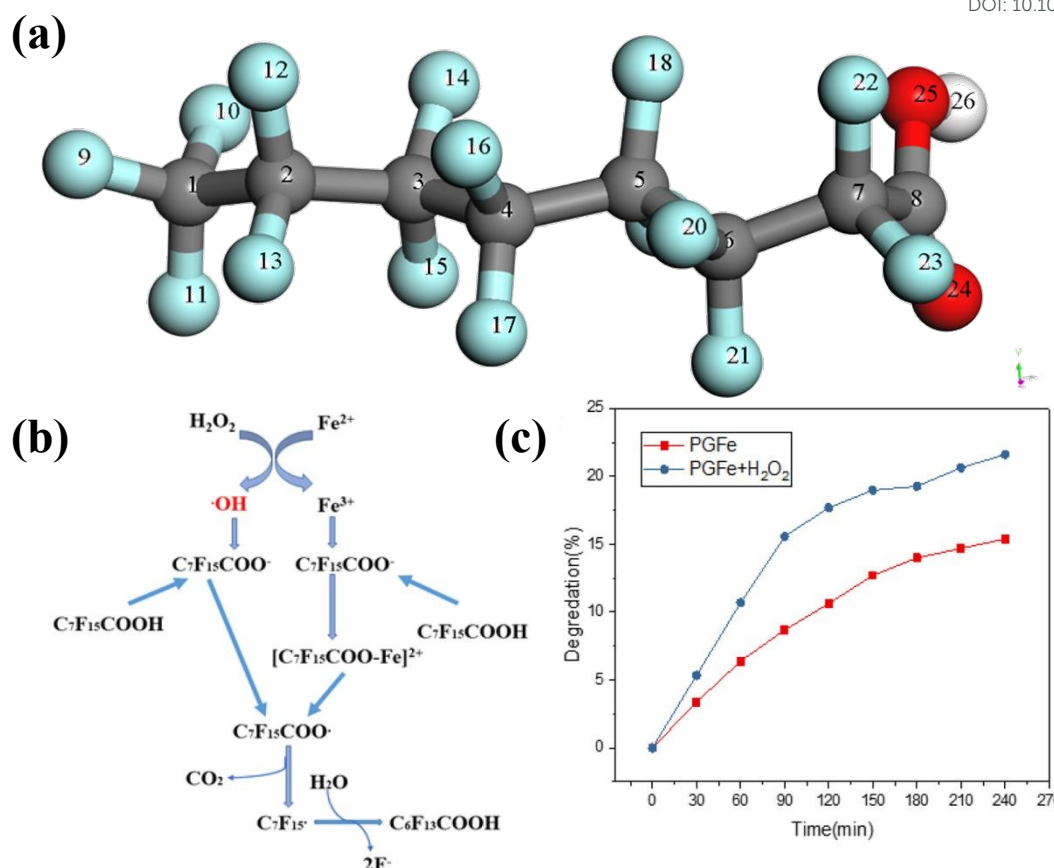


Figure 11. (a) Structure of PFOA denoted by sequence number: 1-8 carbon, 9-23 fluorine, 24-25 oxygen and 26 hydrogen. (b) Schematic diagram of degradation process of PFOA in PGFe/H₂O₂ Fenton system. (c) PFOA degradation rate in PGFe and PGFe/H₂O₂ system.⁸⁵

To further investigate the relationship between material porosity and the degradation rate of PFAS, Zhang et al. developed a layered iron oxychloride (FeOCl) catalyst.⁸⁶ By confining reactive species within a sub-nanometer spatial domain, the hydration coordination number of O₂^{•-} radicals generated from the Fenton reaction was modulated, reducing the average coordination number from 3.3 to 1.89 (Figure 12a and 12b). The decreased coordination number concentrated the negative charge on O₂^{•-},



strengthening its interaction with PFAS molecules. To further enhance spatial effect, the FeOCl was immobilized onto ceramic membranes, the active channels were confined within a 20 nm scale (Figure 12c). As a result, the apparent reaction rate constant (k_{obs}) reached 1.2 min^{-1} (Figure 12d), which was 86 times higher than that of a traditional batch-mode system (0.014 min^{-1}). This study quantitatively demonstrated the performance enhancement of PFAS degradation reactions achieved by confinement effect of high specific surface area materials, and provides a feasible approach for future investigations into the structure–activity relationship for PFAS degradation.

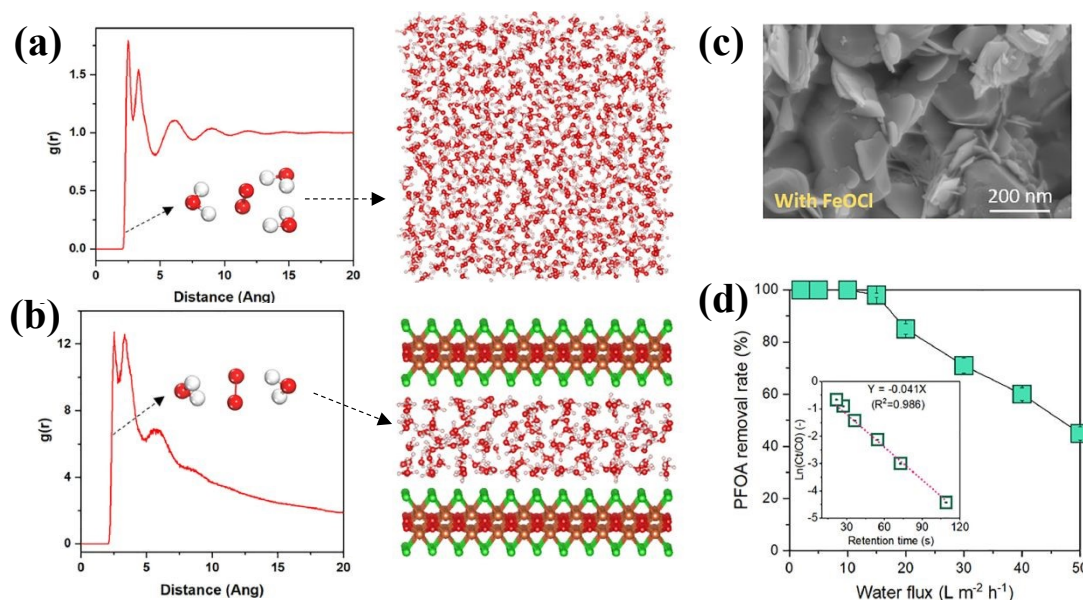


Figure 12. (a) The RDF as a function of distance from free $\text{O}_2^{\bullet-}$ radicals and snapshot of the free $\text{O}_2^{\bullet-}$ radicals in aqueous phase. (b) The RDF as a function of distance from confined $\text{O}_2^{\bullet-}$ radicals and snapshot of the $\text{O}_2^{\bullet-}$ radicals confined inside the FeOCl structure. (c) Cross-sectional SEM images of the FeOCl-incorporated ceramic membrane. (d) Fast degradation of PFOA through heterogeneous Fenton reaction inside FeOCl membrane.⁸⁶



Although structural design of materials can effectively enhance the interaction between reactive radicals and PFAS, numerous unresolved issues remain—such as how the sensitivity of spatial confinement to material dimensions influences radical reactivity, and whether atomic-level features within the catalyst structure affect the confinement effect. Additionally, the deep defluorination remains a challenge, especially for the degradation by-products of short chains.

3.1.3 Radical-mediated phase separation

To address the deep defluorination of PFAS and the accumulation of short-chain byproducts, Santos employed the abundant $\bullet\text{OH}$ generated in the Fenton reaction system to oxidatively modify humic acid (HA) for phase separation of aqueous PFAS and their short-chain byproducts.⁸⁷ The HA molecules contain various functional groups, such as carboxyl and phenolic hydroxyl groups, which may be oxidized or rearranged during the reaction, resulting in the formation of new chemical bonds and larger structural assemblies. Through the oxidative transformation and restructuring of functional groups on HA, the interaction between HA and PFOA was enhanced, ultimately facilitating the transfer of PFOA from the aqueous phase to the solid phase via a co-precipitation and phase separation mechanism (Figure 13a).

As the structure of HA evolves, it may form larger polymeric or network-like aggregates. These aggregates can physically entrap PFOA molecules adsorbed on their surfaces, effectively encapsulating them within the HA matrix (Figure 13b). This encapsulation hinders the re-release of PFOA into the aqueous phase, thereby



facilitating its removal from water. However, this process does not involve the chemical degradation of PFOA; rather, the molecule merely transfers from the aqueous phase to the solid phase. Consequently, the development of effective strategies for the removal of PFAS immobilized in solid phases has emerged as a critical focus area. Materials such as graphene, metal-organic frameworks (MOFs), and covalent organic frameworks (COFs) are being explored as advanced platforms capable of adsorbing PFAS and enabling their subsequent solid-phase separation under catalytic or advanced oxidation conditions.¹¹¹

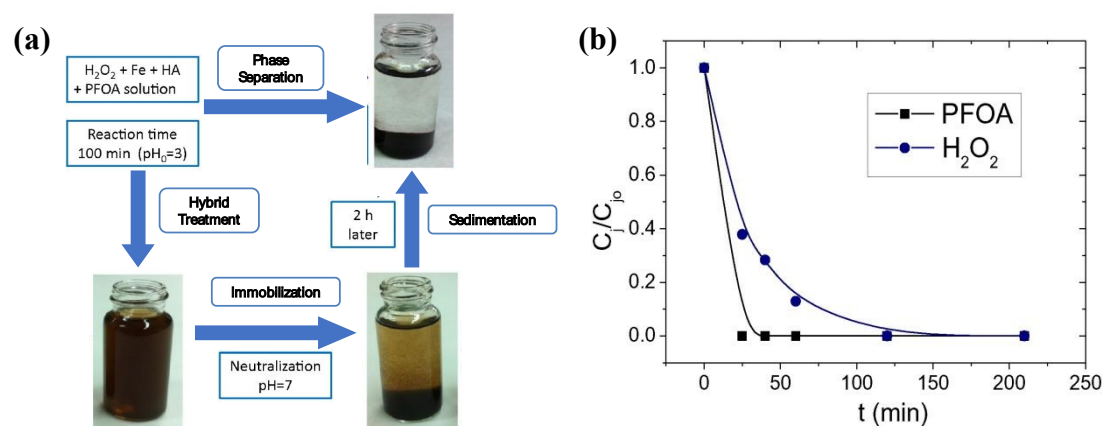
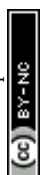


Figure 13. (a) Illustration of HA-coupled Fenton reaction driving multiphase conversion of PFOA. (b) Residual PFOA and oxidant in hybrid treatment of PFOA solution with Fenton like reagent and humic acid.⁸⁷

Substantial progress has been made in understanding the application of chemical-Fenton reactions for PFAS treatment. The chemical-Fenton system offers several advantages, including relatively simple experimental conditions, high selectivity, the synergistic action among multiple reactive radicals, and high achieving efficient PFAS degradation through material structure designs. However, several limitations remain. (1)



The requirement for high concentrations of H_2O_2 (≥ 1 M) not only leads to excessive reagent consumption but also poses significant safety concerns. (2) The system generally exhibits limited capacity to sustain the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox cycle, raising challenges for maintaining long-term Fenton reactivity. (3) Like conventional Fenton systems, chemical Fenton processes have not overcome the inherent pH constraint, typically requiring pre-acidification of the aqueous environment, which further restricts their practical applications.

3.2 *Electro-Fenton reaction system*

The electro-Fenton (EF) process differs from the conventional chemical-Fenton reaction in mechanism. Efficient PFAS mineralization typically requires the initial activation of PFAS molecules into perfluoroalkyl radicals. In the chemical Fenton process, the generation of $\cdot\text{OH}$ alone is often insufficient; therefore, additional more potent oxidation species are needed to achieve effective degradation. In contrast, electro-Fenton systems utilize electrocatalysis—one of the most powerful redox techniques—to directly oxidize PFAS and form perfluoroalkyl radicals, thereby promoting further $\cdot\text{OH}$ generation and overall degradation efficiency. Moreover, the electro-Fenton process offers two additional advantages for PFAS remediation: (1) in-situ generation of H_2O_2 via the oxygen reduction reaction (ORR), reducing reliance on external H_2O_2 dosing; and (2) improved $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox cycling under optimized electrochemical conditions, minimizing the formation of iron sludge (Figure 14).



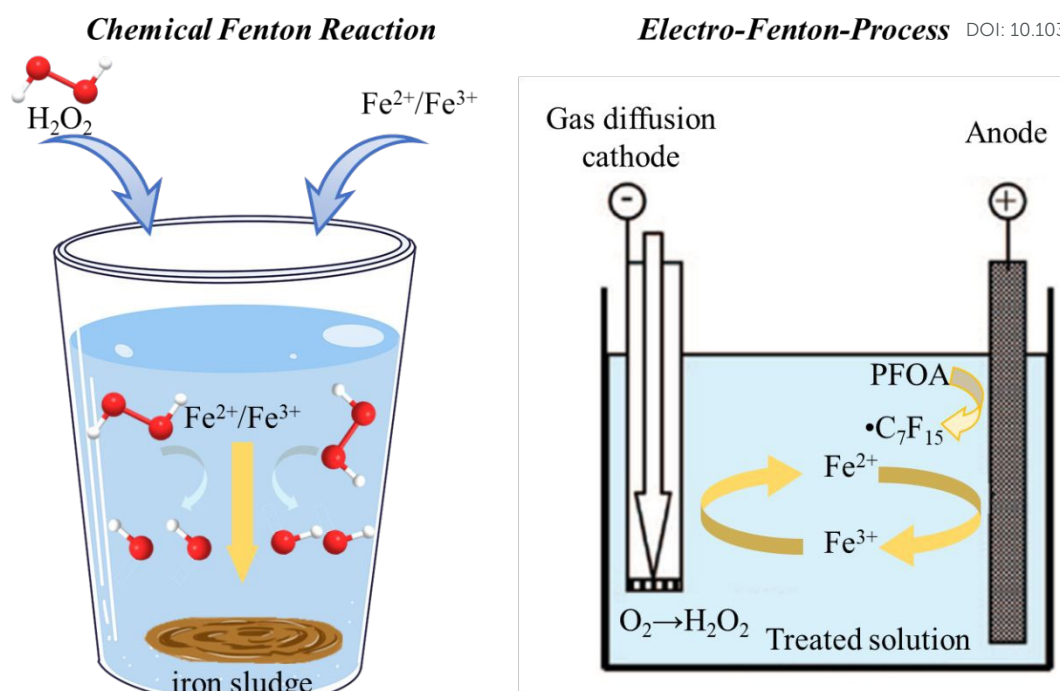


Figure 14. Comparison between chemical-Fenton reaction and electro-Fenton process.

The electro-Fenton reaction represents a synergistic integration of chemical-Fenton and electrochemical method. The anodes used in electro-Fenton systems are commonly boron-doped diamond (BDD) or Magnéli phase titanium suboxides (Ti_4O_7), similar to those in conventional electrochemical oxidation processes. These non-active anode materials are favored due to the following characteristics: (1) high chemical stability and inertness, conferring long operational lifespans;^{112,113} (2) wide potential windows and high oxygen evolution potentials (>2.7 V vs. NHE), conducive to the cleavage of C–F bonds;^{114,115} and (3) excellent corrosion resistance, enabling compatibility with strong acidic or basic environments.¹¹⁶

The anode materials used in electro-Fenton systems are relatively fixed, ongoing research focuses on developing efficient cathode materials to enhance ORR



performance for H_2O_2 generation. In this review, the electro-Fenton systems are categorized based on the cathode materials: iron-containing cathodes and iron-free cathodes.

3.2.1 Iron-containing cathodes

To evaluate the feasibility of a synergistic electro-catalytic system integrating cathodic electro-Fenton and anodic oxidation for effective PFOA removal, Zhao et al. synthesized a Fe–Mn co-doped carbon aerogel material (Fe10MnC). In this system, PFOA was initially activated at the anode, while the cathode facilitated the electro-Fenton reaction to efficiently generate $\bullet\text{OH}$ radicals (Figure 15a). Through the strategic combination of these processes, an effective approach for the synergistic degradation of PFAS was developed.⁸⁸ BDD was employed as the anode material, capable of generating $\bullet\text{OH}$ (H_2O oxidation) with high efficiency. These radicals, alongside direct anodic oxidation, contributed to the cleavage of C–F bonds in PFOA (Figure 15b). Meanwhile, Fe10MnC acted as the cathode, enabling the in-situ electro-generation of H_2O_2 by ORR reaction, which was subsequently activated to produce $\bullet\text{OH}$ under the catalytic effect of Fe and Mn (Figure 15c). Surface valence analysis revealed that Mn improved the selectivity for the two-electron ORR for H_2O_2 production (Figure 15d). This system achieved a 97% PFOA removal rate within 4 hours of electrolysis, without hydrogen peroxide added and no iron sludge produced.



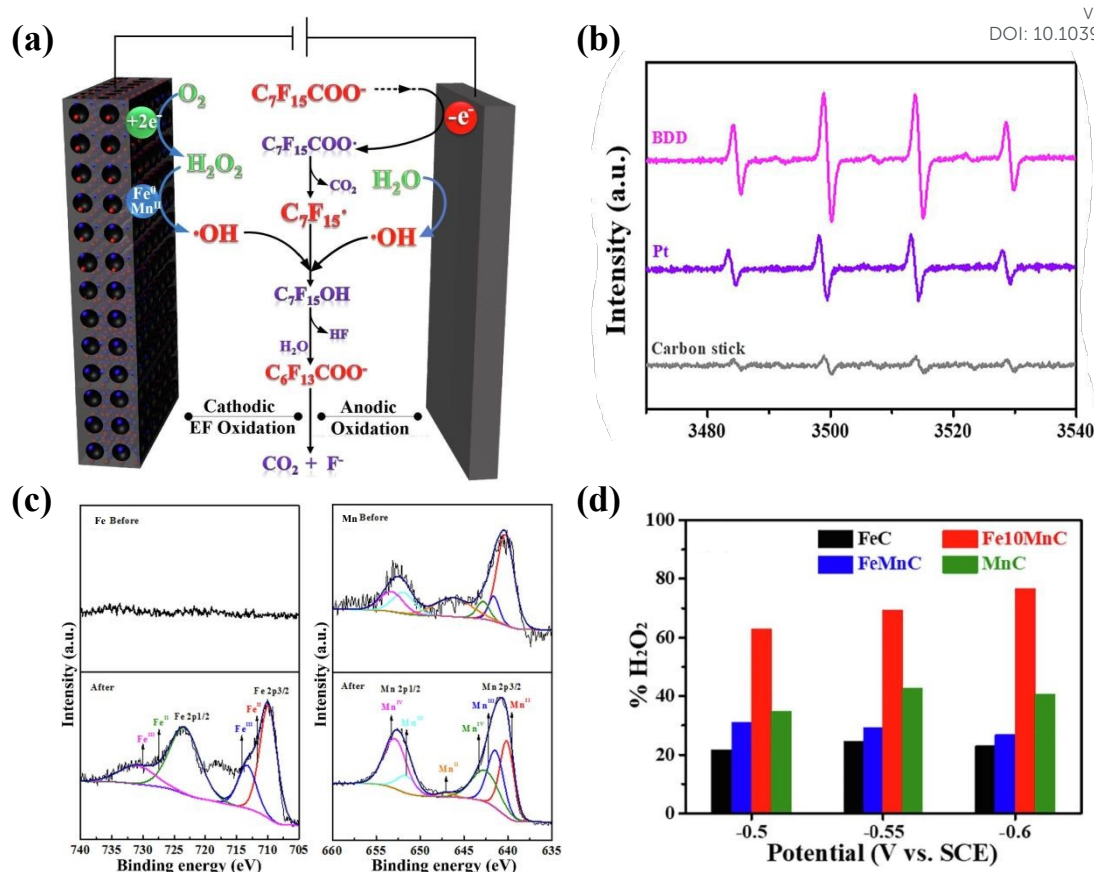


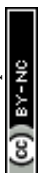
Figure 15. (a) Catalytic mechanism of electro-Fenton oxidation for efficiently removing PFOA with Fe10MnC as the cathode and BDD as the anode. (b) EPR spectra of DMPO•OH adducts with different anodes. (c) Fe and Mn XPS spectra of Fe10MnC before and after PFOA degradation. (d) Productivity for H₂O₂ of different cathodes.⁸⁸

For the purpose of further expanding the range of reactive radicals in electro-Fenton processes, Cai et al. developed an iron–nickel co-doped carbon aerogel (Fe_xNiC), which enabled the coupling of SO₄^{•-} and •OH radicals for effective PFOA degradation (Figure 16a).⁸⁹ Unlike previous studies, a graphite electrode was employed as the anode, which minimized anodic oxidation of PFOA and thus better highlighted the superior performance of the cathodic material in the degradation process. By adjusting the Fe/Ni ratio, the generation rates of SO₄^{•-} and •OH radicals can be



modulated (Figure 16b). While iron is essential for Fenton chemistry, it tends to favor the four-electron reduction pathway in ORR, producing H_2O instead of H_2O_2 .¹¹⁷ Ni doping enhanced the selectivity toward the two-electron pathway, promoting efficient H_2O_2 generation. DFT calculations supported a synergistic degradation mechanism involving $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$: initially, $\text{SO}_4^{\cdot-}$ attacks the carboxylic group of PFOA, forming the carboxyl radical $\text{C}_7\text{F}_{15}\text{COO}\cdot$ ($\Delta G = 139.33 \text{ kJ/mol}$), which undergoes decarboxylation to form the perfluoroalkyl radical $\text{C}_7\text{F}_{15}\cdot$ ($\Delta G = -103.56 \text{ kJ/mol}$). This radical then reacts with $\cdot\text{OH}$ to yield perfluorinated alcohol $\text{C}_7\text{F}_{15}\text{OH}$ ($\Delta G = -443.02 \text{ kJ/mol}$), which undergoes HF elimination ($\Delta G = 97.48 \text{ kJ/mol}$) and hydrolysis (Figure 16c), leading to stepwise chain shortening and eventual complete mineralization.

In real wastewater treatment scenarios (Figure 16d), for raw effluent from a fluorochemical plant in Sichuan (PFOA = 8.69 mg/L), electro-Fenton treatment achieved promising performance after biochemical treatment, with 81% degradation and 52% defluorination within 4 h (Effluent II). Even for raw wastewater without biochemical pretreatment, comparable results were obtained under the same conditions, with 75% degradation and 58% defluorination after 4 h (Effluent I), clearly demonstrating the application potential of this method. In terms of chemical oxygen demand (COD) reduction, the process was likewise effective: for Effluent II, COD decreased from 47.7 mg/L to 26.4 mg/L, while for Effluent I, COD was reduced from 1060 mg/L to 540 mg/L, meeting the Chinese Surface Water Quality Standard (GB3838-2002). Notably, the energy consumption for the treatment of Effluents I and II was approximately 0.39 and 0.018 kWh g^{-1} , respectively, further underscoring the



viability of this approach for industrial applications.

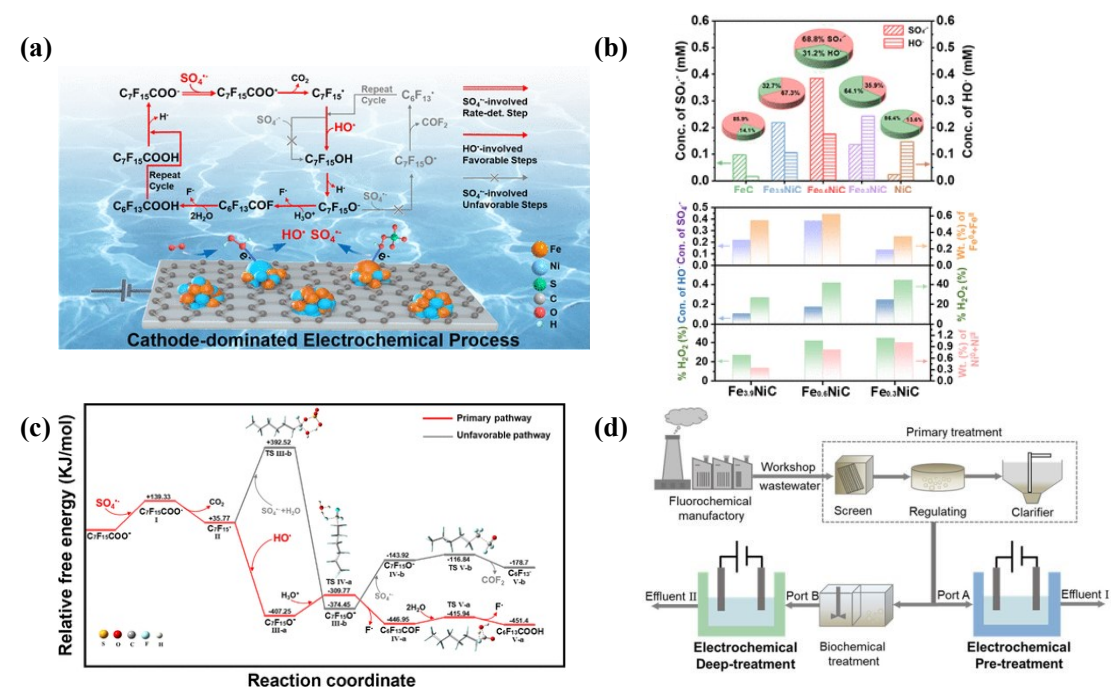


Figure 16. (a) Schematic of PFOA degradation in cathode-dominated electro-Fenton process. (b) The quantitative and accumulate concentration of $\text{SO}_4^{\bullet-}$ and $\text{HO}^{\bullet}$ in different cathodes. (c) Profile of the potential energy surfaces for the PFOA degradation dominated by $\text{SO}_4^{\bullet-}$ and $\text{HO}^{\bullet}$. (d) Flowchart of fluorochemical manufactory wastewater treatment.⁸⁹

In order to highlight the positive contribution of cathodic electro-Fenton reactions for effective degradation of PFOA, Han et al. synthesized a bifunctional single-atom catalyst with a Co-CN_2 configuration supported on an Fe_2O_3 substrate ($\text{Co-CN}_2\text{-Fe}_2\text{O}_3$) (Figure 17a).⁹⁰ The critical role of the cathode in enhancing the generation of reactive oxygen species and improving overall system performance were investigated. A platinum anode was used to eliminate contributions from anodic oxidation, enabling a focused assessment of cathodic degradation. In this system, the Co-CN_2 single-atom

layer facilitated the two-electron ORR for efficient H_2O_2 generation (Figure 17b and 17c). The low-coordination Co sites in the Co-CN_2 structure weakened O_2 adsorption and prevented O–O bond cleavage, thereby improving H_2O_2 selectivity. The Fe_2O_3 substrate functioned as the Fenton catalyst to activate the in-situ generated H_2O_2 into $\bullet\text{OH}$. This system achieved 96% PFOA degradation (Figure 17d) and defluorination (Figure 17e) within 120 minutes, representing near-complete mineralization. Long-term stability tests confirmed >95% degradation and defluorination over 10 cycles (Figure 17f), while avoiding the formation of iron sludge commonly associated with traditional Fenton systems.

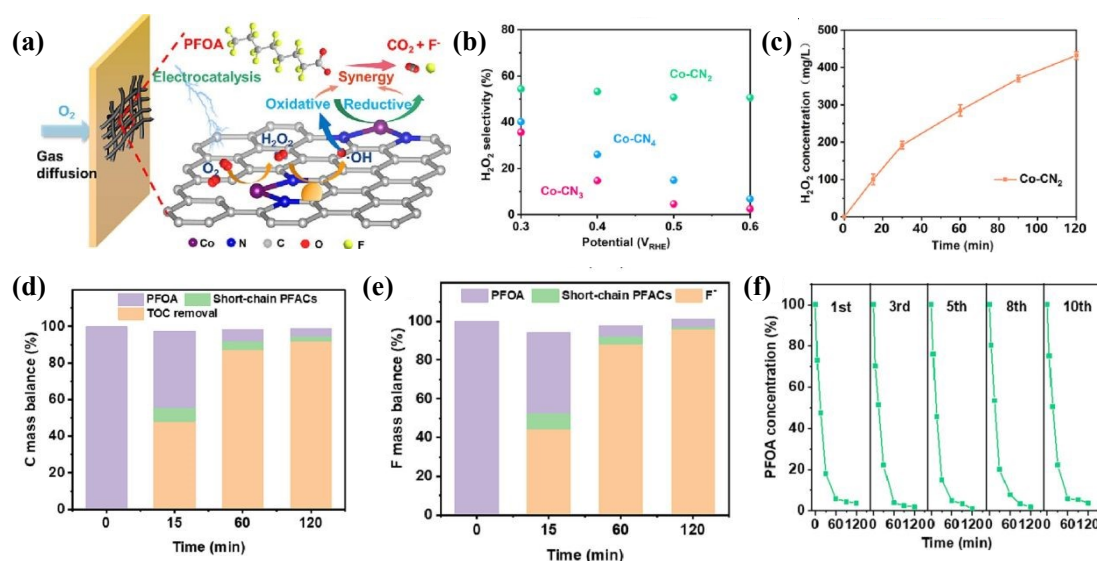
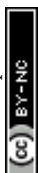


Figure 17. (a) Schematic of PFOA degradation in $\text{Co-CN}_2\text{-Fe}_2\text{O}_3$ cathode electro-Fenton process. (b) The calculated H_2O_2 selectivity as a function of the applied potentials. (c) Concentrations of H_2O_2 produced with Co-CN_2 as a function of electrolysis time. (d) C and (e) F mass balance during PFOA degradation over $\text{Co-CN}_2\text{-Fe}_2\text{O}_3$. (f) The recyclability of $\text{Co-CN}_2\text{-Fe}_2\text{O}_3$ for electro-Fenton PFOA degradation.⁹⁰



With the intention of elucidating the interaction mechanisms underlying PFOA degradation in the electro-Fenton reaction, Yu et al. conducted a systematic investigation on a Fe/N co-doped graphene electrode (Fe/N-GE@GF) (Figure 18a).⁹¹ A synergistic electrochemical process at the cathode was proposed, and key factors influencing the efficiency of the electro-Fenton reaction were scientifically explored. The co-doping of Fe and N introduced significant lattice distortion and structural defects in the graphene framework, resulting in increased surface area and abundant microporosity (Figure 18b). These features exposed more active sites for PFAS degradation. Moreover, N-containing precursors such as pyridine promoted uniform Fe dispersion and the formation of a robust three-dimensional porous structure. The presence of N also enabled PFAS molecules to interact with the electrode material, facilitating their enrichment near the reactive zones. Through precise spatial overlap of radical generation sites and PFAS accumulation regions (Figure 18c), a “Focused Active Reaction Region” that significantly improved degradation efficiency was established. This system achieved 95% PFOA degradation, 90% total organic carbon (TOC) removal, and 80% defluorination within 3 hours. Notably, the Fe/N-GE@GF electrode was capable of generating $\bullet\text{OH}$ in neutral conditions by leveraging singlet oxygen ($^1\text{O}_2$) as a supplementary oxidant (Figure 18d), thereby overcoming the classical Fenton system’s dependence on pH environment. Under neutral conditions (pH = 7), the PFOA degradation efficiency of Fe/N-GE@GF was nearly identical to that observed under acidic conditions (pH = 3), reaching 92.7% compared to 92.8%. In contrast, a marked decrease in degradation efficiency was observed under alkaline



conditions (pH = 10), though a considerable efficiency of 58.8% was still achieved (Figure 18e).

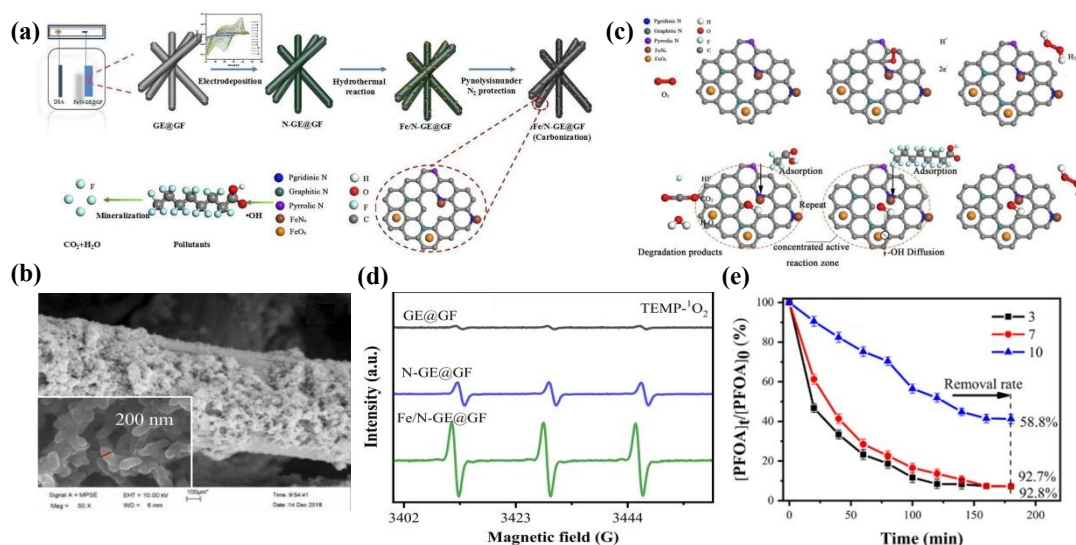


Figure 18. (a) Schematic diagram of Fe/N-GE@GF preparation and degradation experiments. (b) SEM images of N-GE@GF. (c) Possible catalytic mechanism of Fe/N-GE@GF for PFOA degradation. (d) DMPO-¹O₂ by GE@GF, N-GE@GF and Fe/N-GE@GF cathode in electrocatalytic process. (e) PFOA adsorption performance of Fe/N-GE@GF at different pH.⁹¹

3.2.2 Iron-free cathodes

While iron-containing cathodic materials have attracted considerable attention, certain unique structural features of iron-free cathodes also exhibit interactions relevant to PFAS degradation. Wang et al. developed an iron-free biomass-derived nitrogen and sulfur self-doped porous carbon electrode (NSGC) for electro-Fenton degradation of hexafluoropropylene oxide dimer acid (GenX) (Figure 19a), a widely used substitute for the banned PFOA.⁹² Previous studies have demonstrated that fluorine–fluorine



(F $\cdots$ F) interactions between perfluorinated polymers and the perfluoroalkyl chains of PFOA play a critical role in enhancing adsorption from aqueous solutions (Figure 19b).¹¹⁸ The incorporated perfluoropolyether into the NSGC framework exhibited hydrophobic and fluorophilic, and significantly enhanced performance for GenX removal, that is consistent with the DFT calculation results, where the adsorption energy of Gen-X on F-NSGC was significantly enhanced from -35.93 kJ/mol to -46.91 kJ/mol in the presence of F–F interactions (Figure 19c). In the electro-Fenton system, F-NSGC achieved an electro-adsorption efficiency of 59% for GenX within 60 minutes, followed by a degradation efficiency of 96% and a defluorination efficiency of 63% after 180 minutes (Figure 19d). These results indicate both excellent degradation capacity and promising mineralization potential. The presence of competing anions exhibited negligible impact, with removal efficiencies exceeding 95% in all tested scenarios (Figure 19e). When applied to real water samples—including lake water, secondary effluent from a municipal wastewater treatment plant, and tap water—the system consistently achieved over 90% GenX removal within 180 minutes (Figure 19f). To further explore the application potential of this method, the reaction setup was adapted to continuous-flow reactors. Under a flow rate of 5 mL/min with a circulation time of 180 min, the GenX removal efficiency of up to 94% was achieved. However, excessively low flow rates reduced the contact between GenX and the catalytic material, thereby limiting the overall degradation efficiency.



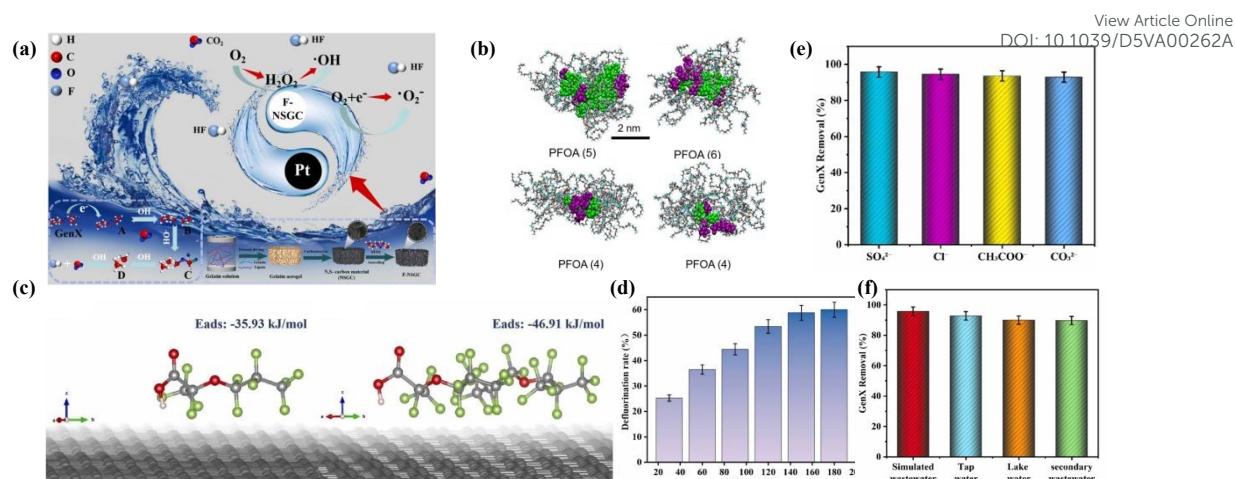


Figure 19. (a) Degradation mechanism of GenX by F-NSGC in electro-Fenton system. (b) Snapshots of molecular dynamics simulations of association of PFOA molecules with the self-assembled block copolymers ¹¹⁸. (c) DFT simulations to calculate the adsorption energy of GenX by NSGC (left) and F-NSGC (right). (d) F- concentration after degradation. (e) Influence of different anions on GenX removal. (f) Influence of different water on GenX removal.⁹²

With the aim of broadening the applicability of combined electro-oxidation and electro-Fenton systems for PFAS treatment, Luu et al. conducted a comprehensive evaluation of the Fenton-assisted electrochemical advanced oxidation process for the removal of 29 representative PFAS compounds, including both long- and short-chain species, as well as linear and branched isomers.⁹³ Ti/BDD and Ti/IrO₂ were used as anode materials for comparison, with Pt serving as the cathode. Fe₃O₄ nanoparticles were directly introduced into the reaction system as catalysts to enhance Fenton reactions. The researchers systematically optimized operational parameters such as pH, Fe₃O₄ concentration, current density, electrolysis duration, and electrolyte



concentration. Under optimized conditions, removal efficiencies ranging from 86% to 100% were achieved within 120 minutes, with a low energy consumption of just 9.0 kWh/m³ (Figure 20a and 20b). Following the attainment of high PFAS removal efficiencies, the study further investigated intermediate products and degradation pathways. Using mass spectrometry and kinetic modeling, the plausible mineralization mechanisms were proposed (Figure 20c). These mechanistic insights provide valuable references for treating other recalcitrant organic pollutants using electro-Fenton-based approaches.

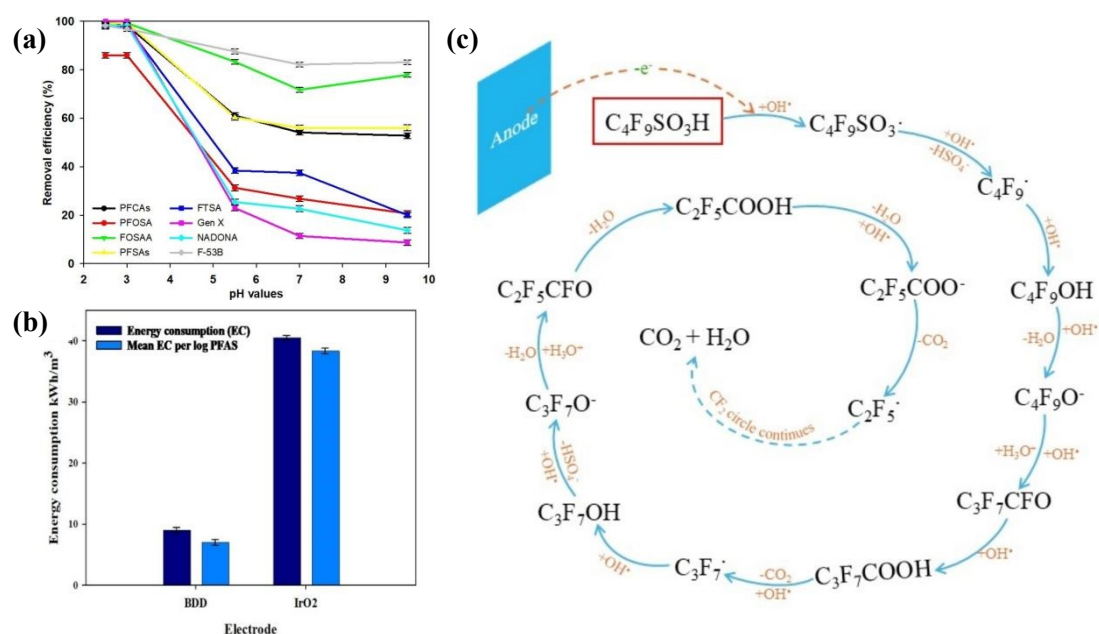


Figure 20. (a) PFAS removal efficiency via the Fenton-assisted electrochemical oxidation process. (b) Energy consumption via the Fenton-assisted electrochemical oxidation process. (c) Intermediate compounds and degradation pathway of PFBS.⁹³

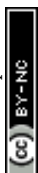
Electro-Fenton reactions have demonstrated the capability for rapid PFAS degradation, accompanied by significant improvements in defluorination efficiency.



Notably, by expanding the sources of oxygen, the electro-Fenton process has overcome the pH limitations inherent to traditional chemical Fenton systems, enabling the in situ generation of $\bullet\text{OH}$ under neutral conditions without the need for external H_2O_2 addition, while also substantially reducing the formation of iron sludge. However, several challenges remain. One of the primary limitations is the high energy consumption associated with the electro-Fenton process, which has increasingly drawn attention focused on techno-economic assessments. Reducing energy demand thus represents a critical direction for future development. Additionally, improvements in the durability and stability of electrode materials are necessary to achieve more favorable life-cycle performance. At present, most research remains at a preliminary or laboratory scale, and there is a pressing need for comprehensive evaluation data on the treatment of large-scale contaminated water systems.

3.3 Photo-Fenton reaction system

Compared to electro-Fenton systems, which rely on externally applied electric power to drive electron transfer processes, photo-Fenton reactions are generally considered to be a greener and more environmentally friendly class of AOPs (Figure 21).^{119,120} In a photo-Fenton system, UV or visible light irradiation facilitates the photoreduction of ferric complexes to Fe^{2+} , thereby accelerating the decomposition of H_2O_2 . Specifically, under mildly acidic conditions (pH 2.8–3.5), Fe^{3+} forms light-responsive ferric hydroxo complexes, such as $[\text{Fe}(\text{OH})]^{2+}$,^{68,121} which can undergo ligand-to-metal charge transfer (LMCT) excitation, regenerating Fe^{2+} and promoting



further $\bullet\text{OH}$ production.¹²² Recent studies have also shown that Fe^{3+} can form complexes with PFAS anions, and these complexes may exhibit enhanced photo-response under irradiation, facilitating PFAS degradation.

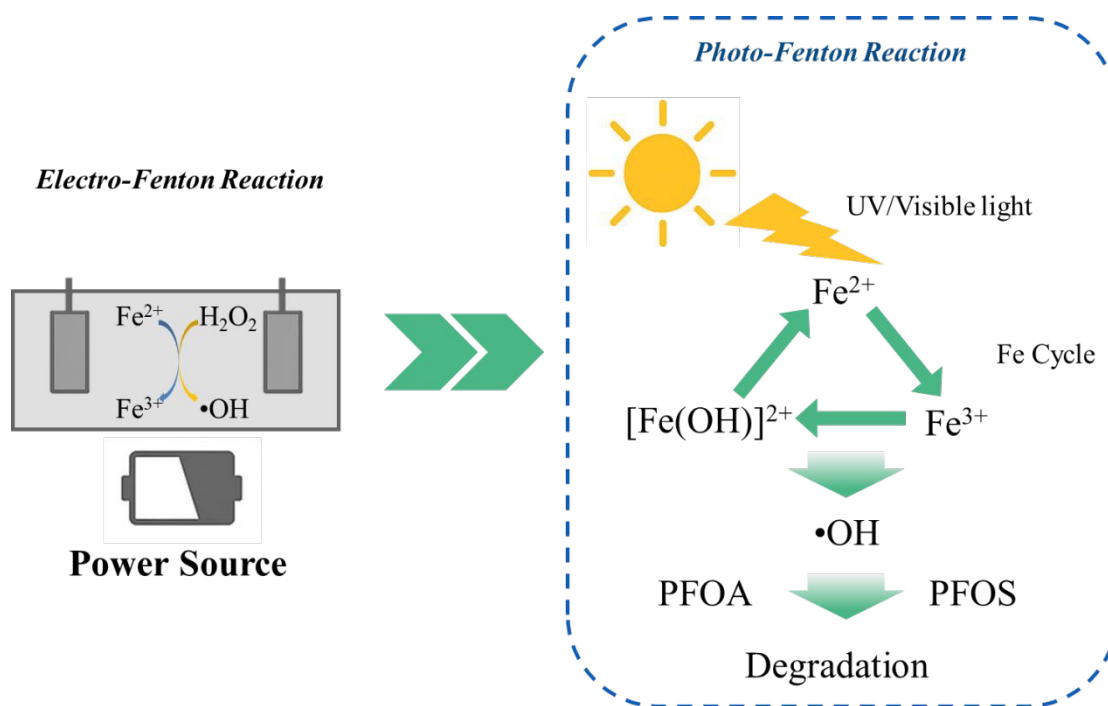


Figure 21. Comparison between electro-Fenton and photo-Fenton for the degradation of PFAS.

Although solar light is more widely available and cost-effective, the efficient control and utilization of photonic energy remain a key research challenge in photo-Fenton systems.¹²³ These systems are typically classified into homogeneous and heterogeneous processes, depending on the physical state of the catalyst. In homogeneous photo-Fenton systems, both the catalyst and reactants are dissolved in aqueous media, providing high dispersibility and intimate contact with contaminants. However, the generally poor light absorption capacity of homogeneous species limits their degradation efficiency, making this a focus for further optimization. In contrast,



heterogeneous photo-Fenton systems exhibit greater capability for absorbing and converting light into chemical energy. Photoinduced holes generated on solid catalyst surfaces can effectively participate in PFAS degradation. Nonetheless, rational design of the catalyst surface and optimization of PFAS mass transfer to reactive sites remain essential considerations for performance improvement.

3.3.1 Homogeneous photo-Fenton systems

Homogeneous photo-Fenton reactions were developed earlier than their heterogeneous counterparts due to no complex catalyst design or synthesis steps required.¹²⁴ The fundamental mechanism of PFAS degradation in homogeneous photo-Fenton systems has been relatively well elucidated. However, limited solubility and recovery challenges of homogeneous catalysts have constrained the application for PFAS degradation.

To verify the feasibility of PFAS degradation via the photo-Fenton process, Tang et al. developed a homogeneous ultraviolet-assisted photo-Fenton system with ferric and ferrous sulfate dissolved in PFOA solution (Figure 22a).⁹⁴ The influence of reagent stoichiometry (i.e., concentrations of Fe^{2+} and H_2O_2) and solution pH on PFOA degradation efficiency were systematically investigated. An optimal Fe^{2+} concentration of 2.0 mM was identified: at this level, more $\bullet\text{OH}$ radicals were generated to enhance both PFOA degradation and defluorination (Figure 22b). However, excessive Fe^{2+} could also act as a scavenger for $\bullet\text{OH}$, thereby reducing the availability of reactive species for PFAS oxidation. Solution pH was found to play a critical role (Figure 22c).



At pH < 2.0, H₂O₂ is readily protonated to form H₃O₂⁺, decreasing its reactivity with Fe²⁺. At pH > 4.0, Fe³⁺ tends to hydrolyze rapidly, forming Fe(OH)₃ precipitates, which hinder both light penetration and complexation with PFOA. Accordingly, the optimal pH range for homogeneous photo-Fenton reactions was determined to be between 2.8 and 3.5.

In addition to the •OH, the interaction between Fe³⁺ and PFOA contributed to the enhancement of the degradation process. A two-stage degradation mechanism was proposed (Figure 22d). In the initial stage, •OH is present in sufficient concentrations to directly activate PFOA anions, forming •C₇F₁₅ radicals. These radicals further react with •OH to generate C₇F₁₅OH, which undergoes hydrolysis and HF elimination to yield short-chain PFAS intermediates, CO₂, and HF. In the second stage, once •OH is depleted, Fe³⁺ forms a [C₇F₁₅COO–Fe]²⁺ complex with PFOA, which, under UV irradiation, is photo-reduced to Fe²⁺ and a carboxyl radical (C₇F₁₅COO•), initiating another degradation cycle with the limited •OH available.



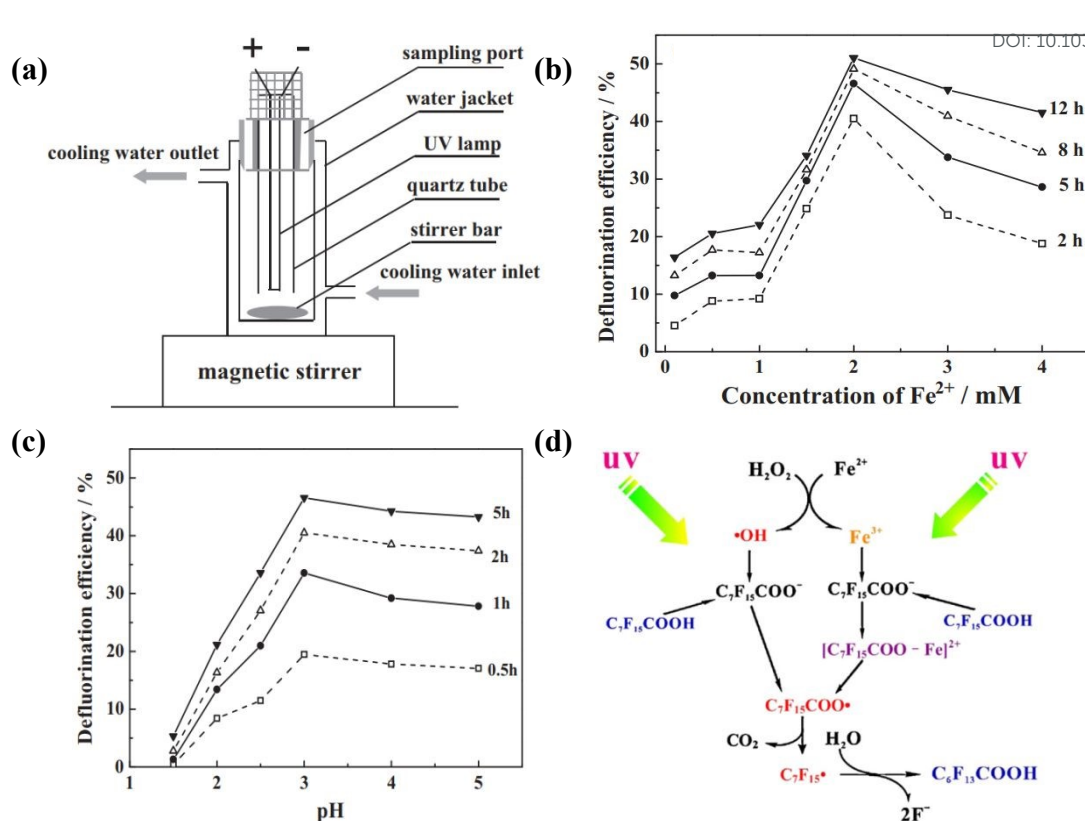


Figure 22. (a) The diagram of the experimental set-up for homogeneous photo-Fenton degradation of PFOA. (b) Effects of initial Fe^{2+} concentration on the defluorination efficiency of PFOA. (c) Effects of H_2O_2 concentration on the defluorination efficiency of PFOA. (d) A two-stage mechanism for the degradation of PFOA in the homogeneous photo-Fenton process.⁹⁴

In order to further broaden the spectral utilization of the photo-Fenton process, Alvarez et al. extended the conventional UV-based photo-Fenton system by introducing visible light as an alternative irradiation source.⁹⁵ The potential of utilizing visible light to effectively drive the photo-Fenton degradation of PFOA was proved. Visible light, as one of the most green and renewable energy sources, offers significant advantages for photo-Fenton degradation of PFOA. It greatly reduces the energy consumption of



the reaction, enhances operational safety, and lowers equipment requirements.

Therefore, visible light is considered an ideal energy input for such advanced oxidation processes. Electron paramagnetic resonance (EPR) spectroscopy confirmed that $\bullet\text{OH}$ was the primary reactive species (Figure 23a and 23b). However, the process required prolonged treatment—28 days—to achieve 98% PFOA degradation (Figure 23c), with only 13% defluorination, highlighting limitations in efficiency, particularly for the degradation of short-chain PFAS. A plausible mechanism for PFAS degradation via the photo-Fenton process was also proposed, which is generally consistent with those suggested in previous studies. In this mechanism, $\bullet\text{OH}$ not only directly attack PFOA but may also target the $[\text{C}_7\text{F}_{15}\text{COO-Fe}]^{2+}$ complex. Fe^{3+} is believed to further reduce the activation energy barrier for $\bullet\text{OH}$ -mediated PFOA degradation. Additionally, a more detailed pathway for the formation of intermediates was presented, indicating broader recognition of this mechanism. (Figure 23d).



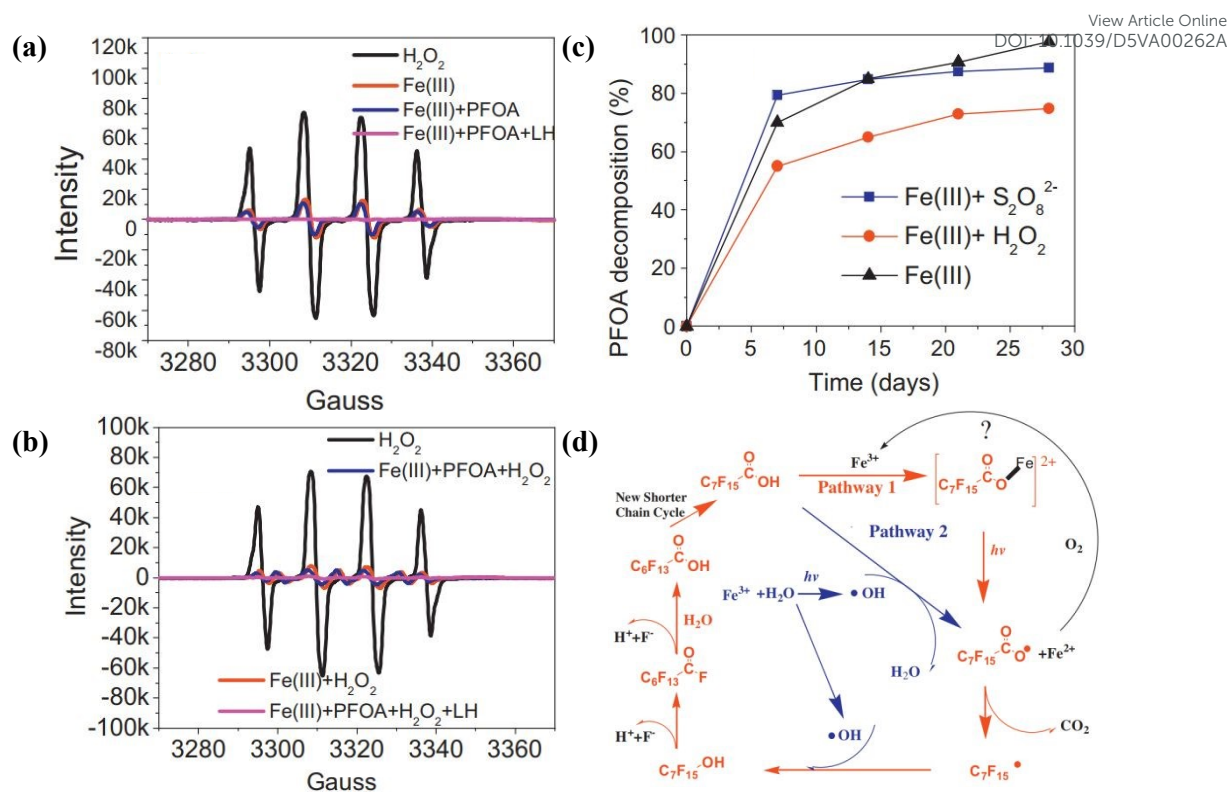


Figure 23. (a) EPR spectra of radicals generated in different experimental groups. (b) EPR spectra of radicals generated in $\text{Fe(III)} - \text{H}_2\text{O}_2$ (2 mM) system; EPR samples were taken after 10 min UV irradiation. (c) Comparison of PFOA degradation by different reaction systems. (d) Proposed PFOA degradation pathway in the presence of Fe(III) and sunlight.⁹⁵

To further enhance the degradation efficiency of the homogeneous photo-Fenton reaction and to gain a more comprehensive understanding of its underlying mechanism, Zhang et al. developed a hybrid system combining Fe^0 /granular activated carbon (Fe^0/GAC) microelectrolysis with a vacuum UV-Fenton (VUV-Fenton) process for PFOA mineralization.⁹⁶ In this system, Fe^0/GAC was first mixed with PFOA to generate numerous microscale galvanic cells that continuously supplied electrons and Fe^{2+} ions, facilitating the initial breakdown of the PFOA structure through enhanced electron



transfer (Figure 24a). Following a pre-activation step, the photo-Fenton reaction was conducted under UV irradiation at 254 nm (Figure 24b), resulting in a defluorination efficiency of 47%, which represents a notable improvement compared to the 39% achieved using the VUV-Fenton system alone (Figure 24c). High-performance liquid chromatography tandem mass spectrometry (HPLC/MS/MS) was employed to identify and quantify degradation intermediates. The detected short-chain perfluorocarboxylic acids (PFCAs)—including PFHpA (C7), PFHeA (C6), PFPeA (C5), PFBA (C4), PFPrA (C3), and TFA (C2)—further confirmed the proposed degradation mechanism of PFOA under photo-Fenton conditions.

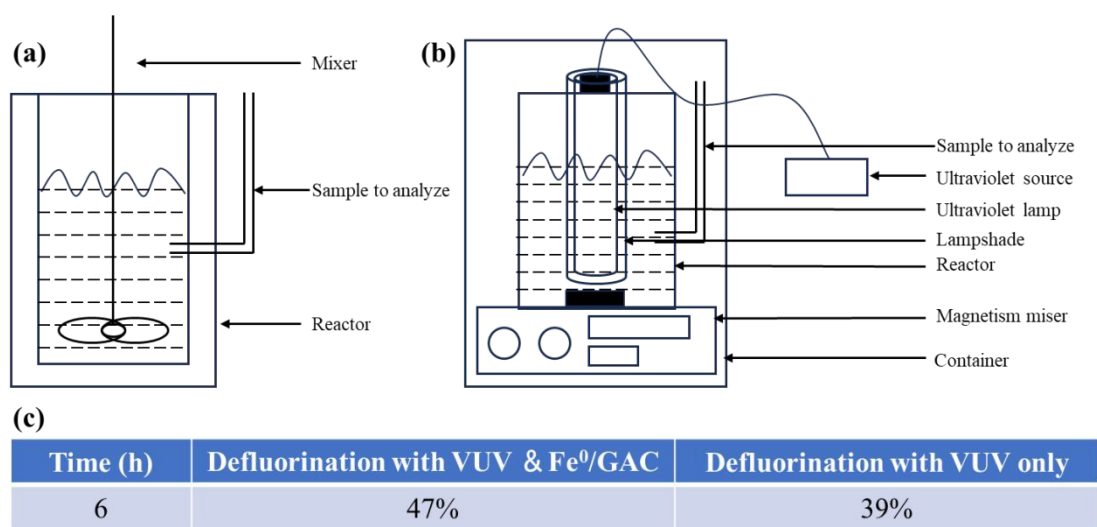


Figure 24. (a) Schematic representation of reactor iron carbon micro-electrolysis and (b) VUV-Fenton. (c) Photochemical defluorination ratio under VUV and Fe⁰/GAC micro-electrolysis and VUV-Fenton systems.

3.3.2 Heterogeneous photo-Fenton systems

Compared to homogeneous photo-Fenton reactions, heterogeneous photo-Fenton systems typically utilize iron-containing catalysts, which can reduce the need for

additional anions and facilitate catalyst recovery through the magnetic properties of solid-phase iron. Based on this concept, Urtiaga et al. employed a TiO_2 /reduced graphene oxide composite catalyst (95% TiO_2 /5% rGO) for the photo-Fenton degradation of PFOA.⁹⁷ After 12 hours of UV–visible irradiation using a mercury lamp, the PFOA degradation efficiency of TiO_2 –rGO reached $93 \pm 7\%$, representing a substantial improvement compared with TiO_2 photocatalysis ($24 \pm 11\%$ removal) and direct photolysis ($58 \pm 9\%$) (Figure 25a). It was reasonably hypothesized that rGO effectively captured photogenerated electrons from TiO_2 , thereby suppressing electron–hole recombination (Figure 25e). This process promoted PFOA degradation through direct oxidation by photogenerated holes or via reactive radical pathways. The progressive decomposition mechanism was further supported by the identification of short-chain perfluorocarboxylic acids (Figure 25b) and the release of fluoride ions (Figure 25c), which closely matched the reduction in total organic carbon (Figure 25d), in line with a stepwise degradation pathway mediated by photogenerated hydroxyl radicals. These findings strongly verified the critical role of $\bullet\text{OH}$ radicals and the stepwise degradation mechanism in PFOA removal by TiO_2 –rGO. Moreover, kinetic studies revealed a clear correlation between degradation efficiency and molecular structure, as the apparent first-order rate constants for UV–visible degradation of PFOA and its intermediate perfluorocarboxylic acids increased with decreasing carbon chain length (Figure 25b). In summary, the development of a heterogeneous photo-Fenton system based on TiO_2 –rGO provides a feasible strategy for PFAS degradation and offers detailed mechanistic insights, thereby laying a solid scientific foundation for



future research.

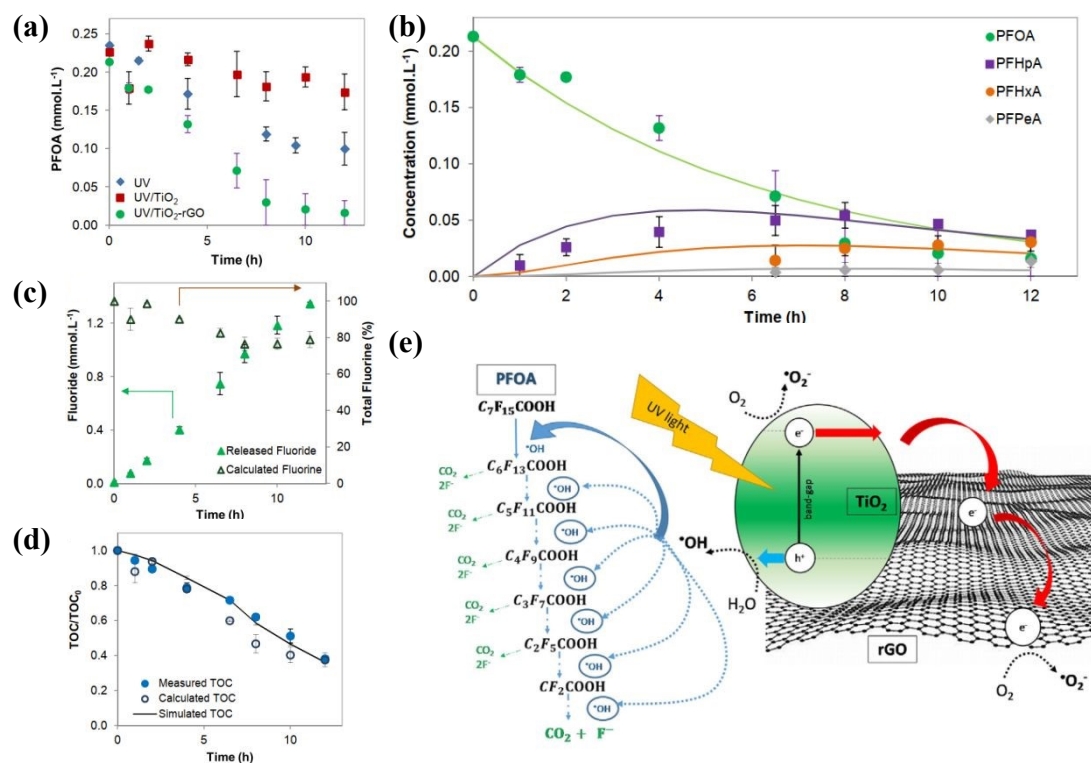


Figure 25. (a) Evolution of PFOA concentration with irradiation time by photolysis and photocatalysis using TiO₂ and TiO₂-rGO. (b) Evolution of PFOA, PFHpA, PFHxA and PFPeA, and their simulated concentrations using the pseudo-first order estimated kinetic parameters. (c) Fluoride in solution and calculated total fluorine. (d) Measured TOC/TOC⁰, calculated TOC/TOC⁰ from the analyzed PFAS, and simulated TOC/TOC⁰ using the simulated PFAS concentrations. (e) Photocatalytic pathways of PFOA decomposition using the TiO₂-rGO catalyst.⁹⁷

In order to achieve a more uniform distribution of iron on the catalyst surface and to elucidate the mechanism of heterogeneous photo-Fenton degradation of PFAS, Wang et al. synthesized a cellulose-based membrane (Co₃O₄@Fe₃O₄) by coating Co₃O₄ nanoparticles onto rod-like MOF-derived Fe₃O₄ and incorporating the composite into a



cellulose solution (Figure 26a). This membrane was then applied in a visible-light-driven photo-Fenton system,⁹⁸ where efficient energy conversion and a rich reactive radical environment enabled effective PFOA degradation. The degradation mechanism relied on the synergistic interplay among photogenerated electrons, holes (h^+), and various reactive species rather than a single dominant species. The photogenerated h^+ directly attacked the carboxylic group ($-\text{COOH}$) of PFOA, initiating decarboxylation and forming $\text{C}_7\text{F}_{15}\bullet$ radicals. The electrons (e^-) reduced dissolved oxygen to $\text{O}_2\bullet^-$, which contributed to further degradation, and also regenerated Fe^{2+} from Fe^{3+} , maintaining $\bullet\text{OH}$ production (Figure 26b). The $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4$ membrane demonstrated outstanding performance, achieving 95% PFOA degradation, maintaining 80% efficiency after five cycles (Figure 26c), and exhibiting minimal metal leaching (Fe: 0.05 ppm; Co: 0.49 ppm). These results were attributed to the material's architecture: regenerated cellulose formed a 3D porous network under alkaline/urea/thiourea conditions, which helped disperse the $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4$ nanoparticles and prevent aggregation (Figure 26d). This study provides valuable experimental and theoretical insights into the rational design of heterogeneous photo-Fenton catalysts.



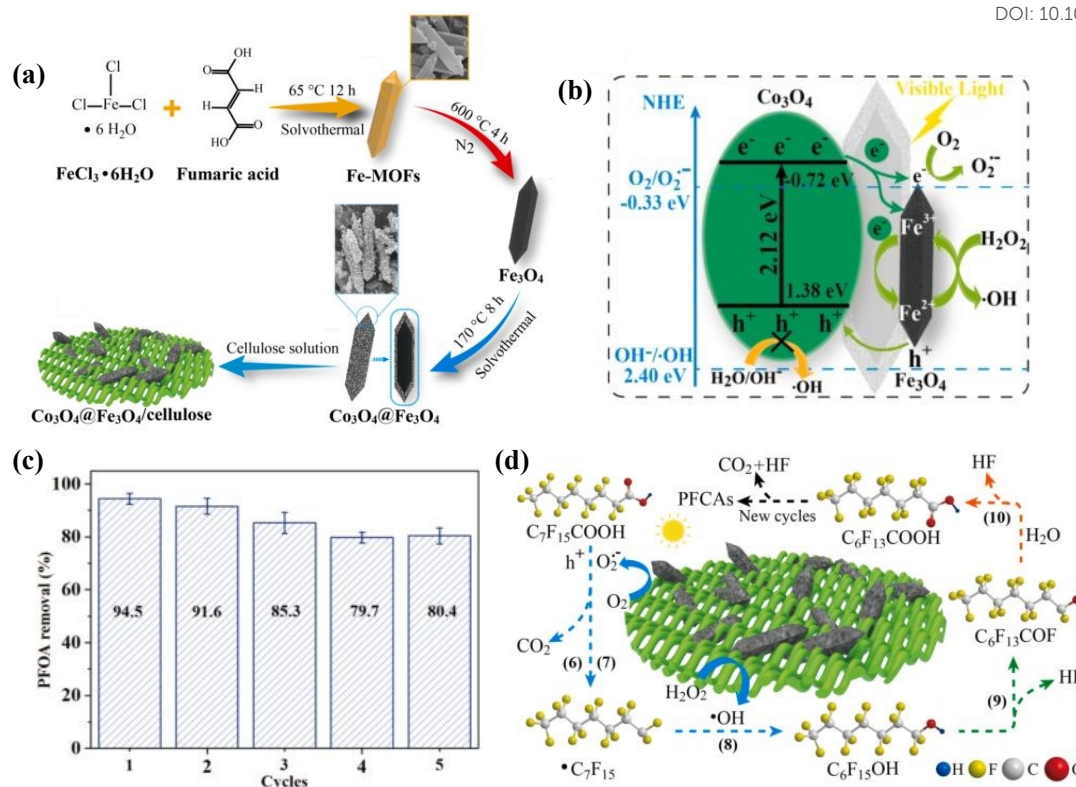


Figure 26. (a) Schematic illustration of the steps to prepare $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}$ blend membranes. (b) Type-II heterojunction reaction mechanism. (c) Reusability of blend membrane. (d) Proposed degradation pathway of PFOA in the $\text{H}_2\text{O}_2/\text{membrane}/\text{visible light}$ system.⁹⁸

To elucidate the synergistic mechanism between PFAS adsorption and photoactivity, Zhang et al. developed $\text{ZIF-67}@\text{C}_3\text{N}_4$ and $\text{MIL-100(Fe)}@\text{C}_3\text{N}_4$ composites with high specific surface areas and adsorption capacity for photo-Fenton degradation of PFOA (Figure 27a and 27b).⁹⁹ Experimental results revealed that $\text{ZIF-67}@\text{C}_3\text{N}_4$ and $\text{MIL-100(Fe)}@\text{C}_3\text{N}_4$ achieved PFOA removal efficiencies of 79.2% and 60.5% (Figure 27c and 27d), respectively—substantially higher than unmodified C_3N_4 . Quenching experiments indicated that photogenerated holes (h^+) played the primary



role in photo-Fenton PFOA degradation, mainly by directly attacking PFOA molecules adsorbed on the catalyst surface and oxidizing water to produce $\cdot\text{OH}$ (Figure 27e). Beyond the photon-induced pathways, PFOA adsorption and charge separation mechanisms also contributed to the high degradation efficiency, such as. The catalyst's ability to accumulate PFOA near photoactive C_3N_4 sites, the enhanced visible-light absorption and charge separation induced by heterojunctions.

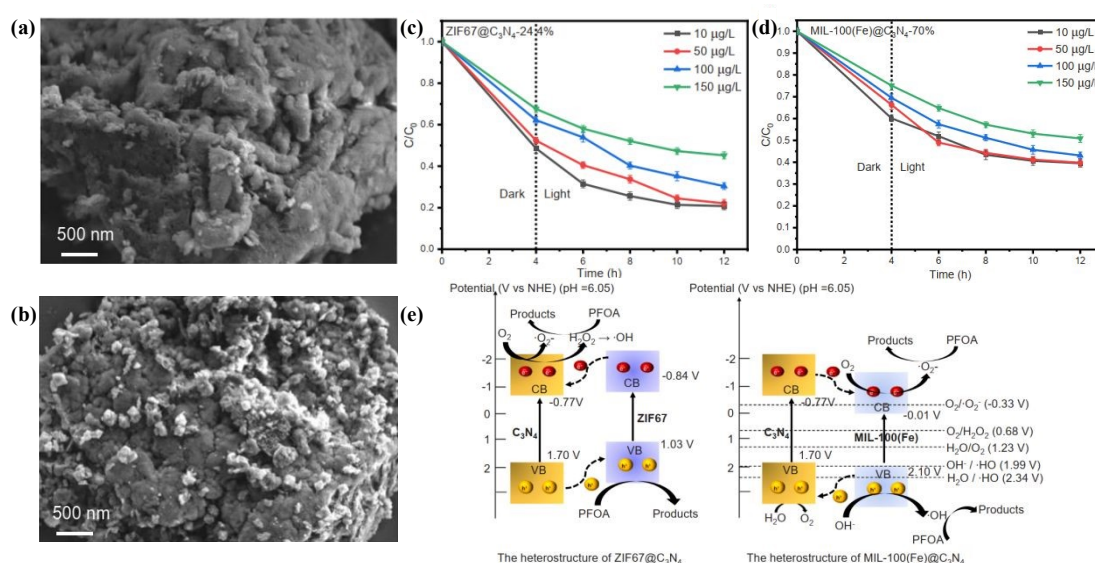
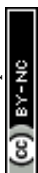


Figure 27. SEM images of C_3N_4 (a) and $\text{MIL-100(Fe)}@\text{C}_3\text{N}_4$ (b). Photodegradation of PFOA with the presence of $\text{ZIF67}@\text{C}_3\text{N}_4$ -24.4% (c) and $\text{MIL-100(Fe)}@\text{C}_3\text{N}_4$ -24.4% (d) with different initial concentrations of PFOA. (e) The heterojunction of $\text{ZIF67}@\text{C}_3\text{N}_4$ and $\text{MIL-100(Fe)}@\text{C}_3\text{N}_4$.⁹⁹

Integrating the heterogeneous photo-Fenton reaction and material structure design for enhancing the radical reactivity, Chen et al. developed Fe(III)-saturated porous montmorillonite (Fe-MMT) as a heterogeneous catalyst to enhance the photo-Fenton reaction.¹⁰⁰ The pore structure microenvironment facilitates effective collisions



between $\bullet\text{OH}$ and PFOA, thereby establishing an alternative strategy for PFOA degradation. In a system containing 1 g/L Fe-MMT and 24 μM PFOA, approximately 90% of the initial PFOA was degraded within 48 hours. The enhanced degradation was attributed to the generation of reactive oxygen species and LMCT mechanism involving Fe species in the interlayer of MMT. Fe^{3+} coordinated with the carboxylate group ($-\text{COO}^-$) of PFOA to form a PFOA- Fe^{2+} complex (Figure 28a). Upon UV irradiation, electrons were transferred from the PFOA ligand to the Fe^{3+} center, producing $\bullet\text{C}_7\text{F}_{15}\text{COO}$ radicals and Fe^{2+} . This LMCT process significantly lowered the activation free energy for PFOA oxidation from 163 to 59.3 kJ/mol (Figure 28b). Further experiments demonstrated that the UV/Fe-MMT system maintained high PFOA removal efficiency even in the presence of natural organic matter and inorganic ions, indicating strong anti-interference capability (Figure 28c and 28d) and potential for practical applications in diverse wastewater treatment scenarios. Moreover, the Fe-MMT catalyst could be regenerated and reused, offering an economic advantage for industrial-scale PFOA remediation (Figure 28e).



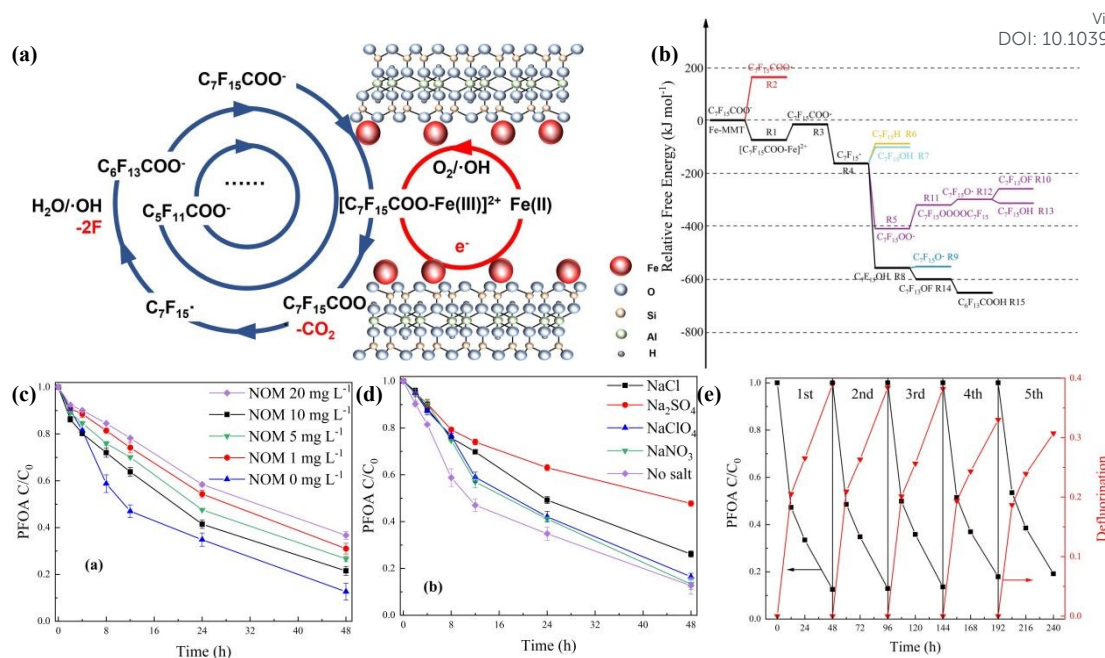


Figure 28. (a) Proposed reaction mechanism for the photo-decomposition of UV/Fe-MMT Fenton system. (b) Scheme of the potential energy surface for the degradation of PFOA in the presence of Fe-MMT. Effect of NOM (c) and inorganic ions (d) on PFOA degradation in UV/Fe-MMT Fenton system. (e) PFOA degradation (black) and defluorination (red) in consecutive batch runs of UV/Fe-MMT Fenton system.¹⁰⁰

Besides experimental validation of scientific hypotheses, theoretical modeling also plays a crucial role in guiding experimental design. Zúniga-Benítez et al. systematically optimized the key parameters (ferrous ion concentration and hydrogen peroxide concentration) for the ultraviolet photo-Fenton (UV/photo-Fenton) degradation of PFOA using response surface methodology (Figure 29a and 29b).¹⁰¹ Under optimal conditions ($\text{Fe}^{2+} = 0.1675 \text{ g/L}$, $\text{H}_2\text{O}_2 = 14.0 \text{ g/L}$, pH 3.0), a 99% removal efficiency was achieved within 60 minutes (Figure 29c). Interestingly, the presence of natural water matrices (e.g., $\text{TOC} = 2.895 \text{ mg/L}$, nitrate) enhanced degradation



efficiency. In untreated surface water, the degradation rate was approximately 30% faster than in deionized water. When UV irradiation was replaced with natural sunlight ($\lambda > 290$ nm), the system still achieved a 95% removal rate within 60 minutes under optimized conditions (Figure 29d), suggesting that solar photo-Fenton processes offer a low-energy alternative particularly suited for sun-rich regions.

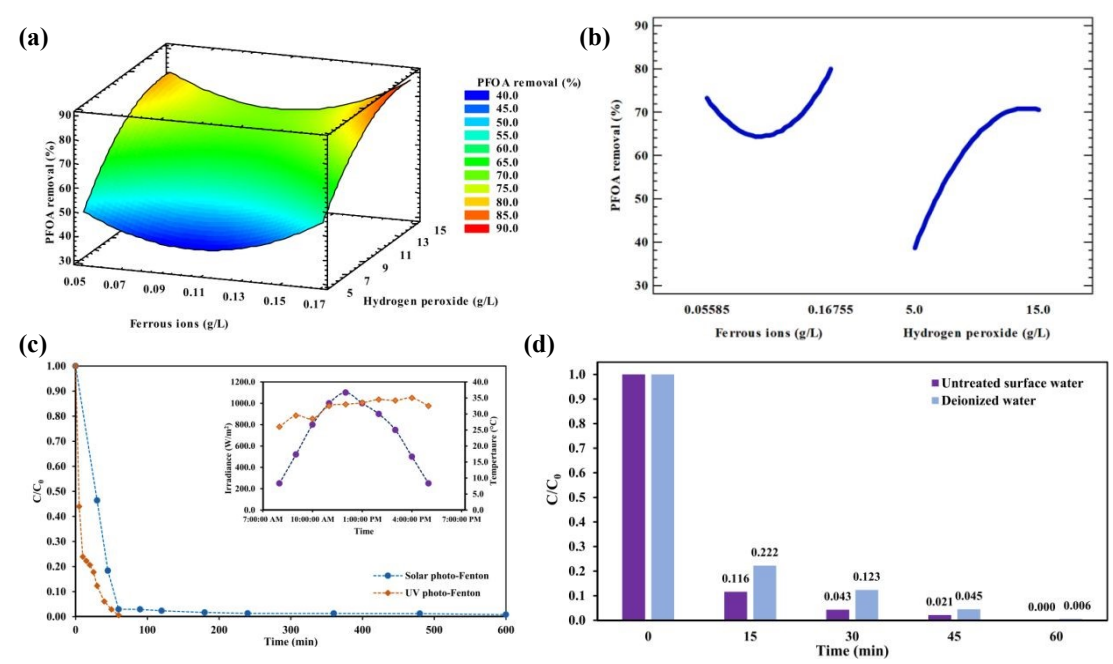


Figure 29. (a) Response surface for PFOA removal using photo-Fenton system. (b) Main effects plot for PFOA removal using photo-Fenton system. (c) PFOA removal under optimized conditions using photo-Fenton and direct solar radiation. (d) Effect of the water matrix in the PFOA removal using photo-Fenton system.¹⁰¹

Homogeneous photo-Fenton reactions offer important mechanistic insights into the degradation pathways of PFAS, while heterogeneous photo-Fenton systems further reveal the structure-activity relationships between material architecture and degradation performance. One of the most significant advantages of photo-Fenton processes is their

use of renewable light energy, aligning closely with the principles of green and sustainable chemistry. However, compared to electro-Fenton systems that enable in situ H_2O_2 generation, the requirement for external H_2O_2 addition in photo-Fenton reactions remains a notable limitation. Furthermore, current research is predominantly focused on UV light-driven systems, which, although effective, often entail higher energy consumption. Although visible light has also been demonstrated to activate photo-Fenton processes for PFAS degradation, the technological maturity of such systems still requires further advancement. Additionally, the scope of photo-Fenton treatment must be broadened to a wider range of PFAS species, particularly those with more complex molecular structures and diverse chemical bond types, which demand more robust and efficient degradation strategies.

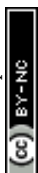
3.4 Solar Photo-Electro-Fenton (SPEF) system

SPEF systems represent a promising and emerging advancement in the development of Fenton-based processes. By integrating the benefits of photo-assisted and electrochemical Fenton mechanisms, SPEF systems build upon traditional chemical Fenton reactions to offer a greener and more energy-efficient approach for pollutant degradation. In particular, 2e^- -ORR generates in situ H_2O_2 , reducing the need for external Fenton reagents. Simultaneously, photoinduced electron-hole transfer further enhances oxidative efficiency while minimizing energy input.¹²⁵ One of the major challenges in SPEF technology lies in the system design,¹²⁶ which must accommodate the simultaneous requirements of both photo-Fenton and electro-Fenton



processes, posing considerable demands on catalyst architecture and operational compatibility.

As an initial attempt to apply photo-electro-Fenton reactions for PFAS degradation, Yu et al. developed a magnetic $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-BiOBr}$ (FSB) composite, which was integrated into a dielectric barrier discharge (DBD) reactor and employed as a heterogeneous Fenton-like photocatalyst for PFOA degradation.¹⁰² The system effectively established a photo-electro-Fenton framework. Compared to DBD alone, the DBD-FSB system enhanced PFOA removal from 74% to 93% and TOC removal from 29% to 63% within 60 minutes (Figure 30a and 30b). The energy efficiency also increased significantly from $46.4 \text{ mg kW}^{-1}\cdot\text{h}^{-1}$ to $72.5 \text{ mg kW}^{-1}\cdot\text{h}^{-1}$. This performance was attributed to multiple reactive species pathways: (i) generation of $\bullet\text{OH}$, H_2O_2 , and O_3 by DBD plasma; and (ii) light-induced Fenton-like reactions on FSB. Multiple PFOA degradation pathways were proposed (Figure 30c), including: (1) hole-driven decarboxylation and radical formation on FSB; (2) direct oxidation in the plasma discharge; and (3) hydroxyl radical attack at the $\alpha\text{-CF}_2$ site, triggering defluorination. The synergistic design improved both degradation efficiency and mechanistic understanding.



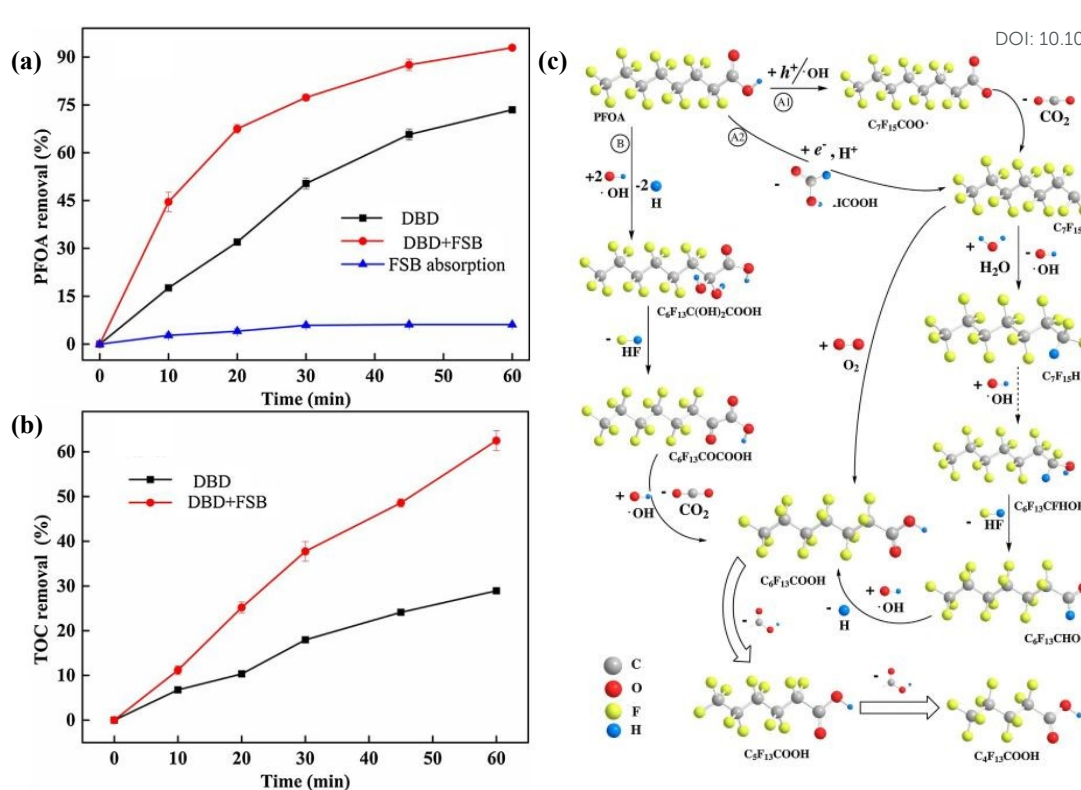


Figure 30. (a) PFOA removals in different treatment processes. (b) TOC removals in different treatment processes. (c) Proposed mineralization mechanism of PFOA in the DBD-FSB system.¹⁰²

Subsequently, to further refine the photo-electro-Fenton system and expand the variety of reactive radical species, Lin et al. successfully fabricated a graphene oxide–titanium dioxide (GO-TiO₂) photoelectrode.¹⁰³ The efficient energy input of a photoelectrochemical (PEC) system and the synergistic effects of multiple reactive radicals, significantly enhanced the Fenton reaction efficiency and PFOS remediation (Figure 31a). The process involved electron transfer, hydroxyl radical generation, and superoxide anion radicals. The degradation pathway was investigated through identification of 25 intermediate products, including perfluoroalkyl sulfonates (PFSAs) (Figure 31b and 31c), perfluoroaldehydes (PFALs), and hydrofluorocarbons (HFCs).

Two primary mineralization routes were proposed (Figure 31d): one via stepwise conversion to shorter-chain PFSA, and another involving initial transformation to PFOA-like structures followed by PFOA degradation. PFALs and HFCs were confirmed as oxidation byproducts of perfluoroalkyl radicals (Figure 31d). The study also showed that shorter-chain PFAS displayed lower degradation rates, indicating stronger resistance and competitive inhibition in PFAS mixtures.

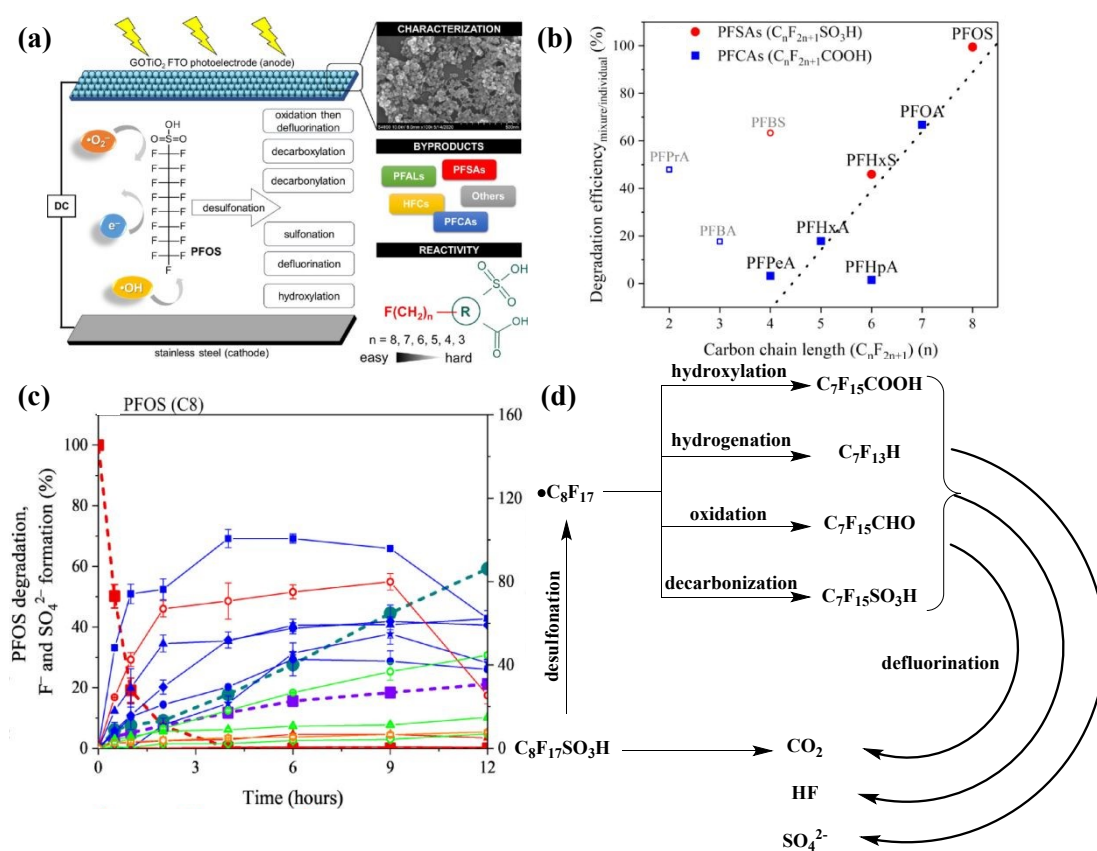


Figure 31. (a) Schematic of PFOS degradation in photoelectrochemical system. (b) The relationship between the carbon chain length and degradation efficiency ratio ($\eta_{\text{mixture}}/\eta_{\text{individual}}$) of PFAS. (c) Formation of the transformation byproducts, F^- and SO_4^{2-} from PFOS degradation in PEC systems.¹⁰³ (d) Proposed degradation pathway of PFOS in the PEC system.



The photo-electro-Fenton system was then further advanced into SPEF system by utilizing a more sustainable and readily available light source—sunlight. Following the design principles of SPEF, Wang et al. introduced a dual-function MOF/carbon nanofiber (MOF/CNF) composite membrane (Figure 32a) for efficient solar photo-electro-Fenton degradation of PFOA.¹⁰⁴ The bifunctional cathode was fabricated by solvothermal growth of Fe/Co bimetallic MOFs onto electrospinning PAN-derived CNFs, exhibiting both photo- and electrocatalytic activity. EPR analysis confirmed enhanced $\bullet\text{OH}$ generation under solar irradiation. The system achieved 99% PFOA removal within 120 minutes (Figure 32b). XPS analysis revealed valence changes of Fe and Co, and a corresponding mineralization mechanism was proposed (Figure 32c). In 2022, the same group advanced this design by integrating a glucose fuel cell (GFC) with the SPEF system to create a sustainable biomass-powered platform for PFOA degradation (Figure 32d).¹⁰⁵ Oxygen-deficient CoFe alloy nanoparticles were anchored onto CNFs (CoFe-OVs@CNF), enabling dual-function cathodes (Figure 32e). The toxicity evolution of degradation intermediates was evaluated, confirming the system's potential to degrade PFOA and other persistent pollutants while mitigating toxic risks (Figure 32f).



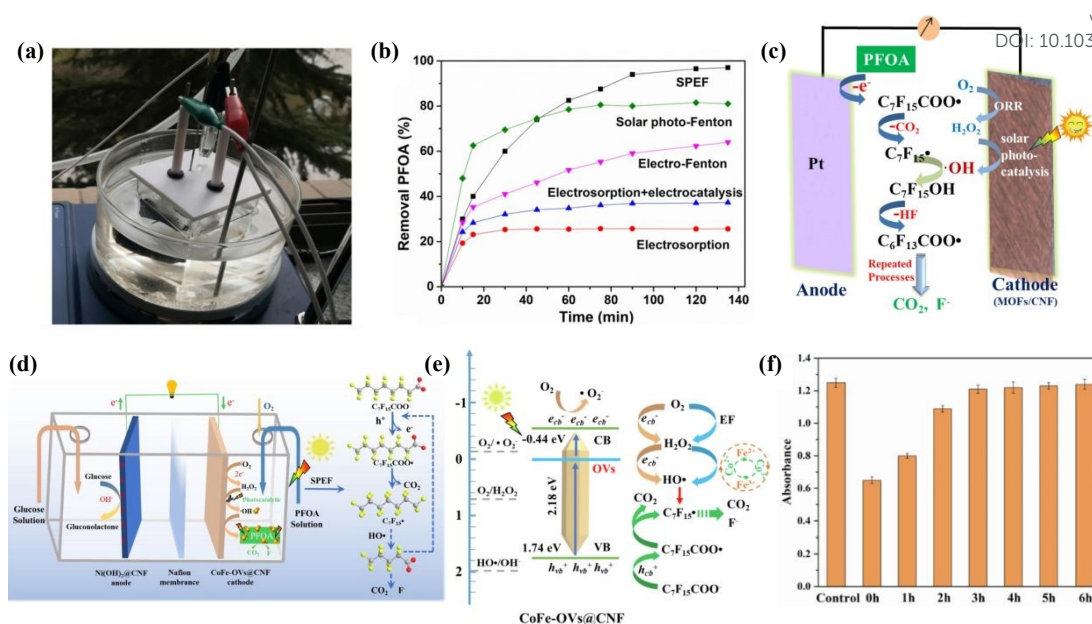


Figure 32. (a) SPEF degradation of PFOA under the natural solar light in outdoors conditions. (b) Removal of PFOA by SPEF, electro-Fenton, electrocatalysis and electrosorption, and electrosorption was conducted under N_2 . (c) Mechanism of PFOA mineralization by the MOFs/CNF constructed SPEF system.¹⁰⁴ (d) Glucose fuel cell driven SPEF process for the degradation of PFOA. (e) Proposed mechanism of solar-photocatalytic coupled Electro-Fenton process for PFOA degradation in GFC-SPEF system. (f) MTT assay for the cell viability of L-02 cells incubated with various degradation time (0–6 h) of PFOA.¹⁰⁵

To further expand the application scope of the SPEF system for PFAS degradation, Hou et al. developed a Cu-based peroxidase-mimicking colorimetric sensor integrated with an SPEF system for PFOA detection and removal (Figure 33a).¹⁰⁶ The flexible, freestanding CNF-Cu/C membrane was synthesized via solvothermal processing, secondary seeding, and in situ thermal reduction (Figure 33b). Derived from MOF/PAN precursors, the resulting 3D carbon network exhibited excellent conductivity,



dispersion, and cycling stability (Figure 33d). The CNF-Cu/C membrane showed strong peroxidase-like activity and enabled rapid PFOA detection via inhibition of TMB chromogenic reactions (Figure 33c), with a detection limit of 0.133 μM . Under optimized conditions, the Cu-SPEF system achieved 98% PFOA removal within 180 minutes. This work illustrates a successful integration of SPEF degradation and real-time detection, with significant practical potential.

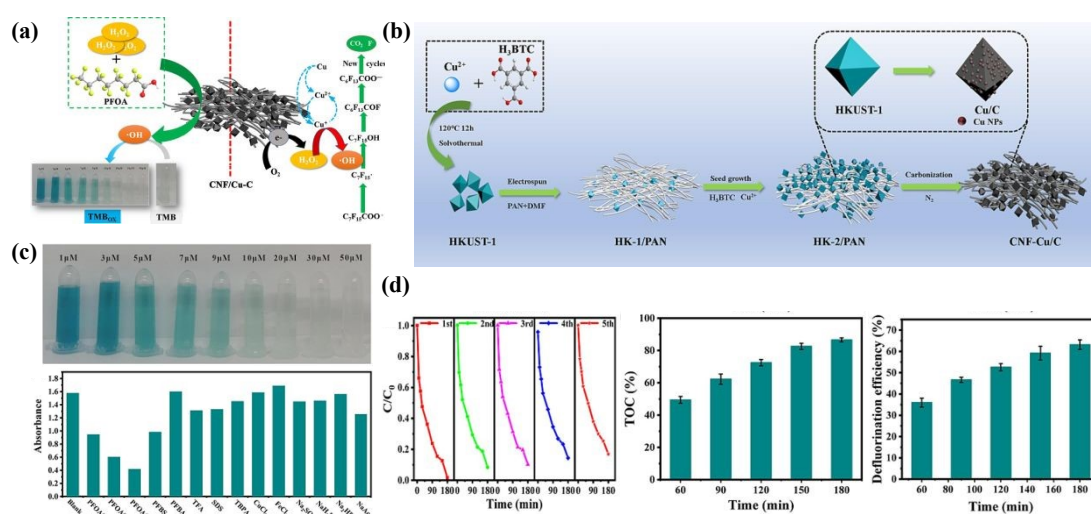


Figure 33. (a) Schematic illustration of PFOA degradation via MOFs-derived Cu/Carbon membrane. (b) Schematic diagram demonstration of the preparation of CNF-Cu/C. (c) Corresponding photographs for the colorimetric detection of PFOA (top) and selectivity of PFOA with other interfering substance (bottom). (d) Degradation rates at different conditions: reusability tests of CNF-Cu/C-800 in SPEF (left), TOC removal efficiency (mid), and defluorination efficiency (right).¹⁰⁶

In order to further elucidate the relationship between the structural characteristics of catalytic materials and PFAS degradation efficiency in SPEF systems, Hou et al. designed two-dimensional layered MOF-based CoFe nanosheets as



photoelectrocatalysts.¹⁰⁷ The material featured abundant unsaturated coordination sites, which facilitated rapid mass and charge transport (Figure 34a). Notably, low-temperature synthesis introduced oxygen vacancies (OVs) that modulated orbital interactions between Fe d-bands and O LUMO states, enhancing PFOA adsorption and reactivity (Figure 34b and 34c). These OVs reduced the bandgap and improved charge separation, significantly boosting photoelectrocatalytic performance (Figure 34d). The catalyst achieved effective degradation even in complex ionic matrices and real water samples (Figure 34e), advancing the practical applicability of SPEF systems and deepening mechanistic understanding at the molecular interface.

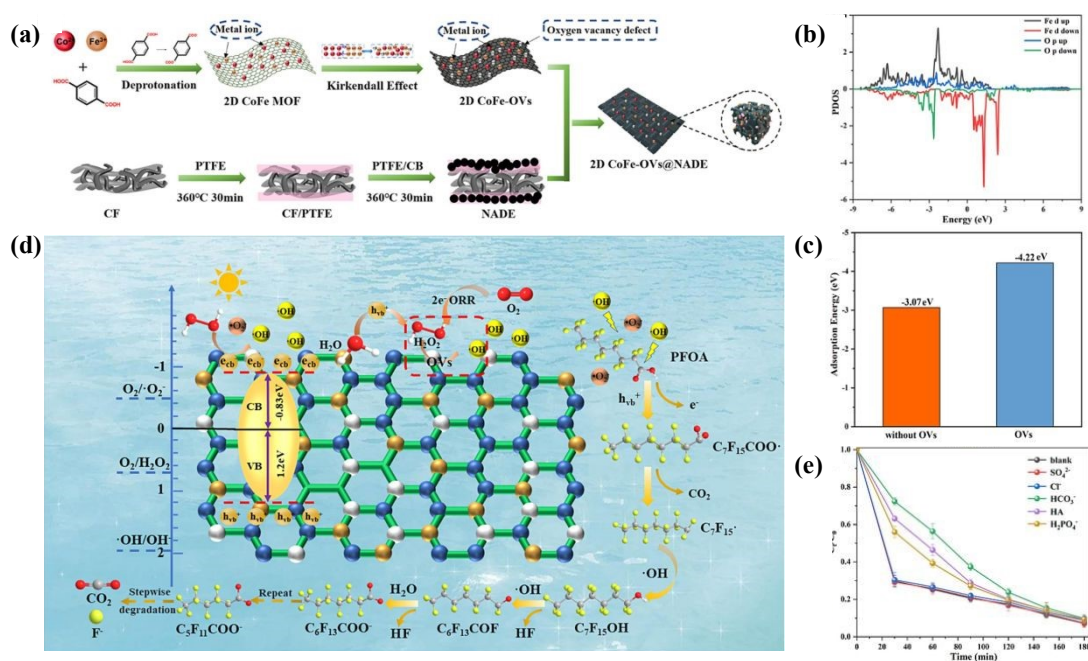


Figure 34. (a) The preparation process of 2D CoFe-OVs@NADE cathode and the construction process of SPEF system. (b) The density of states in 2D CoFe-OVs. (c) The adsorption energy between PFOA and two materials. (d) Mechanism of solar-photocatalytic coupled EF process for PFOA degradation in SPEF system. (e) The effect of coexisting substances in the SPEF system.¹⁰⁷

The solar photo-electro-Fenton (SPEF) system integrates the advantages of both photo-Fenton and electro-Fenton processes by utilizing solar energy as a sustainable light source to generate photogenerated holes for PFAS activation, while simultaneously enabling the *in-situ* generation of H₂O₂ and maintaining a stable Fe²⁺/Fe³⁺ redox cycle inherent to electro-Fenton systems. This allows for efficient and environmentally friendly PFAS degradation without the need for external H₂O₂ addition. Moreover, SPEF systems can be coupled with colorimetric reactions to develop highly sensitive, real-time detection platforms for PFAS, highlighting their significant potential for future applications. However, the development of SPEF faces considerable challenges. Due to the complexity of the integrated system, there are stringent requirements for the structural design of materials used within the reaction framework. Achieving optimal performance demands materials that can simultaneously fulfill the distinct requirements of both photo-Fenton and electro-Fenton processes, which remains one of the most critical barriers to the broader application of SPEF technologies.





Table 1. Recent studies on degradation of PFAS by Fenton reaction.

Catalysts		Target PFAS	[PFAS] ₀	Experimental Conditions	Degradation	Defluorination	Oxidant reactive species	Ref.
Chemical -Fenton reaction	ZVI	PFOA	100 mg/L	ZVI (3.6 mM); PS (5.0 mM); 90 °C; microwave irradiation	68%	23%	SO ₄ ^{•-} ; •OH	80
	Fe(III)	PFOA	100 µg/L	Fe(III) (0.5 mM); H ₂ O ₂ (1.0 M); pH=3.5; 20 °C	89%	\	•OH, O ₂ ^{•-} , and HO ₂ [•]	81
	MD	PFOA	10 mg/L	HP (0.5 M); PS (0.3 M); MD (0.5 g in 60 mL solution);	69%	\	SO ₄ ^{•-} , •OH,	82



				pH=9.0			and O ₂ ^{•-}	
				Pb-BFO/rGO (1.0 g/L);				
Electro-Fenton reaction	Pb-BFO/rGO	PFOA	50 mg/L	H ₂ O ₂ (44.0 mg/L); microwave (300.0 W); 5.0 min	95%	\	•OH	83
	PGFe	PFOA	50 mg/L	PGFe (1.0 g/L); H ₂ O ₂ (15.0 mM); pH=6.0; 25 °C	22%	\	•OH	85
	FeOCl	PFOA	20 mg/L	FeOCl (1.0 g/L); H ₂ O ₂ (2.0 mM); pH=5.2	57%	\	•OH and O ₂ ^{•-}	86
	HA	PFOA	41 mg/L	HA (600.0 mg/L); H ₂ O ₂ (165 mM); Fe ³⁺ (3 mM); pH=3.0	100%	\	•OH	87
	Fe10MnC	PFOA	50 mg/L	Fe10MnC as cathode and BDD as anode; O ₂ (100 mL/min); Na ₂ SO ₄ as electrolyte; pH=3; j=2.85 mA/cm ²	97%	\	•OH	88



	FexNiC as cathodes, graphite sheet							
	FexNiC	PFOA	50 mg/L	as anode; O ₂ (100 mL/min);	81%	\	SO ₄ ^{•-} and	89
	KHSO ₅ (40 mM); pH=3.0; I=25 mA							
	Co-CN ₂ -Fe ₂ O ₃	PFOA	10 mg/L	Co-CN ₂ -Fe ₂ O ₃ as cathodes, Pt as	96%	96%	•OH	90
				anode; O ₂ (10 mL/min); Na ₂ SO ₄ (0.05 M); pH=2; V=-0.06V				
	Fe/N-GE@GF	PFOA	20 mg/L	Fe/N-GE@GF as cathodes, DSA as anode; Na ₂ SO ₄ (0.05 M); pH=7	95%	80%	•OH	91
	F-NSGC	GenX	20 mg/L	F-NSGC as cathodes, Pt as anode; Na ₂ SO ₄ (0.05 M); pH=3	96%	63%	•OH	92
Photo-Fenton reaction	Fe(II)	PFOA	8 mg/L	Fe(II) (2.0 mM); H ₂ O ₂ (30.0 mM); pH=3.0;UV lamp (9W)	95%	53%	•OH	94
	Fe(III)	PFOA	20 mg/L	Fe(III) (1 mM); H ₂ O ₂ (2.0 mM);	98%	13%	•OH	95



UV light (4 W)								
Solar Photo- Electro-	Fe ⁰ /GAC	PFOA	50 mg/L	Fe ⁰ (7.5 g/L); GAC (12.5 g/L); H ₂ O ₂ (22.8 mM); pH=3; VUV light	\	47%	•OH	96
	TiO ₂ -rGO	PFOA	10 mg/L	TiO ₂ -rGO (0.1 g/L); pH=3.8; Hg lamp	93%	98%	•OH and O ₂ ^{•-}	97
	Co ₃ O ₄ @Fe ₃ O ₄	PFOA	20 mg/L	Co ₃ O ₄ @Fe ₃ O ₄ /cellulose as membrane; H ₂ O ₂ (30 mM); pH=3;	95%	\	•OH and O ₂ ^{•-}	98
Xenon lamp (300 W)								
Solar Photo- Electro-	Fe-MMT	PFOA	10 mg/L	Fe-MMT (1.0 g/L); HClO ₄ (0.1 M); pH=3; Hg lamp (36 W)	90%	\	•OH and O ₂ ^{•-}	100
	DBD/FSB	PFOA	20 mg/L	FSB (100 mg/L); pH=4.28; 22 kV peak voltage	93%	32%	•OH	102
	GO-TiO ₂	PFOS	250 µg/L	NaClO ₄ (50 mM); pH=5.64;	99%	20%	•OH	103



Fenton system	MOF/CNF	PFOA	20 mg/L	$j=20\text{ mA/cm}^2$ Na_2SO_4 (50 mM); pH=3; V=-0.6 V	99%	59%	and $\text{O}_2^{\bullet-}$ $\bullet\text{OH}$	104
	CoFe-OVs@CNF	PFOA	20 mg/L	Na_2SO_4 (50 mM); pH=3; O_2 purge; Xenon lamp (300 W)	95%	70%	$\bullet\text{OH}$ and $\text{O}_2^{\bullet-}$	105
	CNF-Cu/C	PFOA	20 mg/L	Na_2SO_4 (50 mM); pH=3; O_2 purge; Xenon lamp (300 W)	98%	63%	$\bullet\text{OH}$, $\text{O}_2^{\bullet-}$, and	106
	CoFe-OVs@NADE	PFOA	20 mg/L	Na_2SO_4 (0.5 M); pH=3; O_2 purge; Xenon lamp (300 W)	93%	67%	$\bullet\text{OH}$ and $\text{O}_2^{\bullet-}$	107

4. Summary and outlook

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The degradation of PFAS is inherently challenging due to the high bond dissociation energy of C–F bonds, which requires not only large quantities of $\bullet\text{OH}$ but also effective activation of PFAS molecules to form reactive $\bullet\text{C}_n\text{F}_{2n+1}$ intermediates. Fenton reactions, owing to their ability to stably generate $\bullet\text{OH}$, naturally emerged as a leading strategy. However, $\bullet\text{OH}$ alone is often insufficient to initiate PFAS activation. To overcome this limitation, multiple innovative approaches have been proposed.

Recent advances in Fenton-based strategies for PFAS degradation have been systematically summarized (Table 1), providing a more intuitive comparison of the relationships among reaction systems, operating conditions, and degradation efficiencies. Distinct reaction systems rely on different oxidative reactive species, which in turn lead to significant variations in PFAS degradation behaviors. In traditional Fenton systems, various radical precursors have been introduced to promote synergistic radical generation for enhanced PFAS degradation. Alternatively, spatial confinement strategies have been employed to restrict PFAS and $\bullet\text{OH}$ interactions to confined catalytic environments, thereby increasing the local radical concentration and reactivity. Additionally, several physical techniques—including electro-Fenton, photo-Fenton, and SPEF—have been developed to facilitate PFAS activation through direct oxidation or electron-hole transfer, thereby enhancing coupling with $\bullet\text{OH}$ and subsequent defluorination steps. These hybrid methods not only circumvent the limitations of chemical Fenton systems, such as excessive H_2O_2 requirements, poor catalyst stability, and strict pH conditions, but also open up new possibilities for the



sustainable treatment of PFAS. However, these advancements come with new challenges—particularly in the rational design of catalytic systems that can meet multiple performance criteria.

Considerable research efforts are still required to fully understand and optimize Fenton-based PFAS degradation. Continued exploration of Fenton-derived AOPs is essential to broaden the scope of PFAS treatment and to proactively address the challenges posed by emerging PFAS variants in future environmental scenarios. Among these developments, multi-strategy coupled Fenton systems, such as the recently proposed SPEF process, are regarded as some of the most promising approaches. By integrating multiple mechanisms, these systems can overcome the limitations inherent to individual methods. However, such integration also significantly increases the complexity of system design and material engineering. Based on the content of this review, the following research gaps and perspectives are proposed:

(1) Most existing studies have focused on the degradation of PFOA and PFOS, which are typically present at the highest concentrations in contaminated water. However, the PFAS concentrations (~10-50 mg/L) used in laboratory-scale experiments are far higher than those typically found in natural waters. Therefore, future research should focus on low-concentration PFAS degradation under environmentally relevant conditions to better meet real-world treatment demands.

(2) Current Fenton-based degradation systems have been primarily developed for PFOA, whereas studies on other PFAS species with diverse functional groups or backbone structures remain limited. Expanding the applicability of Fenton reactions to



a broader range of PFAS is therefore an important direction for future research.

Moreover, the influences of PFAS functional groups, backbone architectures, and spatial conformations on the degradation efficiency, degradation pathways, and byproduct formation in Fenton-based systems require further systematic investigation.

(3) Although novel Fenton-based systems have shown impressive performance, achieving over 95% PFAS degradation within a few hours, the formation of diverse transformation products—including short-chain intermediates, functional group modifications, and possible backbone alterations—remains a major concern. The limited identification of these byproducts and the lack of comprehensive toxicological assessment raise the risk of secondary pollution. Addressing this challenge calls for integrated, multidisciplinary frameworks that link degradation efficiency with systematic analyses of byproduct formation, toxicity, and environmental fate. Future research should therefore move beyond removal rates toward holistic evaluations that ensure both treatment effectiveness and long-term environmental and biological safety.

(4) The development of increasingly sophisticated multi-method coupled Fenton systems presents considerable challenges for catalyst design and material selection. Future work should aim to elucidate the structure-activity relationships between catalyst composition and PFAS degradation performance. Establishing general design principles will enable the development of more effective catalytic materials specifically tailored for PFAS treatment.

(5) Despite widespread attention to Fenton-based AOPs for PFAS degradation, their performance in complex environmental waters has not been systematically evaluated.



Moreover, current Fenton systems typically operate at relatively small treatment volumes. Large-scale water treatment applications require comprehensive studies of process scalability and techno-economic performance. In this context, life cycle assessment (LCA) and techno-economic analysis (TEA) should be considered in future evaluations of PFAS treatment technologies.

Author contributions

Zhicong Huang: Conceptualization; Data curation; Visualization; Validation; Writing – original draft; Writing – review & editing. **Xi Huang:** Investigation. **Kang Liu:** Supervision. **Junwei Fu:** Conceptualization; Funding acquisition; Project administration; Resources; Supervision; Writing – review & editing. **Min Liu:** Supervision.

Conflicts of 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:

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

