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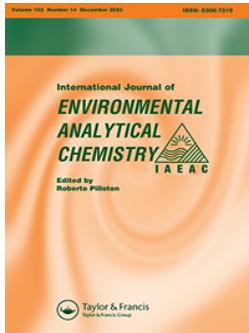


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REVIEW ARTICLE



Per- and polyfluoroalkyl substances degradation using hydroxyl- and sulphate- radical-based advanced oxidation from water matrices: which one is the best approach?

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ABSTRACT

This review investigated the efficiency and mechanism of per- and polyfluoroalkyl substances (PFASs) removal using advanced oxidation processes. Boron-doped diamond (BDD) electrodes in the electrochemical oxidation process are considered one of the ideal anode materials for the oxidation of PFAS compounds due to their high oxidation power with weak electrode-hydroxyl radical interactions. The degradation of PFAS by the combined process of foam fractionation combined with BDD electrochemical oxidation treatment showed that the overall degradation of long-chain PFAS was 77% against 22% of short-chain PFAS in the leachate water treatment plant. The experimental data revealed that photochemical oxidation is moderately efficient for perfluorooctanoic acid (PFOA) but inadequate for Perfluorooctanesulfonic acid (PFOS) removal. Moreover, photochemical oxidation relies heavily on hydroxyl radical oxidation, which is unsuccessful in PFAS breakdown. The review is expected to improve our current understanding of research about PFAS and hence aid in the selection of suitable advanced oxidation processes for PFAS management. Regarding the persulphate method, it has been shown to be effective in the elimination of PFOA, but not PFOS, since the sulphonate group is substantially less electron-dense than the carboxylic group, making PFOS resilient to oxidation by sulphate free radicals.

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PFAS; degradation mechanism; health risk assessment; sulphate radical; hydroxyl radical

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are chemicals utilised in commercial and industrial goods since the 1940s. PFAS are formed of a polar head group (lipophilic tail) and fluorinated alkyl chain (hydrophobic tail), giving them surfactant-like qualities (refer to Figure 1 for a better understanding of the molecular structure of PFAS). It should be

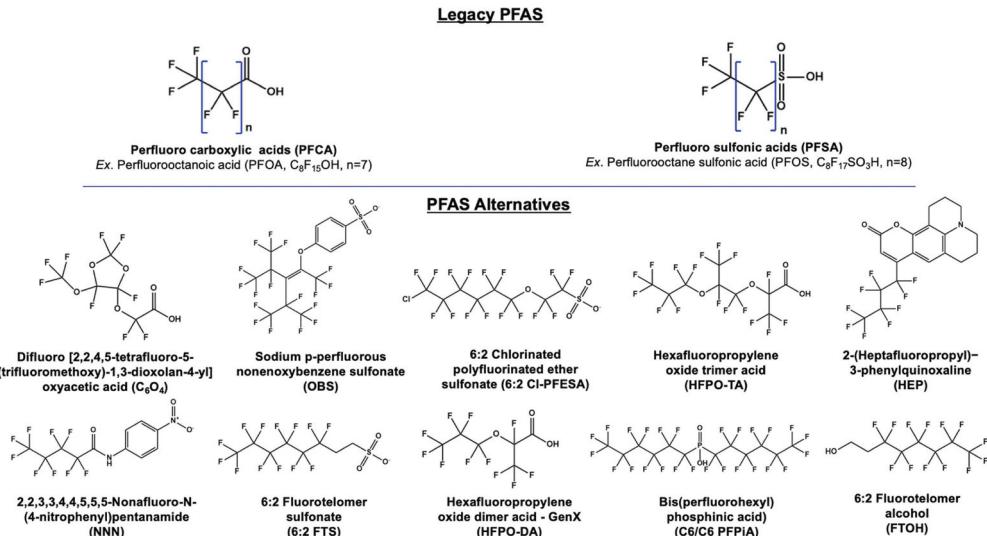


Figure 1. Structures and examples of legacy and alternative PFAS substances. Many alternative and legacy PFAS are not included in this list, although they are considered as similarly critical substances for environmental monitoring and treatment. Modified after ref [1].

noted that their hydrophobicity characteristic is recognised to be greater by the chain length increase. They can endure severe temperatures and are resistant to both grease and water. These substances can pass into the environment from point sources of contamination from production plant [2], industrial wastewaters [3], military firefighting foams [4,5], and landfill leachates [6]. They have been detected in these matrices [7]. Figure 2 shows possible releases, uptake pathways, and their final destruction ways. PFAS have a limited removal efficiency, which results in bioaccumulation in people [8] and animals [9]. Their omnipresence and endurance, together with their detrimental health impacts like endocrine and metabolic disruption or even cancer, necessitate monitoring these compounds in drinking water, food, and other environmental matrices [10]. Long-chain PFAS have been banned from manufacture since their health risks were discovered, thanks to the Stockholm Convention. After the ban, manufacturers began making structural adjustments to PFAS to make them more readily excretable and/or biodegradable. These substitutes for PFAS have structures with ether linkages or chlorinated carbons and shorter fluoroalkyl chains (Figure 1).

Physical, chemical, and biological treatments are used to remediate PFAS contamination. The physical treatment removes PFAS contamination using anion exchangers or carbon-based sorption materials. Removing the pollutant alone isn't enough for comprehensive treatment since it merely moves PFAS from one medium to another; it doesn't degrade or eliminate them. Chemical remediation degrades PFAS through electrochemical, photochemical, and plasma processes. The biological treatment destroys PFAS using bacteria and plants. Their biodegradation can be conducted by enzymes that immediately eliminate fluorine atoms from these substances, either by attaching oxygen across the F-C bond (oxidation) or by trying to add electrons throughout the F-C bond (reduction), letting other usual assimilation enzymes split the remaining compound. Also, under aerobic or anaerobic circumstances, there are identified bacteria that may break down an F-C bond [1,11].

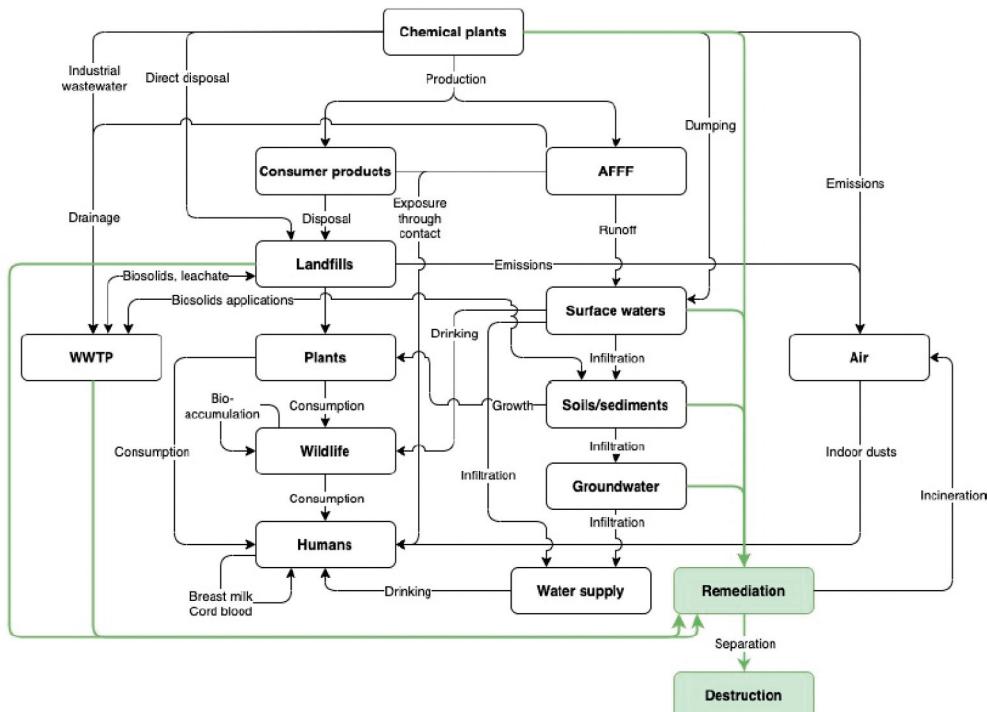


Figure 2. PFAS release and exposure pathways (WWTP=wastewater treatment plant, AFFF= Aqueous film-forming foams).

Phytoremediation has also been utilised to remediate PFAS. While PFAS are not completely destroyed by phytoremediation, bioaccumulation in plants could be a pathway for PFAS removal [12]. Physical treatment combined with the biological or chemical method can minimise remediation costs and efforts [11]. This review investigated PFAS removal by two approaches based on advanced oxidation processes. Knowing the PFAS transfer and conversion mechanisms can enhance understanding of chemical treatment methods. Effective remediation strategies must address legacy, new, and unwanted transformation products of PFAS in the water supply. Physical treatment can remove PFAS from the source and drinking water. PFAS removal provides an excess of contaminated substances that need permanent disposal. Leachate from these materials can include PFAS, making disposal expensive and difficult. Recent research has studied plasma reactors, photocatalytic defluorination, and hydroxyl radical processes.

Advanced Oxidation Processes (AOPs) are a group of technologies that use chemical reactions to break down and remove PFAS from contaminated water. AOPs typically involve the use of strong oxidising agents, such as ozone, hydrogen peroxide, or UV radiation, to generate reactive oxygen species that can oxidise and destroy PFAS molecules. These processes are considered 'advanced' because they can effectively treat even highly persistent and toxic PFAS compounds that are resistant to conventional treatment methods [13]. Various oxidising chemicals can be used in the PFAS oxidative degradation process. Much as there are other review articles about several treatment strategies for PFAS removal, the comparison of such methods and removal mechanisms are overlooked. Herein, this comprehensive review has been undertaken to evaluate the ability of

hydroxyl radical and sulphate radical-based AOPs such as potassium permanganate, hydrogen peroxide, electrochemical oxidation, ultraviolet light, chlorine, chlorine dioxide, and ozone for PFAS degradation. The disadvantages of the former, such as acidic pH and radical scavenging by NOM, and that of the latter, such as inadequate mineralisation efficacy, are also discussed. Furthermore, the study assesses the environmental and health risks of PFAS for a better understanding of their complex behaviour and basic science, as well as their severe health and environmental consequences. Finally, knowledge gaps in using advanced oxidation processes for the treatment of PFAS are reviewed, and recommendations for further research are offered [13,14].

2. Hydroxyl radical-based advanced oxidation processes

Ozonation is an advanced oxidation process in which ozone gas is used as the oxidant. The primary reaction of ozone with organic molecules is due to its high selectivity [15,16]. There are several operational factors that influence removal efficiency [17]. In addition to pH, temperature, and organic matter concentration, the water matrix influences ozone's stability [18]. Hydroxyl radicals, which are even more powerful than molecular ozone, are non-selective and extremely reactive [19,20]. Yang et al. [18] discovered the same outcome for PFOS treated with alkaline ozonation. Under equal conditions, 6:2 FTSA was converted to 13% residual. According to Table 1, Mitchell et al. [21] oxidised PFOA using the Fenton method, in which 1 molar hydrogen peroxide and 0.5 mM iron were used, resulting in 89% PFOA reduction in 150 minutes. Although the Fenton method itself reportedly cannot degrade PFAS, it has been fruitful for PFOA removal [21]. Similarly, Lin et al. [22] replicated Schröder's alkaline ozonation experimental conditions and observed effective decomposition of PFOA and PFOS with 33% and 43% elimination, respectively. The authors found a rise in the removal rate to 90% PFOA and 85% PFOS after a 15-minute first ozonation at pH = 4–5, which was then adjusted to 11. They showed that proxone treatment (O_3/H_2O_2) reduced both substances by more than 99% after four hours [22].

Schröder and Meesters [31] reported that perfluorooctanesulfonic (PFOS) is resistant to ozone, as well as O_3/UV and O_3/H_2O_2 . The Fenton reaction produces hydroxyl radical, ferric ion, hydroxyl ion, and ferrous ion from hydrogen peroxide and iron. The photo-Fenton method, which is a Fenton reaction integrated with UV irradiation, improves conventional Fenton performance [31]. The electro-Fenton technique, which electrochemically generates in-situ hydrogen peroxide, reduces the limitations of the conventional Fenton process. Also, it can be progressed by incorporating UV light into it. Increasing Fe^{2+} and hydrogen peroxide concentrations often can promote contamination degradation. Fenton-based treatment processes can remove PFAS because they are able to degrade larger concentrations of pollutants efficiently [31]. Olvera-Vargas et al. [23] tested the electro-Fenton breakdown of GenX, a short-chain hexafluoropropylene oxide dimer acid, utilising a graphene-Ni-foam (Gr-Ni-foam) cathode coupled with electro-oxidation employing a boron doped diamond (BDD) anode. They discovered that homogenous $\cdot OH$ radicals generated by electro-Fenton had little reaction with the GenX molecule. Instead, direct electron transfer at the surface of BDD anode triggered GenX degradation, which was then continued and accelerated by homogenous $\cdot OH$. Fluorine doped tin oxide (FTO) and Pt anodes, on the other hand, did not promote GenX degradation. They suggested a mineralisation mechanism for GenX that involves two distinct paths

Table 1. Summary of hydroxyl and sulphate radical-based advanced oxidation approaches in treating PFAS.

Approach	Process	Critical factors	Target pollutant	Advantage	Disadvantage	Key points	Ref.
CHP	Time: 150 minutes	PFOA	Hydroperoxide as a strong nucleophile, attacks electron-deficient carbon atoms, thereby rapidly degrading PFOA.	Superoxide was less effective in PFOA degradation.	Fenton method (1 M H ₂ O ₂ and .5 mM iron) resulting in 89% reduction	Mitchell et al. [21]	
Hydroxyl radical-based AOPs	pH: 4-5, Time: 15-minutes & 4-hours	PFOA/PFOS PFOS	Rapidly treated by ozonation under alkaline condition	Energy required by alkaline ozonation treatment are much higher than alkaline-peroxone O ₃ /H ₂ O ₂ ; both substances removed by more than 99%. O ₃ /H ₂ O ₂ ; both substances removed by more than 99%.	Ozonation: 90% PFOA and 83% PFOS removal achieved. O ₃ /H ₂ O ₂ ; both substances removed by more than 99%.	Lin et al. [22]	
EF using a Gr-Ni-foam cathode paired with a BDD anode	Time: 6 hours	GenX	Gr-Ni-foam proved an effective cathode for H ₂ O ₂ generation.	Pt and FTO anodes did not favor GenX degradation.	92.2% of GenX mineralization achieved under 16 mA cm ⁻² using combined EF and BDD oxidation compared to 9.2% by EF and 73.6% with BDD standalone.	Olvera-Vargas et al. [23]	
Synergic EC and EF	Time: 4 hours	PFOA	BDD had a significant contribution of anodic oxidation ability in synergic electrochemical process.	It took more than 4 hours to remove PFOA.	A novel cathode employing iron/manganese-doped carbon as cathode and BDD as anode which achieved 97% removal.	Wang et al. [24]	
Metal ions mediated photochemical decomposition	-	PFOA	The concentration of ferric ion Mg ²⁺ , Zn ²⁺ or Cu ²⁺ only slightly enhanced the decomposition rate of PFOA.	8.2% degradation achieved using Fe ³⁺ under 254 nm UV radiation.	Wang et al. [25]		

(Continued)

Table 1. (Continued).

Approach	Process	Critical factors	Target pollutant	Advantage	Disadvantage	Key points	Ref.
Activated persulfate oxidation	UV/H ₂ O ₂ , UV/Cl ₂ , UV/TiO ₂ , and O ₃ /H ₂ O ₂	-	PFAS	-	hydroxyl radical-based AOPs are inefficient for the treatment.	An increase of PFOA from 5.7 ng/L in the influent to 11 ng/L in the AOP effluent during UV/Cl ₂ treatment.	Venkatesan et al. [26]
Sulfate radical-based AOPs	Microwave-hydrothermal using ZVI	pH:2.5, PS:10 mmol.L ⁻¹ , temperature: 90°C time: 2 h	PFOS	UV/H ₂ O ₂ was found to be the most effective condition with 4.2%.	Further increase in amounts of S ₂ O ₈ ²⁻ caused insignificant improvement in PFOS defluorination due to elimination of sulfate radicals under high concentration of S ₂ O ₈ ²⁻ .	Sulfate radicals oxidation and hydrolysis were the main mechanisms involved in defluorination process of PFOS.	Yang et al. [27]
Activated persulfate oxidation	pH:2.0, temperature: 50°C, molar ratio of PFOA to persulfate: 1:100, reaction time: 100 h	PFOA	The combined use of ZVI and PS lead to more efficient decomposition of PFOA at lower reaction temperature within a shorter reaction time.	The standalone PS had slowly decomposed of PFOA at the end of 8 h	Microwave activated persulfate degrade 77% of PFOA.	PFOA degradation efficiency achieved 89.9%.	Lee et al. [28]
Heat-activated persulfate	Time: 12 hours	PFOA and PFOS	PFOA degradation efficiency was yielded with higher temperature, higher persulfate dosage and a longer reaction time under acidic conditions.	The corresponding DF ratio of 23.9% was much less than the PFOA degradation efficiency, indicating that not all PFOA degradation is achieved via fluorine removal.	PFOA degradation efficiency achieved	Yin et al. [29]	
				PFOS remained unaltered even under higher temperature (85 and 90°C) at 60.5 and 84 mM S ₂ O ₈ ²⁻ .	PFOS is oxidized by heat-activated persulfate within 72 h at 50°C.	Park et al. [30]	

O₃: ozonation; H₂O₂: hydrogen peroxide; PS: persulfate; ZVI: zero-valent iron; PFOA: Perfluorooctanoic acid; PFOS: Perfluorooctane sulphonlic acid; EF: Electro-Fenton; EC: electrochemical; GenX: hexafluoropropylene oxide dimer acid; Gr: Graphene; BDD: boron doped diamond; FTO: fluorine doped tin oxide; DF: defluorination; CHP: catalysed H₂O₂ propagation.

beginning with electron transfer at the GenX molecule's carboxylic and ether groups [23]. Further research is needed for the application of advanced Fenton processes, such as electro-Fenton, photo Fenton, electrophoto-Fenton, and their combinations with other processes, for the degradation of PFAS.

BDD electrodes in the electrochemical oxidation process are considered one of the ideal anode materials to oxidise PFAS compounds. This is because BDD is characterised by high oxidation power with a weak electrode – hydroxyl radical interactions, which leads to a high current efficiency for organic oxidation and a low electrochemical activity for oxygen evolution. In the same vein, the mechanism of PFAS oxidation (Figure 3) is such that the rate-limiting step is the direct electron transfer at the surface, which leads to the

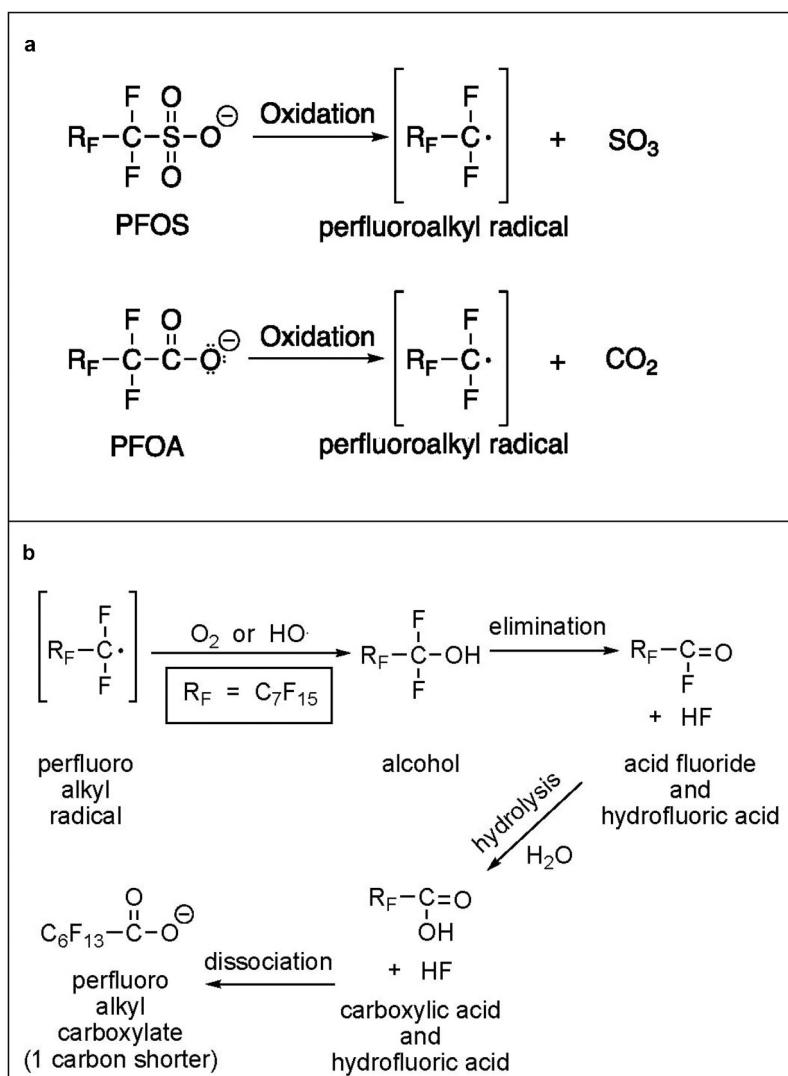


Figure 3. The mechanism of PFAS compounds oxidation in EO process: (a) Rate-limiting step for the treatment of PFOS versus PFOA to the perfluoroalkyl radical; (b) subsequent degradation of perfluoroalkyl radical.

cleavage of the head group ($-COOH$ vs. $-SO_3H$) to produce the corresponding perfluoroalkyl radical. After that, the perfluoroalkyl radical can quickly react with $\bullet OH$, O_2 , or H_2O and degrade to the one-carbon shorter per-fluoro-heptane-carboxylate. The 1-carbon shorter carboxylate undergoes the same degradation cycle as the original PFOA, sequentially converting the carboxylic acid head to carbon dioxide (CO_2), fluorine atoms to hydrogen fluoride (HF), and CF_2 to another carboxylic acid group [32].

Electrochemical oxidation has been gaining popularity for treating water and wastewater due to its ability to decompose resistant organic pollutants, like perfluorinated compounds [33]. Advantages of electrochemical oxidation include the feasibility of being operated at room temperature, no need for chemicals, and producing no waste [34]. It can be conducted through direct and indirect anodic oxidation. In direct electrolysis, pollutants are adsorbed onto and decomposed at the electrode directly. Through indirect electrolysis, impurities are destroyed in the bulk fluid in interactions with electrode-formed oxidising mediators [34]. Due to its chemical, mechanical, and thermal stability, boron-doped diamond (BDD) has been employed in most PFAS removal studies. Schröder et al. [35] explored PFAS elimination as part of a multi-pronged approach that included ozone treatment and heterogeneous catalysis. They found that the combination of O_3 and celite had lower removal rates by 14% and 53% for PFOA and PFOS, respectively, rather than Fenton/UV by 73% (PFOA) and 62% (PFOS). Titanium oxide (TiO_2), lead dioxide (PbO_2), and tin oxide (SnO_2) are also declared to remediate water contaminated with PFAS better than platinum (Pt) and iridium oxide (IrO_2) as the latter are recognised as more inactive substances [35,36].

In respect of low conductivity TiO_2 , electrooxidation processes can be facilitated by the use of Ebonex®. Ebonex® is a non-stoichiometric titanium oxide mixture containing Magneli phase titanium oxides Ti_4O_7 . Ti_4O_7 is often preferred as a new material over TiO_2 due to its higher electrical conductivity, larger specific surface area, and better stability under high potentials. Ti_4O_7 also exhibits superior catalytic activity for various oxidation reactions, making it a promising material for use in electrochemical oxidation applications [37]. In Lin et al. [38] the concentrated PFAS waste stream was treated by novel porous Ti_4O_7 ceramic anode through a Magnéli phase. As shown in Figure 4, compared to the Ce- PbO_2 and BDD electrodes, two well-known 'non-active' anodes that have been proven effective for PFOA degradation, the Ti_4O_7 ceramic anode exhibits almost complete mineralisation and

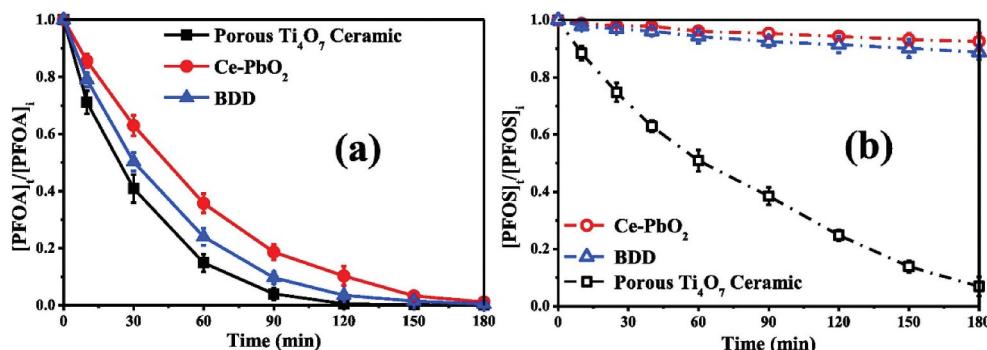


Figure 4. The degradation of PFOA and PFOS via electrooxidation by the Ce- PbO_2 , BDD, and porous Ti_4O_7 ceramic anode at a constant current density of 5 mA cm^{-2} . Reproduced with permission from ref [38]. Copyright © 2018 Elsevier Ltd.

a faster decay rate for PFOA and PFOS. In the same vein, HO[•] radicals play an important role in PFOS degradation. Since the value of the OH adsorbate on Ti₄O₇ electrode is significantly lower than those on BDD, which showed higher reactivity on Ti₄O₇ than those on BDD. Consequently, this contributes to the higher PFOS removal rate on Ti₄O₇ than on BDD [39].

In the electrochemical oxidation of PFAS, operational parameters such as temperature, pH [38], electrode distance [39], current density, electrolyte type have significant contributions [40], and initial PFAS dosage [41]. Boron-doped diamond, PbO₄, SnO₂, and TiO₂ could be preferable due to their strong electron transfer capacity and the capability of their atoms to maintain an equal oxidation status during reactions, whereas active anode atoms continually cycle during oxidation [42]. EAOPs have been found to be particularly beneficial for the total removal of persistent organic contaminants that are not degradable by standard treatment approaches, as well as the complete mineralisation of different organic compounds such as dyes, pesticides, nitrophenols, and chlorophenols [43]. They have also been demonstrated to be useful for treating industrial wastewater that is mixed heterogeneously. Another advantage of EAOPs is the possibility of using heterogeneous catalysts for the efficient generation of hydroxyl radicals in an aqueous medium that is recyclable and reusable [44].

However, there are environmental and financial risks involved with the electrochemical oxidation of these components. Toxic byproducts such as bromate, perchlorate, hydrogen fluoride, and lead have been described in studies. The production of perchlorate was noticed during the electro-oxidation of PFAS utilising BDD anodes [45,46]. Because the majority of these electrodes possess harmful heavy metals, the metals may be discharged into the environment, in addition to the comparatively expensive cost of electrodes, which is still a great concern for mass production of them [47].

It was found that during the electro-oxidation of PFOA and PFOS using a Ti/RuO₂ electrode, current density improved PFOA decomposition, and shorter-chain perfluoro carboxylic acids (PFCAs) or no fluoride were found in the final solution [48]. It can be because of the fact that with the progress of electrolysis, PFCAs with short chains could have been degraded to unstable PFCAs like trifluoroacetic acid (TFA) and then entered the gaseous phase [49]. PFOS decomposition slowed over time, indicating anode saturation [50]. PFOS owned the most fluoride retrieval, followed by PFOA. They also found that trace levels of shorter chain PFAS in solution, generated via degradation processes of PFAS on the surface of the anode with little transfer to the aqueous phase [45]. Increased PFOS decomposition using Si/BDD anode with rising the current density was reported in another study, in which parallel plate flow-through reactors degrade PFOS completely compared to spinning disk electrode ones [46]. Liao and Farrell [51] also examined the degrading of perfluorobutane sulphonate (PFBS) and reported practically full elimination [51]. It is also reported that acidic pH degraded PFOA more than alkaline conditions, which can be because of the pH-dependent sorption of PFAS [48]. In an acidic environment, hydrogen ions (H⁺) are adsorbed on the anode surface, and anionic PFAS readily adsorb onto the active areas via electrostatic attraction. Kinetic investigations indicated rising rate constants with chain length, which can be due to easier sorption on the anode. Chain length also increases PFAS hydrophobicity. Increasing the initial PFAS concentration raised rate constants, suggesting that PFOA species may get to the electrode surface more easily at higher concentrations, leading to greater removal rates [52,53].

Trautmann et al. [35] studied the electrochemical oxidation of PFAS-contaminated groundwater from a previous firefighting training location and synthetic groundwater and concluded that PFOS showed more degradation than PFHxS and PFBS, suggesting that chain length increases the rate of degradation [39,54]. Opposed to PFBS, PFBA was completely decomposed, and so they related this to the fact that PFAS with the identical carbon number as PFCA is more difficult to decompose because of their limited mass transfer at the anode due to their electrophilic functional group. Researchers [54] suggested PFAS oxidised in the sequence of perfluorooctane sulphonic acid (PFOS) > perfluorohexane sulphonate (PFHxS) > perfluorobutane sulphonate (PFBS) > 6:2 fluorotelomer sulphonic acid (6:2 FTSA), demonstrating stepwise decomposition (shorter chain length formation). They also observed the production of perchlorate and bromate as byproducts of the electrooxidation of PFAS by BDD anode [54]. Niu et al. [55] used a Ce-doped adapted porous nanocrystalline PbO₂ film electrode to mineralise five PFAS and showed significant PFOA elimination and defluorination. Lin et al. [22] found that with increasing initial PFOA concentration and plate distance, degradation efficiency declined while defluorination efficiency rose. They claimed that increasing plate distance may have decreased the PFAS mass transfer throughout the electrodes, hence reducing degrading efficiency. This can be due to the fact that voltage and PFA mass transfer rates between electrodes are reliant on plate spacing. They also noted that PFOA's C – F energy level is substantial. Therefore a large electrical potential is needed to stimulate electron transfer for defluorination processes. Raising plate distance may have increased voltage between the electrodes, growing the rate of defluorination [22].

A pilot scale study by Smith et al. [56] evaluated PFAS degradation from groundwater and leachate water treatment plant using the foam fractionation (FF) process as a pretreatment of BDD-electrochemical oxidation (EO). As can be seen from Figure 5, due to the short-chain PFAS being low in FF, therefore, the overall degradation efficiency was

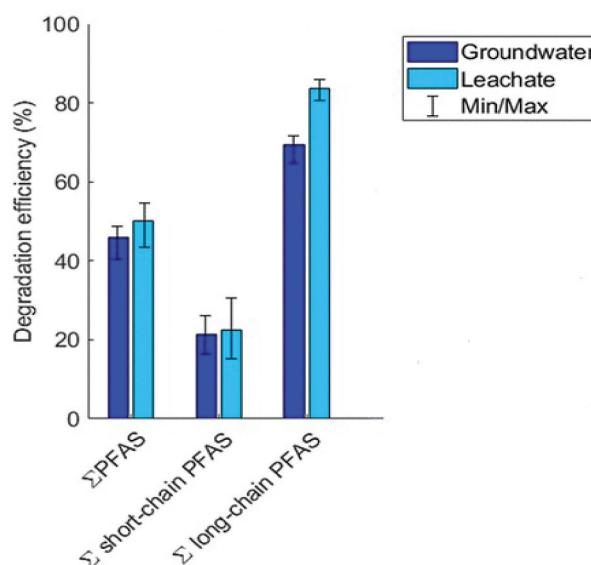


Figure 5. PFAS degradation efficiency (%) of the coupled FF-EO process in groundwater and leachate. Modified after ref [56].

lower in the groundwater. However, the overall degradation of long-chain PFAS (mean 77%) was more than three times higher than that of short-chain PFAS (mean 22%) in the leachate.

Electrochemical oxidation can also be combined with other processes. Zhao et al. [40] noticed an increase in degrading rate when coupling SnO_2 -Sb/carbon aerogel with ultrasound, which was because of more reactivity and fast mass transfer at the electrode surface. Shi et al. [57] used electrocoagulation and electrooxidation to eliminate PFAS from water. They applied Zinc and stainless steel as anode and cathode during electrocoagulation, after which the effluent was transported to the electrooxidation reactor containing the Ti_4O_7 anode. They observed that high current density and/or PFAS concentration during EC generated foam, facilitating the separation of PFAS from the bulk fluid, especially the long-chain ones [52]. However, further study is needed to design cheaper electrodes that restrict toxic byproduct generation and to find the ideal operational parameters to minimise the formation of hazardous byproducts. Also, more studies that mirror low conductivity and PFAS concentration, as well as the incidence of inorganic ions and NOM, ought to be carried out to examine their impact on electrochemical oxidation performance prior to promoting it for the industrial scale [41].

Electro-Fenton is another electrochemical treatment technique that has broadly been investigated, which likewise relies on hydroxyl radical's oxidative ability. The electro-Fenton process is an 'indirect oxidation' approach, unlike electrochemical oxidation, which employs a 'non-active' anode like BDD and SnO_2 electrodes. Wang et al. [24] used electro-Fenton and electrochemical anodic oxidation to increase PFOA treatment efficiency. To accomplish, they created a novel cathode employing iron/manganese-doped carbon (Fe/Mn-C) and used the BDD anode. The hybrid process removed almost all PFOA (97%) in 4 hours. This unique process also reduced TOC by 93%, showing that PFOA was mainly mineralised to fluorine and carbon dioxide. The EF/EO system effectively integrates two advanced oxidation processes that share the same source of electrical energy [55]. It can enhance converting electrical energy into chemical energy by using both the cathode and anode to form reactive radicals at the same time [55]. Hydrogen peroxide, the primary reagent for creating reactive radicals, can be produced spontaneously in this hybrid process, and finally, the conventional electrooxidation configurations can be employed for this purpose as well, with just few adjustments needed regarding cathode material [55].

Partial mineralisation of pollutants can occur during chemical oxidation owing to the development of hazardous intermediates and byproducts. This increases operational expenses due to treatment time or byproduct handling. UV irradiation (natural sunshine or UV lamps) has facilitated easing this matter by accelerating oxidation reactions between free radicals and pollutants, mineralising substances [56]. It can degrade pollutants directly (photolysis) or indirectly (photochemical oxidation) [57]. In the former, pollutants are converted by UV absorption, whereas in the latter, they interact with produced reactive species [24]. Due to their chemical nature, PFAS do not absorb light at wavelengths >220 nm [58]. It is proved that 190 nm (VUV) is needed for effective homolysis of C – F fluorinated compounds [59]. Giri et al. demonstrated PFAS elimination by 185 nm photolysis [60]. $\text{S}_2\text{O}_8^{2-}$, Fe^{3+} , TiO_2 , CO_3^{2-} , heteropolyacid photocatalyst ($\text{H}_3\text{PW}_{12}\text{O}_{40}$), and IO_4^- can breakdown PFAS when paired with UV >220 nm [61]. Reactive and strong molecules such as OH^- , CO_3^{2-} , H, and PFAS-Fe complexes cause this phenomenon. Photochemical degradation of PFAS depends on the source of light (UV or VUV), pH, initial PFAS content, utilised reagent, and temperature [62,63].

Giri et al. [64] removed nearly all PFOA from ultrapure water using 185 nm and 254 nm radiation. Cao et al. [65] studied the degrading of PFOA in aqueous periodate (IO_4^-) under UV (254 nm), and VUV (254 nm and 185 nm) light, and it was observed that VUV irradiation reduced PFOA more effectively than solo UV irradiation. UV irradiation created IO_3^- , which oxidised PFOA when periodate was added [65]. In a study, researchers found efficacious degradation of PFCAs with UV/TiO₂ method at a pH of 3.0 and observed that the rate constant was 46 times larger than in the basic environment [66]. Tang et al. [67] removed PFOA with a UV-Fenton method, but the combination of hydrogen peroxide and UV and also the solo Fenton processes were not fruitful in this regard. Wang et al. [25] achieved 80.2% degradation using Fe^{3+} under 254 nm UV radiation. Zhang et al. [68] studied PFOA photodegradation at different temperatures and observed that increasing temperature under UV irradiation led to higher removal efficiency. They suggested that acidic pH increased PFAS ionisation and believed that heated TiO₂ photo-holes oxidised PFCAs. In another study [69], UV/Pb – TiO₂ system was used to degrade PFOA, and it proposed that Low PFOA degradation without any defluorination was attributable to F adsorption on the TiO₂ surface. Improved PFOA degradation was associated with higher adsorption on the catalyst surface. The modified catalyst collected photo-induced electrons, preventing electron recombination and enhancing degrading efficiency [69,70].

In a recent work conducted by Barisci and Suri [71], the removal of polyfluorinated telomer alcohol was conducted by UV photolysis, UV/H₂O₂, solar irradiation with and without H₂O₂, ozonation, and O₃/H₂O₂, and it was observed that UV photolysis, solar irradiation, UV/H₂O₂, and solar irradiation/H₂O₂ processes were able to remove the contaminant almost completely. When hydrogen peroxide was added to UV processes, the defluorination ratio, as well as the reaction time, were decreased, which was reported to be disadvantageous when added to the ozonation process because of the scavenging effect of hydrogen peroxide. They concluded that the solo ozone process (with the highest defluorination rate) and UV/H₂O₂ were the best methods for the degradation of TFHFSE [71]. Hori et al. [62] assessed the PFOA direct photolysis by both UV radiation (220–460 nm) and UV/H₂O₂. Photochemical oxidation revealed practically complete PFOA abatement with increasing irradiation time, whereas adding hydrogen peroxide exhibited limited PFOA removal [62]. Other investigations have shown successful PFOA degradation using UV/noble metallic nanoparticles modified-TiO₂ [68], UV/transition metal oxidised-TiO₂ [69], and UV/TiO₂-reduced graphene oxide [70]. Overall, degradation rates are poor in comparison with other treatment methods since the photochemical method is largely reliant on hydroxyl radical oxidation, which is almost ineffective in PFAS degradation [71].

Although in a very recent study, it is declared that AOPs are not always effective at treating perfluoroalkyl compounds, and more importantly, field information on their influence on unidentified PFAS precursors through groundwater treatment is lacking [26]. The fate of PFAS in seven pilot-scale AOPs was investigated at four drinking water systems (UV/H₂O₂, O₃/H₂O₂, UV/TiO₂, and UV/Cl₂) in New York State in the United States of America. Seven of 18 PFAS were below 64 ng/L in the influent. The concentration of all identified PFAS increased after AOP treatment, likely due to precursor transformation. The rise in PFAS concentration was reliant on UV and oxidant dose, approving that conversion processes were happening because of AOPs. At one location, PFOA levels surpassed the New York State drinking water threshold of 10 ng/L afterwards treatment but not beforehand, illustrating the necessity of evaluating the influence of AOP on the quality of treated

water when planning treatment structures for issues of compliance. They observed that increased PFAS levels in AOP systems interacted positively with levels of nitrate in groundwater, proposing septic discharges on the spot could be a cause of PFAS pollution in these zones. Researchers suggested that while hydroxyl radical-based AOPs are inefficient for the treatment of PFAS, they can show the true degree of PFAS pollution in source waters. Their work underlined the urgency to undertake TOP or comparable assays to identify the true degree of PFAS pollution, which will enable water purveyors to develop appropriate treatment schemes to fulfill PFAS standards and govern public health [26].

3. Sulfate radical-based advanced oxidation processes

Most of the research into free radicals for PFAS removal has been conducted on activated persulphate, which can remove different contaminants in groundwater, such as pharmaceuticals [67], pesticides [72], herbicides [73], PFAS [74], and chlorinated solvents [75]. Persulphate ($S_2O_8^{2-}$) is a powerful oxidant by means of a redox potential of 2.01 V that degrades pollutants via activation through free radicals or direct electron transfer [76]. To create free radicals in-situ, various ways have been utilised to activate persulphate, most notably chemical or heat activation. Persulphate produces sulphate radicals (2.6 V) and hydroxyl radicals (2.7 V) when activated [76]. Because of the interaction of sulphate radicals with chloride, hydroxyl radical is the dominant substance in real applications [77]. As a result, most sulphate radicals in normal, natural waters generate hydroxyl radicals [78], which are rarely able to decompose PFAS [58]. It should be noted that in an alkaline environment, the sulphate radical is generated more than the hydroxyl radical. For the activation, either energy or catalysts can be employed. Heat, UV, or ultrasonic can be used as energy sources [79]. Among the various activating processes available, the chemical reaction between the carbon precursor and an alkaline hydroxide (such as NaOH or KOH) yields the most effective activation results for preparing activated carbon of transition metals, non-metals such as carbonaceous materials [80]. It has also been stated that SO_4^{2-} may be produced electrochemically from sulphate ions using electrodes such as boron-doped diamond (BDD) [81]. OH^- may also be produced in SR-AOPs at high pH levels by the reaction of hydroxyl ions with SO_4^{2-} [82].

Park et al. [78] tested heat activated persulphate under in-situ groundwater treatment conditions for the oxidation of PFOA, 6:2 fluorotelomer sulphonate (6:2 FTSA), and PFOS. According to their findings, PFOA oxidation obeyed the unzipping breakdown pathway (chain depolymerisation) of PFCAs to fluoride and shorter chain length molecules, whereas 6:2 FTSA was oxidised to PFHxA and PFHpA. Even at greater temperatures, there was no modification of PFOS. Pollutants such as BTEX (Benzene, Toluene, Ethylbenzene, and xylene) did not appear to have any impact on the rates of PFOA decomposition. Other researchers found an analogous formation of degrading intermediates, confirming the successive loss of units of CF_2 [83]. However, at very high temperatures, the sulphate radicals were vigorously scavenged, while an acidic pH inhibited PFOA breakdown, which can be because of the fact that at these conditions (low pH and/or high temperature), radicals tend to react with other radicals rather than contaminants [28,84,85].

The generated hydroxyl radical inhibits the reaction between PFOA and sulphate radicals because its rate constant is higher [86–88]. Yin et al. [29] found that at low pH, activated persulphate oxidised PFOA in groundwater and also that raising persulphate

dosage, temperature, and duration improved degradation performance. Defluorination effectiveness dropped at pH > 5.0, suggesting sulphate free radicals were more effective in PFOA breakdown than hydroxyl radicals. They also discovered that hydrochloric acid reduced the defluorination ratio in comparison with sulphuric acid. This can be due to the reaction between sulphate radicals and chloride, which creates ineffective hydroxyl radicals [29]. Lee et al. [89] investigated PFOA degradation utilising a microwave-activated persulphate method. At pH 2.5, PFOA was degraded effectively, although alkaline pH and chloride ions slowed the pace due to scavenging sulphate radicals. They also studied PFOA degradation at lower temperatures (20°C – 40°C) and observed satisfactory defluorination and nearly full PFOA decomposition at acidic pH and raised persulphate content. In another study, almost 100% PFAS and PFOA degradation utilising microwave-hydro-thermal persulphate technique was reported [86]. Furthermore, the combination of potassium persulphate and sodium hydroxide was tested for the decomposition of per- and polyfluoroalkyl ether acids for validating a full oxidizable precursor assay and showed a substantial result [87]. The reaction blend remained for 6 hours at 85°C and pH greater than 12, converting persulphate ($S_2O_8^{2-}$) to sulphate radical ($SO_4^{\cdot-}$) at higher temperatures, and these radicals quickly react to create hydroxyl radicals at larger pH levels [90].

Lutze et al. [74] demonstrated that sulphate radicals broke down PFCAs, whereas PFAS persisted in resisting the attack of sulphate radicals in their most current work on the mechanistic decomposition of PFAS utilising UV/ $S_2O_8^{2-}$ method. According to the results, the reaction kinetics of PFCAs were not dependent on C-F chain length, and the decomposition trail featured an unzipping reaction in which more than one unit of CF_2 was transformed to F^- and CO_2 per each attack of the radicals. The scientists discovered that the effectiveness of the UV/ $S_2O_8^{2-}$ the combination was reduced in the existence of solutes like bicarbonate, chloride, and organic matter, which exist in real water, resulting in a great energy requirement for PFCA destruction [74]. In another study, adding persulphate to the combination of ozonation and catalyst for degradation of 18 analysed PFAS improved removal rates dramatically, as can be seen in Figure 6 [88].

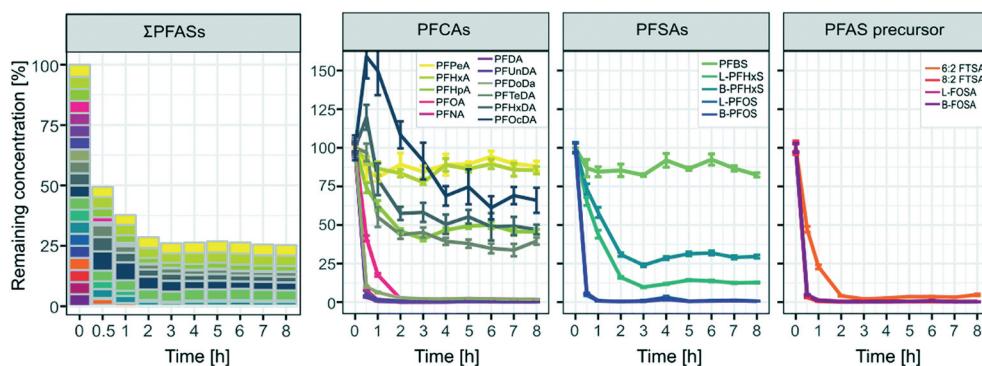


Figure 6. Concentrations of all spiking PFAS that remained [%] over time in the pilot-scale ozonation experiment. The values were calculated using the mean concentrations of duplicate samples taken at each time point. The error bars represent the mean deviation from the mean of the duplicate samples. All computations were standardized to quantities obtained in samples taken at 0 h, immediately before introducing ozone into the system. Reproduced with permission from ref [88]. Copyright 2010 Taylor & Francis.

Based on studies, PFOS does not disintegrate through oxidation by persulphate oxidation [91,92]. Yang et al. [27], on the other hand, showed PFOS oxidative defluorination by persulphate that was activated hydrothermally. Raising the persulphate dose enhanced the defluorination of PFOS; however, after a certain threshold, the growth in the persulphate dose had little influence. As oxidation intermediates, PFAS with carbon chain length numbers ranging from 0 to 6 were discovered. PFBS and PFHxS were measured at low concentrations and continued to be consistent throughout the reaction period, which was suggested to be because of $\text{CF}_3(\text{CF}_2)_5^-$ and $\text{CF}_3(\text{CF}_2)_3^-$ recombination with a set of SO_3^- . It is also worth noting that environmental matrices like chloride and carbonate can decrease the efficacy of the process of activated persulphate.

4. Main mechanisms involved in PFAS degradation by AOPs

Advanced oxidation processes are famous methods for the elimination of numerous organic pollutants in groundwater, including chlorinated solvents and new toxins like petroleum hydrocarbon soil and 1, 4- dioxane. As previously stated, oxidation of hydroxyl radicals is insufficient to break C-F bonds in PFAS, despite the fact that frequent oxidative reagents, like ozone, hydrogen peroxide, peroxide/ozone, sodium persulphate, and peroxide/permanganate, have been investigated for their potential decomposition [89]. Hydrogen peroxide, either used alone or combined with Fenton's reagent (iron (II), Fe^{2+}) as well as UV light, produces hydroxyl radicals that have been used in water and wastewater treatment for the oxidation of organic contaminants [90]. In general, Fenton's reagent performs better around pH 3–4 because H_2O_2 and Fe^{2+} are more soluble in acidic conditions than at pH 7 [90]. If hydrogen atoms are present in an organic compound, excellent electron-withdrawing groups, hydroxyl radicals, can easily react with them, resulting in the production of water ($E_0 = 2.7 \text{ V}$). PFAS, on the other hand, are devoid of any accessible hydrogen atoms. As a result, oxidation methods relying only on hydroxyl radicals are insufficient to break C-F bonds in PFAS. Nevertheless, when other radicals like superoxide radical anion and per hydroxyl radicals are joined with hydroxyl radicals, they have a synergistic impact that leads to PFAS breakdown [91].

As the potential mechanisms are summarised in Figure 7, the oxidative degradation mechanism for PFAS comprises a consistent degradation pathway independent of the method used or the free radicals' source. The electron transfer route proceeds through the breaking of the C-C bonds between the COOH group and PFCAs (decarboxylation) or the C-S bonds among the SO_3^- group and PFAS (desulfonation) to create perfluoroalkyl radicals ($\text{C}_n\text{F}_{2n+1}\cdot$) that are unstable [27,92,93]. It should be noted that PFAS breakdown proceeds in electrochemical oxidation by direct electron transfer from the sulphonate (SO_3^-) or carboxyl (COO^-) group to the anode surface [30]. The subsequent unstable perfluoroalkyl radicals combine with water to generate hydroxyl radicals, which then results in forming alcohol that is thermally unstable ($\text{C}_n\text{F}_{2n+1}\text{OH}$). Then, hydrogen fluoride is eliminated from the alcohol to generate $\text{C}_{n-1}\text{F}_{2n-1}\text{COF}$; a hydrolysed form of PFAS without a CF_2 unit. Before the full mineralisation to CO_2 , SO_4^{2-} , and F^- , the shorter chain PFAS proceeds to go through this sequence of reactions (stepwise breakdown by the removal of CF_2 units) [94,95].

Even though other researchers have suggested alternative PFAS breakdown mechanisms involving activated photochemical oxidation, persulphate, and electrochemical oxidation [96,97]. They predicted that the produced perfluoroalkyl radicals would react with

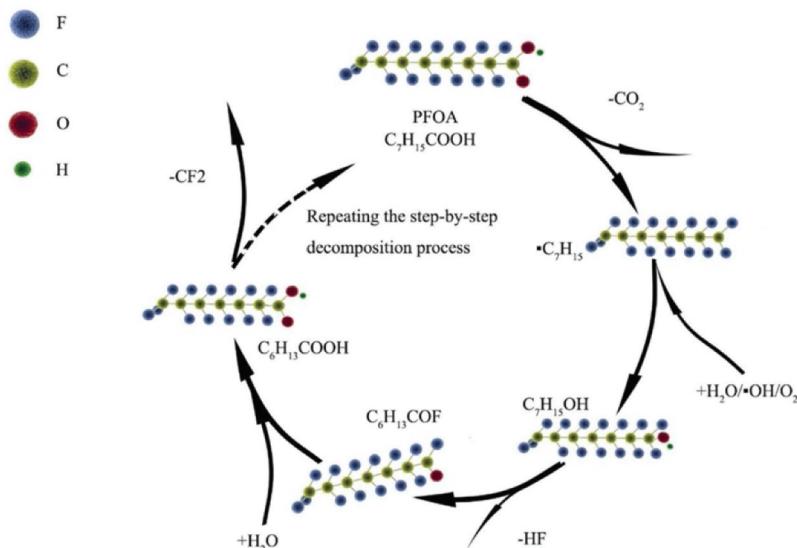


Figure 7. The oxidative degradation pathway of PFAS and mechanisms involved.

molecular oxygen produced by the electrolysis of water, yielding a radical of perfluoroperoxy. When one perfluoroperoxy radical interacts with the other one, a perfluoroalkoxy radical is formed, which subsequently combines with additional radicals to generate perfluorinated alcohols, and then the previously described set of events (degrading step wisely) occurs. In the UV-Fenton system, a PFAS-iron complex may emerge before decarboxylation or desulfonation, releasing a perfluoroalkyl radical [98,99] (Figure 8).

According to Zhuo et al. [100], during electro-oxidation of 6:2 FTSA, its carbon to carbon (C-C) bond or carbon to hydrogen (C-H) bond combines with hydroxyl radicals, creating $C_6F_{13}COO^-$, which subsequently experiences the CF_2 disengaging PFAS breakdown process. The majority of investigations have proposed a pseudo-first-order model for the kinetics of PFAS electrochemical oxidation [100]. Regardless of the mechanism, the oxidative techniques all follow the equivalent pattern of degrading to shorter chain molecules.

According to the recent research conducted by Zeidabadi et al. [101], a possible pathway was proposed for PFOA degradation (Figure 9). The results revealed that in the primary transformation of PFOA with SO_4^{2-} contribution, the oxidation is initiated by an electron transfer from the carboxyl head group to the surface of the anode and/or SO_4^{2-} to form the highly reactive PFCA radical. This radical undergoes Kolbe decarboxylation and produces perfluoroalkyl radical ($C_7F_{15}^{\cdot}$). $C_7F_{15}^{\cdot}$ then follows three reaction pathways, which include at first, the reaction of $C_7F_{15}^{\cdot}$ with $\cdot OH$. This reaction produces an unstable alcohol, $C_7F_{15}OH$, which undergoes hydrolysis and release of HF to form the shorter chain PFCA. Further, $C_7F_{15}H$ undergoes hydrolysis by $C_7F_{15}^{\cdot}$ to form $C_6F_{13}COO^-$ with subsequent reactions with $\cdot OH$ and release of HF. The $C_6F_{13}COO^-$ produced further degrades to shorter chain PFCAs in a similar pathway. Finally, the produced $C_7F_{15}^{\cdot}$ may react with oxygen produced from water electrolysis to form the perfluoroalkyl peroxy radical ($C_7F_{15}OO^{\cdot}$).

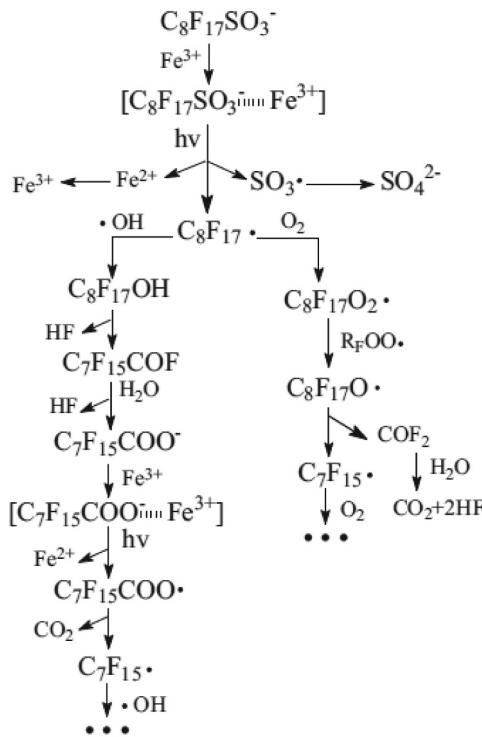


Figure 8. The suggested pathway for PFOS degradation by UV with the addition of ferric ion. Reproduced with permission from ref [27]. Copyright © 2013 Public Library of Science.

5. Health and environmental risk assessment of PFAS

Toxicology and bioaccumulation of PFAS have been extensively investigated; nevertheless, the toxicity of the mixtures of PFAS as they occur in the environment is still ambiguous [102,103]. Since they stand as the most commonly utilised arrangements and unchanging final products of other PFAS precursors, perfluorooctanoic acid (PFOA) and perfluorooctane sulphonic acid (PFOS) are the most frequently investigated PFAS [104].

In areas where pollution from a point source is alarming, PFAS impacts on animal and plant health have been investigated. Kwak et al. [105] revealed that *V. radiata* and *O. sativa* grow fewer roots in PFOA-contaminated soil. Nematode reproduction rates dropped after 1 day in soils contaminated with PFOA (equal to or above 300 mg/kg dry soil) in comparison with the soil without PFOA. The existence of above 600 mg/kg PFOA in dry soil diminished the number of earthworms [105]. Lettuce exposed to 500 and 5000 ng/L PFOA and PFOS for 28 days was tested for phytotoxicity [106], and it was observed that PFOA accumulated 4.0–4.3 times more than PFOS. At 500 and 5000 ng/L PFOA and PFOS exposure, a metabolomics investigation found significant alterations in the carbon energy metabolome. The citric acid cycle, decarboxylate, glyoxylate, and pyruvate pathways affected carbon metabolism. The existence of PFOA stressed the amino acid metabolome, while PFOS altered linoleic acid metabolism. PFOA and PFOS exposure triggered four plant defence mechanisms. 8-Hydroxy-

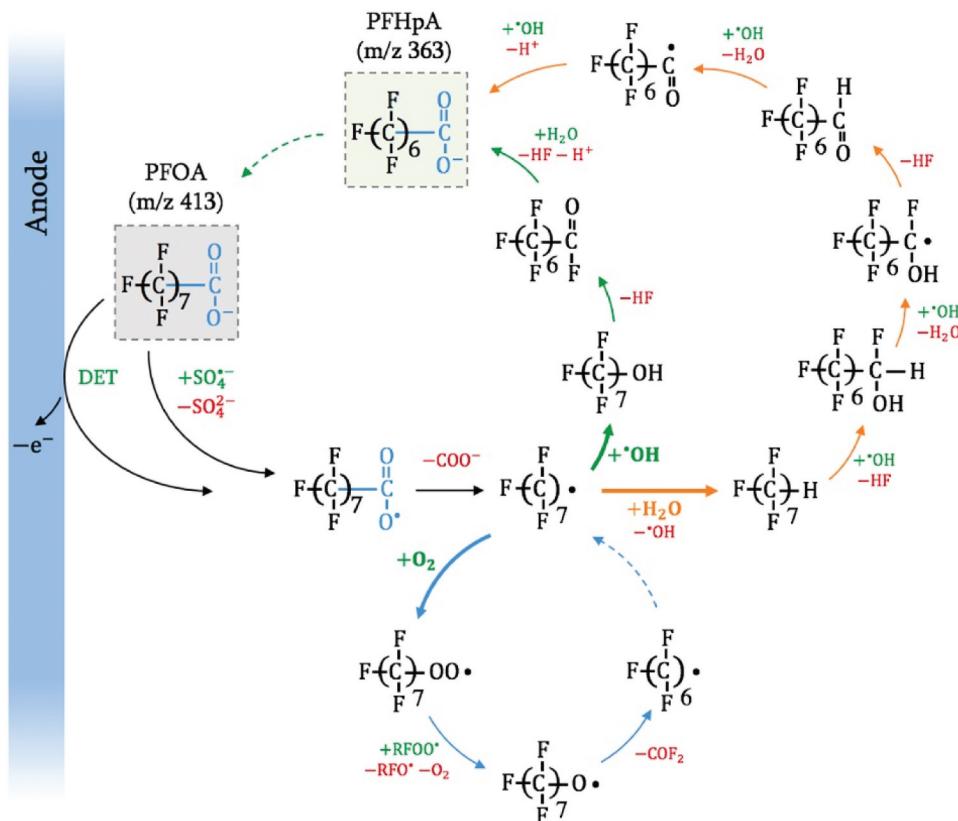


Figure 9. Mechanism of PFOA degradation through oxidation by sulfate radicals. Reproduced with permission from ref [101]. Copyright © 2023 Elsevier Ltd.

deoxyguanosine, a biomarker for oxidative DNA damage, was significantly elevated by PFOA and PFOS exposure, 2.0–4.1-fold above the control. The applied metabolomics methodology offered multiple cases of the effects of PFAS pollution on plants that would not have been completely noticed if only phenotypic alterations or biomass had been investigated. This study's modest PFAS exposure levels did not affect lettuce development [107]. After incubation with PFOS-polluted soil, the distributions of PFOS in water, pore water, sediment, suspended particulate matter, and three benthic species were investigated [108]. The benthic invertebrates accumulated 2% of the total PFOS mass, while up to 80% were retained in sediment. Bioturbation by *C. kiiensis* did not affect the redistribution of PFOS, whereas *H. azteca* and *L. hoffmeisteri* did, which showed that benthic creatures like the latter could change the bioavailability of PFAS in soils [109].

The influence of PFAS on flora and fauna has also been analysed. Metabolomics was applied to compare difluoro [2,2,4,5-tetrafluoro-5-(trifluoromethoxy)-1,3-dioxolan-4-yl]oxyacetic acid (C_6O_4) and PFOA on *Ruditapes philippinarum* clams [110]. Both pollutants reduced haemocyte count and size. The alternative PFAS induced haemocyte and gill biomarker variations and DNA damage at lower doses than PFOA [111]. Also, sodium p-perfluorous nonenoxybenzene sulphate (OBS) and 6:2

chlorinated polyfluorinated ether sulphonate were contrasted to PFOS in zebrafish embryos at 1 M [112]. PFOS exposure has a greater influence on zebrafish oxidative liver stress than 6:2 Cl-PFESA and OBS. All three PFAS were examined regarding disrupted gut microbiota, anti-inflammatory, and immune-related gene expression [102]. Early mouse and rat PFAS exposure investigations indicated liver, spleen, and other organ damage. Since PFAS have been converted to PFAS, determining their side effects on organisms is crucial. PFAS impairs protein function, according to these findings [113]. Augmented reactive oxygen species (ROS) at cellular and suppression of superoxide dismutase contribute to nephrocyte death. PFDA's hydrogen bonding actions on Cu/Zn-SOD caused morphological alterations and lowered enzymatic activity, which increased oxidative stress. Hexafluoropropylene oxide trimer acid (HFPO-TA), another PFAS alternative, was tested on male mouse liver mitochondrial function and biogenesis [114]. Following the exposure of mouse liver to HFPO-TA spiked drinking water (2, 20, and 200 g/L) for 6 weeks, metabolomics, genomics, histological examination, and transmission electron microscopy were performed. HFPO-TA affected liver weight, cell shape, and inflammation. After 200 g/L HFPO-TA exposure, mitochondrial RNA and DNA linked to division and fusion increased. HFPO-TA is utilised instead of PFOA and has been found in surface waters, which is alarming because this study suggests it can affect liver functionality and cause liver cancer [114]. These animal studies on PFAS toxicity can also inform data on human investigations.

Long-term investigations have indicated potentially negative health consequences of PFAS [115], and research into its human health implications has directed to growing concern and legislation in nations. Several major, continuous biomonitoring investigations are also now underway, most remarkably Nutrition Examination and the National Health Survey run by the Centers for Disease Control and Prevention in the United States [116]. Several decades of research have yielded significant discoveries, including proof of PFAS in the blood serum of chemical labourers, which was discovered in the 1980s [117]. Because PFAS are water-soluble, they react differently in the human body than many other organic contaminants. They, for instance, have a significant proclivity to interact with serum and tissue proteins like albumin, which may contribute to their existence in the liver, kidneys, and blood [118]. Longitudinal human research has revealed that PFAS causes changes in kidney and thyroid function [119]. Several epidemiological investigations undertaken in recent years have shown potential consequences such as endocrine disruption, cancer, immunotoxicity, and metabolic disturbance [120]. PFAS goes into the human body through drinking water because of its high solubility. Longer exposure to PFAS compounds increases risk due to omnipresent absorption and high dosages [111]. PFAS toxicity and the threshold values at which they constitute a severe health concern are poorly understood. Moreover, this link lacks an interpretation of the relationship between PFAS exposure and effect, as no precise information can describe the impact's durability, frequency, and intensity. While the guidelines share agreement on using human health as a framework for any governing values, there looks to be a substantial disparity in defining uniform PFAS standards since the PFAS level and rate are variables within one nation and throughout the world [120]. These divergences originate from variances in PFAS sources, toxicological judgements, and exposure amounts, where PFAS compounds can change from one to the other and transit with sediment and water far

from the source, producing spatial and temporal dissimilarity. This review suggests the need for more studies to establish the features, fate, severity, and treatment of PFAS in future works.

6. Conclusions and future prospects

The present knowledge state of advanced oxidation processes for PFAS remediation was covered in this review paper. The effectiveness of PFAS abatement in water and wastewater was observed to differ across multiple reaction variables, including initial PFAS content and other operational factors. Because of these variables, comparing the competence of each method is difficult. However, overall, electrochemical oxidation performed better than Fenton-based processes (Fenton, electro-Fenton, and photo-Fenton), photochemical oxidation, ozonation, hydrogen peroxide addition, and activated persulphate for PFAS removal on the basis of initial PFAS concentration and reduction extent. Experimental scale investigations have demonstrated that PFCA, PFAS, and polyfluorinated compounds can be successfully eliminated by electrochemical oxidation, even though the application and wider industrial use it is restricted because of energy consumption, the expense of producing efficient electrodes, and harmful by-products. The combination of electrochemical oxidation and electro-Fenton is recommended for future works targeting PFAS degradation since it can be conducted with minor changes in the cathode while using the same energy source. Also, the drawbacks of both processes can be overcome by the usage of the hybrid process. Photochemical oxidation is moderately efficient for PFOA but inadequate for PFOS removal. Moreover, photochemical oxidation relies heavily on hydroxyl radical oxidation, which is unsuccessful in PFAS breakdown. Furthermore, the incidence of scavengers that eat hydroxyl radicals frequently competes with pollutants, and as most actual water systems include these elements, achieving reasonable efficiency with photochemical oxidation is usually difficult. However, there is still a lot to do in this scope as hydroxyl radical based-AOPs have not always been successful in the degradation of PFAS. Regarding the persulphate method, it has been shown to be effective in the elimination of PFOA (PFCAs), but not PFOS (PFAS) since the sulphonate group is substantially less electron-dense than the carboxylic group, making PFOS resilient to oxidation by sulphate free radicals. Persulphate systems create radicals that can alter polyfluorinated compounds (precursors) into PFCAs, making cleanup easier. Degradation of PFOA often requires increased concentrations of persulphate, elevated temperatures, or the introduction of acidic or basic conditions.

Recommendations for future works are as follows:

- More PFAS classes must be studied for their environmental and human toxicity, as well as the effectiveness of removal and treatment methods.
- Many AOPs that have been explored for PFAS removal have been conducted on the lab scale rather than in actual wastewater treatment plants. Commercial-scale wastewater treatment systems should be the focus of future research.
- More study is required to identify PFAS decomposition by-products and their toxicity.

- New AOPs should be developed that do not require significant volumes of chemicals (such as electrochemical oxidation) and have minimal operation and installation costs.
- Degrading PFAS necessitates the development of new photocatalysts or electrode materials.
- To properly remove and degrade PFAS, a hybrid system comprising AOPs and other treatment methods can be used.
- There should be more research about PFAS degradation by novel Fenton processes, including bi-Fenton, electro-Fenton, or photo/solar-electro-Fenton techniques.
- Combining two or more advanced oxidation processes, especially when UV is applied, can be fruitful for the removal of PFAS.

Overall, PFAS removal effectiveness in the aqueous phase varies with reaction parameters such as initial PFAS content, environmental matrix, and other process variables. These factors make comparing technological efficiency difficult.

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