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Recent advances on PFAS degradation *via* thermal and nonthermal methods

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Abstract

Per- and polyfluoroalkyl substances (PFAS) are a set of synthetic chemicals which contain several carbon-fluorine (C–F) bonds and have been in production for the past eight decades. PFAS have been used in several industrial and consumer products including nonstick pans, food packaging, firefighting foams, and carpeting. PFAS require proper investigations worldwide due to their omnipresence in the biotic environment and the resulting pollution to drinking water sources. These harmful chemicals have been associated with adverse health effects such as liver damage, cancer, low fertility, hormone subjugation, and thyroid illness. In addition, these fluorinated compounds show high chemical, thermal, biological, hydrolytic, photochemical, and oxidative stability. Therefore, effective treatment processes are required for the removal and degradation of PFAS from wastewater, drinking water, and groundwater. Previous review papers have provided excellent summaries on PFAS treatment technologies, but the focus has been on the elimination efficiency without providing mechanistic understanding of removal/degradation pathways. The present review summarizes a comprehensive examination of various thermal and non-thermal PFAS destruction technologies. It includes sonochemical/ultrasound degradation, microwave hydrothermal treatment, subcritical or supercritical treatment, electrical discharge plasma technology, thermal destruction methods/incinerations, low/high-temperature thermal desorption process, vapor energy generator (VEG) technology and mechanochemical destruction. The background, degradation mechanisms/pathways, and advances of each remediation process are discussed in detail in this review.

Keywords

PFAS; Thermal degradation; Nonthermal degradation; Incineration; Mineralization

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Declaration of Competing Interest
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1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are synthetic compounds with unique properties including high chemical and thermal stability, making them resistant to degradation and oxidation [1]. Since the 1940s, PFAS have been utilized in numerous consumer products, industrial applications, and aqueous film-forming foam deliveries operated for aerial firefighting [2,3]. The carbon-fluorine (C-F) bond in PFAS is thermodynamically robust and provides persistence, inertness, and stability to the perfluorinated molecule [4]. Therefore, PFAS are not readily biodegradable. These chemicals can enter the water cycle either via point sources (e.g., industrial, and municipal wastewater treatment plant sewage, industrial facilities, and firefighting training sites) or through atmospheric accumulation or nonpoint causes (e.g., groundwater and drainage penetration) (Fig. 1) [5,6]. Humans can be exposed to PFAS by consuming contaminated water and food, which can cause adverse health effects including thyroid disease, liver damage, and cancer [7]. The existence of perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) in groundwater have raised concerns including developmental effects to the fetus during pregnancy or nursing, liver effects, cancer, thyroid effects, and immune effects [8]. In response, the U.S. Environmental Protection Agency (U.S. EPA) has specified a new health advisory level of 0.02 ppt (ng/L) and 0.004 ppt for PFOS and PFOA in drinking water, respectively [9]. However, several water bodies near airports, military, and industrial sites exceed the U.S. EPA level [10,11].

Due to the persistence and documented toxic effects of PFAS, their elimination from water and wastewater is critical [12]. Various review articles have focused on PFAS occurrence, fate, transport, and treatment using various in-situ and ex-situ processes [5,6,11,13–19].The elimination of PFAS via adsorption, nanofiltration (NF) and reverse osmosis (RO), biological degradation, thermal degradation, photolysis, electrolysis, chemical oxidation, and reduction have been studied [14, 15,19]. PFAS treatment via adsorption has been studied using granular activated carbon (GAC), powdered activated carbon (PAC), anion exchange (AIX), molecularly imprinted polymers (MIP) and biocompatible materials [20]. Upon the different adsorbents, AIX has shown promise with achieving the highest adsorption capacity [21,22]. Yet, AIX is a costly process limiting its large-scale application. More importantly, adsorption processes require secondary treatment (i.e., regeneration of adsorbent) and waste management (i.e., disposal of spent adsorbent). Membrane separation processes including NF and RO have also shown promise in removing a wide range of PFAS, but their wider implementation is hampered by membrane fouling and high energy requirements [23]. Compared to physiochemical processes, the biological degradation of PFAS is challenged by the persistence of the C-F bond and the high negativity in F^- [18]. From a technological perspective, advanced oxidation processes (e.g., chemical oxidation and reduction) have been successful in the complete mineralization of PFAS [24]. However, operational and technological requirements (e.g., slow reaction rates) have limited their large-scale application.

This review examines the literature for promising PFAS thermal and nonthermal treatment technologies including sonochemical/ultrasound degradation, microwave hydrothermal treatment, subcritical or supercritical treatment, electrical discharge plasma technology, thermal destruction methods/incinerations, low/high-temperature thermal desorption process, and vapor energy generator (VEG) technology.

2. Sonochemical/ultrasound degradation

In water treatment, sonochemistry involves the use of acoustic field to generate radicals to degrade contaminants in various aqueous media [25]. More specifically, acoustic cavitation (i.e., bubbles collapsing in solution due to sound waves) causes high temperature and pressure conditions resulting in the pyrolytic degradation of pollutants including PFAS at the bubble-water phase [13]. Most sonochemical studies for chemical pollutants' degradation in aqueous media have been conducted at lab-scale (i.e., small volume) using ultrasonic irradiation at ambient pressures and temperatures [26–28]. In sonolysis, ultrasonic irradiation creates pressure waves generating small cavities in the aqueous medium [29,30]. More specifically, the soundwaves (i.e., sonowaves) induce localized areas of low- and high-pressure forming vapor bubbles (i.e., cavitation) that continue to grow and finally collapse causing a high temperature and pressure condition [31]. In these bubbles, the average internal vapor temperature increases to 4000 K, while bubble-water interface temperatures are generally between 600 K and 1000 K [32,33]. These momentary high temperatures assist in the *in-situ* pyrolysis of water into hydrogen atoms (H), oxygen atoms (O), and hydroxyl radicals (•OH) in the interfacial and vapor regions of each collapsing bubble [16]. The resulting radicals react quickly with organic molecules at the bubble interface or in the bubble interior gas-phase [34].

Ultrasonic dissociation has also been shown to help eliminate pollutants with high Henry's Law constants that separate into the vapor phase or those pollutants that exist in the air-water interface [35,36]. Table 1 lists a variety of sonochemical treatment technologies that have been investigated for PFAS, primarily PFOA and PFOS. Moriwaki et al. investigated the sonolysis of PFOA (C_0=10 ppm) and PFOS (C_0=10 ppm) under an argon and oxygen atmosphere [37]. Under an argon atmosphere, this process showed promising results with pseudo-first-order rate constants of 0.16 and 0.32 min^{-1} for PFOS and PFOA, respectively. Liquid chromatography-mass spectroscopy (LC/MS) analysis revealed that most of the PFOS and PFOA molecules were decomposed at the interfacial area between the bulk solution and the cavitation bubbles [37]. In another study, the sonochemical degradation of groundwater beneath a landfill containing PFOA, PFOS, volatile organic compounds (VOCs), and dissolved organic matter (DOM) was explored. With organic components present, the sonolytic dissociation rate of PFOA and PFOS was reduced due to the competitive sorption at the bubble-water interface. However, the incorporation of ozonation with ultrasound increased the mineralization of PFOA and PFOS in landfill groundwater treatment [38]. Vecitis et al. also investigated sonolysis degradation of PFOA and PFOS in an aqueous solution. Their technology was determined to be effective for the complete mineralization of PFAS, ranging from 10 nM to 10 μM into carbon dioxide, carbon monoxide, fluoride, and sulfate [39]. The combination of the dual-transducer arrangement of ultrasonic and mega-sonic frequencies was also utilized for the dissociation of aqueous film-forming foam (AFFF) in bulk [40,41]. The presence of sulfate or bicarbonate ions diminished the sonolysis process, but perchlorate or nitrate present in solution increased the mineralization rate of PFAS under ultrasonic irradiation [42]. Additionally, the effect of co-surfactants such as anionic surfactant (e.g., sodium dodecyl sulfate (SDS)), non-ionic surfactant (e.g., octyl phenol ethoxylate (Triton X-110)) and cationic surfactant (e.g., hexadecyltrimethylammonium bromide (CTAB)) in the treatment of PFOA under ultrasonic irradiation was investigated [43]. CTAB enhanced the mineralization of PFOA at a lower pH, while SDS and Triton X-100 decreased the degree of degradation of PFOA. When a reaction mixture of PFOA (120 μM) and CTAB (0.12 mM) was treated under ultrasonic irradiation for 2 h at pH 4, 79% dissociation of PFOA was observed. Vecitis et al. studied the mineralization of PFOS in an aqueous dilution of FC-600 (an AFFF formulation) [44]. FC-600 is an AFFF formulation consisting of a mixture of hydrocarbon (HC) and fluorochemical components with co-solvents, anionic hydrocarbon surfactants, fluorinated amphiphilic surfactants, anionic fluorinated surfactants, and thickeners such as starch. PFOS was mineralized sonolytically in the scale of FC-600 aqueous dilutions, 65 ppb<[PFOS]<13100 ppb [44]. The degradation rate of the PFOS-AFFF system was found to be identical to PFOS-Milli-Q under the sonochemical condition. These studies showed that, initially, pyrolytic breakage of the carbon-sulfur (C-S) bond of PFOS occurred at the bubble-water interface [44]. Panchangam and his research group reported oxidative photodegradation of PFOA using TiO_2 as a photocatalyst under sonication. This combination of photocatalyst and ultrasonic irradiation showed 65–70% degradation of PFOA (C_0=50 ppm) within 7 h in relatively mild conditions such as ambient temperature and pressure and almost neutral pH [45].

In summary, PFOA and PFOS can be sonochemically degraded *via* pyrolytic reactions at the water-bubble interface. Sonolytic PFAS mineralization is highly effective at a bench scale. However, PFAS treatment under sonication at a large scale has not been studied yet. Additionally, the proper optimization of parameters such as frequency and power should be considered in PFAS mineralization *via* sonication. Furthermore, the co-existence of other organic chemicals (e.g., humic substances) and inorganic chemicals (e.g., bicarbonate, sulfate) could also affect the sonochemical PFAS degradation. However, the integration of other techniques such as vacuum UV light irradiation, adsorption to sonochemical methods may enhance mineralization performance and support in reducing power requirements. For example, Zhao and his research group developed a combined technique of granular activated carbon (GAC) and ultrasound to treat PFAS effectively. The ultrasonic effect increased the adsorption of PFOS (C_0=50 ppm) on GAC from 2.5 to 9 times [48]. Yang et al. also studied the combination of vacuum UV and ultrasonic irradiation for the mineralization of PFOS (10 ppm). This combined technology offered improved treatment of PFAS compared to sonolysis alone [49].

3. Microwave hydrothermal treatment

Microwave-hydrothermal processes have been widely used for their cost-effectiveness in preparing composite materials [50–52]. This process consumes up to 50% less energy and yields higher mineralization rates than conventional hydrothermal treatment methods [26,52,53]. Lee et al. investigated microwave-hydrothermal mineralization of PFOA in the presence of persulfate ($S_2O_8^{2-}$) as an oxidant in the water at various temperatures: 60 °C, 90 °C, and 130 °C [54]. Table 2 summarizes the typical conditions and PFOA removal of various microwave hydrothermal treatment technologies. Persulfate generates active sulfate radicals ($SO_4^{\bullet -}$) with high redox potential (2.6 V) and can degrade most organic pollutants (Eq. 1) [54–56]. PFOA was dissociated to non-measurable levels at 60 °C after 6 h of reaction. Microwave-hydrothermal treatment at higher temperatures increases the PFOA degradation rate. However, at exceedingly high temperatures such as 130 °C, persulfate generates a substantial number of active radicals that further react with residual persulfate (Eqs. 3 and 4), resulting in lower PFOA dissociation. The pH of solutions also affects the dissociation of PFOA. Solutions with higher pH have a slower reaction (Eq. 2) due to the formation of fewer active •OH radicals by the reaction of active sulfate radicals with ^{-}OH (Eq. 2). Hori et al. proposed the PFOA mineralization mechanism (Eqs. 5–(9). In this mechanism, sulfate-free radicals (from Eq. 1) oxidize PFOA ($C_7F_{15}COOH$) via hydrogen atom abstraction to form into the equivalent cationic radical *i.e.* $[C_7F_{15}COOH]^{\bullet +}$ (Eq. 5) which further generates an unstable perfluorinated alkyl radical $^{\bullet}C_7F_{15}$ (Eq. 6) [57]. This alkyl radical reacts with water to generate an unstable perfluorinated alcohol ($C_7F_{15}OH$; Eq. 7) and transforms into $C_6F_{13}COF$ and HF (Eq. 8) [58]. Further, $C_6F_{13}COF$ converts into perfluoroheptanoic acid (PFHpA, $C_6F_{13}COOH$; Eq. 9) *via* hydrolysis [59]. Other perfluorinated acids, such as perfluorohexanoic acid (PFHeA), perfluoropentanoic acid (PFPeA), and perfluorobutyric acid (PFBA), are observed by sequential oxidation of additional CF_2 unit. At the end of the process, sulfate radicals completely mineralize the PFCAs into carbon dioxide (CO_2) and fluoride (F^-) [60].

$$S_2O_8^{2-} + \text{Heat} \rightarrow 2SO_4^{\bullet -} \tag{1}$$

$$SO_4^{\bullet -} + {}^{-}OH \rightarrow 2SO_4^{2-} + {}^{\bullet}OH \tag{2}$$

$$SO_4^{\bullet -} + SO_4^{\bullet -} \rightarrow S_2O_8^{2-} \tag{3}$$

$$SO_4^{\bullet\,-} + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_{8^-} \tag{4}$$

$$SO_4{\bullet}^{-} + C_7\,F_{15}COOH \rightarrow SO_4^{2-} + C_7\,F_{15}COOH^{+} \tag{5}$$

$$C_7\,F_{15}COOH^{\bullet +} \rightarrow {}^{\bullet}\,C_7\,F_{15} + CO_2 + H^{+} \tag{6}$$

$$C_7F_{15} + H_2O \rightarrow C_7\,F_{15}OH + H \tag{7}$$

$$C_7F_{15}OH \rightarrow C_6\,F_{13}COF + F^{-} + H^{+} \tag{8}$$

$$C_6F_{13}COF + H_2O \rightarrow C_6\,F_{13}COOH + F^{-} + H^{+} \tag{9}$$

A lab-scale approach of zero-valent iron (ZVI) and 5 Mm persulfate was examined for the microwave-hydrothermal degradation of PFOA at 60 °C and 90 °C [61]. This approach resulted in 67.6% decomposition of PFOA into short-chain PFCA and fluoride ions. ZVI not only degraded PFOA, but also generated Fe^{2+} (ferrous) ions under both anaerobic and aerobic conditions (Eqs. 10 and 11) [61,62]. These Fe^{2+} ions lower the activation energy of persulfate by generating sulfate free radicals at lower reaction temperature (Eq. 12). The synergetic effect of ZVI and persulfate increased the mineralization of PFOA and reduced the reaction time. Juxtaposing with conventional hydrothermal treatments, the microwave-hydrothermal method with ZVI and persulfate is quicker and a more energy-saving process for the degradation of perfluorinated carboxylic acids. However, scalability remains to be an obstacle of microwave-induced processes due to limited radiation depth and heat loss.

$$\mathrm{Fe}^{0} + 1/2\mathrm{O}_2 + \mathrm{H}_2\mathrm{O} \rightarrow \mathrm{Fe}^{2+} + 2\mathrm{OH}^{-} \qquad (10)$$

$$\mathrm{Fe}^{0} + 2\mathrm{H}_2\mathrm{O} \rightarrow \mathrm{Fe}^{2+} + 2\mathrm{OH}^{-} + \mathrm{H}_2 \qquad (11)$$

$$\mathrm{Fe}^{2+} + \mathrm{S}_2\mathrm{O}_8^{2-} \rightarrow \mathrm{Fe}^{3+} + \mathrm{SO}_4^{\bullet\,-\,-} + \mathrm{SO}_4^{2-} \qquad (12)$$

4. Subcritical or supercritical treatment

Subcritical or supercritical water treatments are eco-friendly and sustainable processes. Supercritical water occurs at temperatures >374 °C and at pressures >22.1 MPa. Alternatively, subcritical water is liquid water under pressure at temperatures between the boiling point, 100 °C, and 350 °C [63–65]. Previous studies have focused on hazardous waste destruction using subcritical and supercritical water [57,66–68]. Hori et al. examined the decomposition of PFOS and other short-chain (C2-C6) PFAS such as nonafluorobutanesulfonate, pentafluoroethanesulfonate, heptafluoropropanesulfonate, and perfluorohexanesulfonate in subcritical water [69]. They also studied the degradation of PFAS in the presence of metals including Al, Cu, Fe, and Zn powder in subcritical water [69]. PFOS showed minimal degradation in pure subcritical water, but the introduction of metal powder increased the PFOS mineralization in increasing order from no-metal ≈Al<Cu <Zn<<Fe (Table 3). The presence of iron supported the most effective PFOS dissociation. On the other hand, the order of redox potential over the series is Cu<Fe<Zn<Al. From these results, Hori et al. concluded that the metal surface and surface area play a greater role than its respective redox potential in the mineralization of PFOS. This phenomenon is applicable for ZVI and fluorinated species (PFOS) adsorbed on the iron surface even at room temperature. The adsorbed PFOS was then degraded into fluoride ions when the temperature was increased above 250°C. When the mixture of iron metal and an aqueous solution of PFOS (93–372 μM) was heated at 350°C for six hours, 46.2–51.4% PFOS degradation was obtained. This technique transformed PFOS into fluoride ions without any PFCA detection, though a small amount of fluoroform (CHF_3) was observed [60]. Similar conditions were utilized for the elimination of perfluorohexanesulfonate (PFHS), an organic pollutant. In pure subcritical water at 350°C, little decomposition of PFHS was observed. On the other hand, in pure supercritical water at 380°C, it degraded into sulfate and fluoride ions. However, the incorporation of ZVI into the reaction process enhanced the degrdation of PFHS significantly [70]. Inspired by these studies, degradation of Nafion NRE-212, a

model perfluorinated ion-exchange membrane applied for fuel cells, was explored in sub- and supercritical water in the presence of metal. The membrane demonstrated minimal decomposition in pure subcritical water, but the introduction of zero-valent metal enhanced the degradation of the membrane in the following order of Al< no metal<Zn<Cu<<Fe. When the mixture of membrane and ZVI were heated under the supercritical condition at 350°C for 17 h, 73.2% of the fluorine content of the membrane was converted into fluoride ions, and other intermediates including CF_3COOH, $HCF(CF_3)OC_2F_4SO_3$, CO_2, and HCF_3 [71]. Hori et al. also investigated the mineralization of perfluorinated ionic liquid anions such as $[(CF_3SO_2)_2N]^-$ and $[(C_4F_9SO_2)_2N]^-$ in subcritical and supercritical water to better understand the retrieval of the fluorine component. Similarly, the presence of ZVI enhanced the dissociation of perfluorinated ionic liquid anions. The mixture of $[(CF_3SO_2)_2N]^-$ and ZVI yielded 69% fluoride ions at 344°C in six hours of reaction. This yield was 186 times higher than the yield without iron. Also, when the reaction time was increased to 18 h and the temperature was increased to 375°C, $[(CF_3SO_2)_2N]^-$ converted 76.8% of the fluorine content into F^- in the presence of ZVI [72].

Overall, sub- or supercritical treatment technology for PFAS mineralization could be an effective process for future applications. However, for industrial applications, additional studies at a large scale are required. Additionally, new methods should focus on improving the system design for low corrosion and salt build up.

5. Electrical discharge plasma technology

Plasma is a moderately or entirely ionized gas formed by electrical discharge [74,75]. It contains free neutrons, electrons, free radicals, ions, and atoms in heightened energy states. In terms of temperature and electron density, plasma systems can be characterized into two groups: nonthermal plasma process and thermal plasma process [76–79]. The nonthermal plasma process is associated with less power (i.e., dielectric barrier discharge, corona discharge, spark discharge, gliding arc discharge, and glow discharge). In the nonthermal generation process, energetic electrons collide with the oxygen (O_2), nitrogen (N_2), water (H_2O) molecules and generate secondary electrons, ions, radicals, and photons [80–82]. Generation of plasma through thermal processes (typically torches or radiofrequency, arc discharge) is characterized by increased energy and plasma elements in thermal equilibrium [83–85]. High energy ions in plasma continuously degrade the carbon chains of PFAS [86]. Yasuoka et al. explored the decomposition of PFOA and PFOS in different plasmas using direct-current plasma produced within small gas bubbles in a solution [87]. The energy efficiency and degradation rate were estimated by determining the sulfate and fluoride ions isolated from PFOS/PFOA. The energy efficiency and concentration of F-ions in the PFOS were 26 mg kWh^{-1} and 17.7 mg/L, respectively, after 4 h of reaction [87]. Additionally, formic acid was introduced as a scavenger of hydrated electrons (e^-_{aq}) and phosphoric acid as a scavenger of hydroxyl radicals (•OH), but these demonstrated little effect on mineralization [87]. Another research group investigated PFOA decomposition using two processes: plasma treatment and sulfate radical anion treatment, where PFOA mineralized into carbon dioxide *via* interfacial reaction with the plasma [88].

Based on liquid chromatography-mass spectrometry studies, these authors proposed a PFOA decomposition scheme, as shown in Fig. 2 [88]. Firstly, PFOA acts as a surfactant and adsorbs to the gas-liquid interface during plasma treatment. Then, the sequential thermal cleavage of the PFOA carbon-carbon bonds occurs on the carbon chain edge, resulting in the generation of fluorocarbon radicals in the bubbles [88]. Further, fluorocarbon radicals react with plasma-produced H and •OH radicals and transform into CO, CO_2, and HF *via* a redox reaction. Due to the high solubility of hydrogen fluoride gas, only carbon monoxide and carbon dioxide are released as the concluding products [88]. Another study explored the connection between the adsorbed amount of perfluorocarboxylic acids (PFCA) and the degree of dissociation by a direct-current plasma. The quantity of PFCA adsorbed at the gas-liquid interface increased for longer carbon chains, which subsequently improved the rate of mineralization [89]. Later, the same research group also investigated the complete degradation of PFOA (C_0=41.4 ppm) and PFOS (C_0=60 ppm) within oxygen bubbles by DC plasma after 3 h and 8 h of operation, respectively [90]. From LC/MS studies, the authors proposed plausible degradation pathways of PFOA (Eqs. 13–18) and PFOS (Eqs. 19–22) using DC plasma [90]. Initially, plasma-generated high-energy ions join with negatively charged ions of PFCAs on the surface of contaminated water. This process produces an electron and an unstable carboxyl radical (Eq. 13) [90]. Then, carbon dioxide and fluorocarbon radicals are formed *via* decarboxylation reaction (Eq. 14). The unstable fluorocarbon radical instantly reacts with water, and the carbon chain decreases by one, yielding PFCAs. In one study, Zhang et al. investigated the carbon-carbon bonds of PFOA cleaved by high energy vacuum ultraviolet light (184nm) [37]. Similarly, in this process, C-C bonds of higher energy ions could be broken (Eqs. 13–22) [90].

$$\mathrm{C_nF_{2n+1}COO^- + M^+ \rightarrow C_nF_{2n+1}COO^\bullet + M^+ + e^-} \tag{13}$$

$$\mathrm{C_nF_{2n+1}COO^\bullet \rightarrow{}^\bullet C_nF_{2n+1} + CO_2} \tag{14}$$

$$\mathrm{\bullet C_nF_{2n+1} + 2H_2O \rightarrow C_{n-1}\,F_{2n-1}COO^- + 3H^+ + 2\,F^- + H^\bullet} \tag{15}$$

$$\mathrm{C_7\,F_{15}COO^- + 2M^+ \rightarrow{}^\bullet CF_3 + \;\bullet C_6H_{12} + COO^- + 2M^+} \tag{16}$$

$$\mathrm{\bullet CF_3 +{}^\bullet COO^- \rightarrow CF_3COO^-} \tag{17}$$

$$\mathrm{\bullet C_7\,F_{12} + 2H_2O \rightarrow C_5\,F_{11}COO^- + 2H^+ + F^- + 2H^\bullet} \tag{18}$$

$$\mathrm{C_8\,F_{17}SO_3^- + M^+ \rightarrow{}^\bullet C_8\,F_{17}SO_3 + M^+ + e^-} \tag{19}$$

$$\mathrm{\bullet C_8\,F_{17}SO_3 \rightarrow{}^\bullet C_8\,F_{17} +{}^\bullet SO_3} \tag{20}$$

$$\bullet C_8F_{17} + 2H_2O \rightarrow C_7F_{15}COO^- + 3H^+ + 2F^- + H^\bullet \tag{21}$$

$$\bullet SO_3 + H_2O \rightarrow 2H^+ + SO_4^{2-} \tag{22}$$

Singh and his research group used ultra-performance liquid chromatograph-quadrupole time-of-flight-high resolution mass spectrometry (UPLC-QTOF-HRMS) analysis to identify the by-products of PFAS mineralization by a plasma treatment process [91]. Based on their studies and the by-products quantified in the liquid phase, they proposed a mineralization mechanism for PFOA and PFOS (Fig. 3). Firstly, plasma-generated reactive species such as aqueous electrons, plasma electrons, and argon ions attack the carboxylic functional group (−COOH) of PFOA and generate unstable perfluoroalkyl radicals ($^\bullet C_7F_{15}$) [91]. This unstable $^\bullet C_7F_{15}$ radical reacts with $^\bullet OH$ and converts into thermally unstable perfluoro alcohols ($C_7F_{15}OH$), which further transform into $C_6F_{13}COF$ and HF by the attack of e_{aq}^-. The water reacts with $C_6F_{13}COF$ and yields $C_6F_{13}COOH$ and HF molecules. Therefore, chain propagation reactions, including oxidative and reductive species following hydrolysis, yield short chain perfluorinated carboxylic acid (PFCA). The mineralization pathway of PFOS seems to resemble that of PFOA. In the chain initiation reaction of PFOS, reactive species attack PFOS and form $^\bullet C_8F_{17}$ radicals by the cleavage of C-S bond [91]. Further, chain propagation reactions of $^\bullet C_8F_{17}$ lead to the generation of short-chain PFCA. The team identified 43 and 35 novel by-products of PFOA and PFOS, respectively, based on accurate mass measurements and isotopic profile [91].

Marouf-Khelifa et al. used TiO_2 to catalyze the nonthermal process (NTP), Glidarc, for the degradation of perfluorinated non-ionic surfactant, Forafac 1110 (C_6F_{13}-$C_2H_4(OC_2H_4)_{11.5}OH$) in aqueous solution [92]. Glidarc is characterized by the generation of an electric arc between two electrodes in a gaseous atmosphere. Reactive species such as NO• and •OH radicals are generated when the Glidarc is introduced to humid air plasma. Then, the NO• radical converts into NO_2, NO_2^- and NO_3^-. These NO species show acidic properties and acidify the reaction, while hydroxyl radicals act as strong oxidizing agents to make Glidarc a robust oxidizer for the decomposition of PFAS [92]. The combination of heterogeneous catalysis (TiO_2) with plasma-chemical treatment gave 96% mineralization of Forafac in one hour. Alternatively, six hours were required to accomplish the same degradation without the TiO_2 catalyst [92].

$$H_2O + e^- \rightarrow {}^\bullet OH + H^\bullet + e^- \tag{23}$$

$$N_2 + e^- \rightarrow N(^4S) + N(^2D) + e^- \tag{24}$$

$$N(^2D) + O_2 \rightarrow NO^\bullet + O \tag{25}$$

$$NO^\bullet + {}^\bullet OH \rightarrow NO_2 + H^\bullet \tag{26}$$

$$NO_2 + HO_2^{\bullet} \rightarrow HNO_2 + O_2 \tag{27}$$

$$HNO_2 + HO^{\bullet} \rightarrow HNO_3 + H_2O \tag{28}$$

Recently, nonthermal atmospheric plasma (NTAP) technology has been studied for the degradation of low concentrations (1 μg/L) of PFAS (mainly PFOA and PFOS) from polluted water samples taken from the soil cleaning process. The NTAP process can degrade 50% of the initial PFAS concentration in less than 200 s, and it can be utilized as an alternative tactic for the mineralization of PFAS [93].

Thus, plasma-based technologies are very efficient in the elimination of PFAS from both drinking water and groundwater. However, the co-existence of organic and inorganic contaminants affects the performance of plasma treatment processes. The assessment of by-products during plasma treatment should be considered for its practicability.

6. Thermal destruction (Incineration)

Incineration is a well-known mineralization pathway for the removal of harmful compounds, mostly toxic organic molecules, using heat [94–96]. Incineration is an energy intensive process, where high temperatures ranging from 600°C to 1000°C are applied to destroy harmful compounds [97,98]. Yet, there is an environmental tradeoff, where gaseous toxic substances can be released into the surrounding environment. Yamada et al. studied the thermal dissociation of a polyester/cellulose fabric substrate treated with a fluorotelomer-based acrylic polymer under conditions similar to a medical waste incinerator (MWI) and municipal waste combustor (MWC) processes in the US [99]. Thermal experiments were performed at non-flame reactor temperature ranging from 600°C to 1000°C. In this process, no detectible amount of PFOA was found using in-line gas chromatography/mass spectrometry (GC/MS). Hence, the burning of these wastes was not thought to be a source of PFOA to the environment [99]. Similarly, the kinetics of thermal degradation of ammonium perfluorooctanoate (APFO) were studied using high-temperature gas-phase nuclear magnetic resonance spectroscopy. However, in this process, volatile and toxic by-products such as 1-H-perfluoroheptane were observed [100]. Therefore, the burning of PFAS and foreign wastes was shown to release toxic substances including furan and dioxins [101,102].

In one study, the combustion of PFOS yielded greenhouse gases such as tetrafluoromethane (CF_4) and hexafluoroethane (C_2F_6) [99]. These greenhouse gases show global warming potentials of 5,700 and 11,900, with long lifetimes of 50,000 and 10,000 years, respectively [103]. The fixation of these toxic by-products can be accomplished using certain additives such as calcium hydroxide [103].

The incineration approach was also utilized to evaluate the fate of PFAS during thermal regeneration of GAC [104,105]. PFOA, PFOS, and PFHxA adsorbed GAC were thermally treated in the nitrogen gas stream [104]. Volatile organic fluorine (VOF) measured 13.2, 5.9, and 4.8% for PFOA, PFOS, and PFHxA, respectively, at 700°C. However, VOF diminished to 0.1% at a higher temperature (1000°C). During reactivation of GAC *via* thermal regeneration, no PFAS were observed in GAC in the temperature range from 700 to 1000°C. Similarly, Xiao and his research group examined the thermal decomposition mechanism of seven perfluoroalkyl carboxylic acids (PFCA), three perfluoroalkyl sulfonic acids (PFSA), and one perfluoroalkyl ether carboxylic acid (PFECA) in different atmospheres (N_2, O_2, CO_2, and air) on spent granular activated carbon (GAC) during thermal reactivation [106]. The proposed thermal decomposition pathways of PFOA based on the organic fluorine species identified by a thermal desorption-pyrolysis system (CDS Analytical) coupled to a gas chromatograph with an MS detector (TD-Pyr-GC-MS) are shown in Fig. 4 [106].

Furthermore, PFAS have been detected in wastewater treatment plant effluent, influent and biosolids worldwide [107]. In one investigation on US biosolids, the major PFAS in biosolids were observed PFOA (34 ± 22 ppm dry weight) and PFOS (403 ± 127 ng/g dry weight) [108]. Research on the potential of pyrolysis and gasification processes to destroy PFAS in biosolids are extremely limited. Recently, in one study, >90% of PFOA and PFOS was safely removed from the biosolids via pyrolysis at the temperature range of 500°C - 600°C as part of a biochar generation process [109].

Ongoing investigations are currently exploring the thermal decomposition of PFAS, including catalytic destruction of PFAS at high temperatures [110]. Thermal treatment for PFAS elimination is under examination at the bench scale in Dandenong South, Victoria. Australia [111]. The environmental impact of incineration and thermal destruction methods for soils includes earth-moving equipment, transporting polluted soil, and storage in landfill. Incineration of contaminated soil is energy extensive. PFAS emissions and by-products from incinerators are currently not well understood. Therefore, further investigations are required to understand better the significance and viability of incineration in PFAS treatment and its generated by-products [111].

7. Low/high-temperature thermal desorption

Besides conventional thermal treatment (e.g., incineration), thermal desorption has been employed to heat contaminated soil *ex situ* or *in* situ, where the vaporized contaminants partition to the air phase. This thermal treatment process would require a polishing step with air filters to remove the vaporized contaminants. Thermal desorption process has been utilized extensively to treat soils contaminated with pesticides with comparable physicochemical properties to perfluorinated compounds [17,112]. Compared to incineration, this technique is less energy intensive and can still achieve high removal for most organic contaminants. For thermal desorption of PFAS, excavated soil has been treated at 500°C to 600°C in a rotary kiln to release PFAS into the gas stream [18, 113,114]. Then, PFAS have been mineralized at >1000°C via catalytic oxidation in the afterburner. The thermal desorption process looks to be a potential tactic for treatment of PFAS-contaminated soils. However, large scale studies have not been conducted on at PFAS specifically. At present, experimental information related to polyfluorinated precursor remediation is not available [18]. Also, for the thermal desorption process assessment, the mobilization cost of large rotary kilns and accompanying treatment rates should be measured. In another approach of thermal desorption, thermopiles have also been utilized. In this process, excavated soil is placed into shielded piles. These covered piles are heated in the range of 500°C-600°C using heater rods or diesel/gas burner to release PFAS into the vapor stream. These covered thermopiles are then secured under vacuum to extricate vapors and further subjected to condensers or thermal oxidizers to mineralize PFAS [18]. However, this method does not seem practical for PFAS mineralization, as the temperature of the soil should be kept between 500°C and 600°C for several weeks for efficient treatment [17,113].

Due to the high-temperature requirement, the thermal desorption process is expensive and requires a high preliminary investment in set-up.

8. Vapor energy generator (VEG) technology

Vapor energy generator (VEG) technology utilizes steam at 1100°C to degrade PFAS from contaminated soils in a chamber [115,116]. In this process, hydrogen gas is produced by the splitting water (H_2O), and carbon monoxide (CO) is generated from the combustion of the organic fraction of soil. Then, the combination of hydrogen gas and carbon monoxide, which is known as syngas (H_2+CO), burns and provides extra heat to the system. This process has a smaller functioning footprint, lower energy costs, and lesser organizational cost than thermal desorption systems. VEG technology was initially proposed by Endpoint Consulting Inc. for the bench-scale mineralization of PFAS in the soil [19]. Endpoint utilized VEG on spiked soil samples to study the treatment capability at 580°C, 595°C, and 950°C. VEG technology yielded 99% PFAS degradation within 30 min of treatment at 950°C. However, the company endorsed new bench-scale and scale-up tests of the VEG technology to establish the best treatment possibility [19]. The VEG process includes a compressed and high-efficiency steam generator patented by Endpoint Consulting Inc. (South San Francisco, CA). This is an ex-situ thermal desorption and mineralization method. Previously, VEG has been utilized for improved oil recovery for a range of intractable pollutants such as petroleum hydrocarbons, heavy-end oils, polychlorinated biphenyls, pesticides, selected metals (arsenic, zinc, and mercury), and polycyclic aromatic hydrocarbons, with ~45 full-size plants accomplished in the US [116].

To the best our knowledge, VEG’s full-scale application has not been studied precisely regarding PFAS. However, promising small-scale investigations on PFAS mineralization using VEG technology have been performed. VEG technology has been employed at several full-scale programs for non-PFAS toxins.

9. Mechanochemical destruction

Ball milling technology has been explored to treat PFAS-contaminated solid media, such as contaminated soils or residuals from desolvation of concentrated waste streams. The milling process is conducted at modest temperatures and pressures in the presence of co-milling reagents (e.g., potassium hydroxide [117], calcium oxide [118], alumina [119], sodium persulfate, and zero-valent iron [120]). The mechanochemical degradation of PFAS and the rapture of C–F and C–C bonds may be achieved either by amorphization of the crystal structure of PFAS and/or deforming valence bonds and angles under mechanical stress.

Thus, the final milling powders would contain environmentally safe inorganic salts for disposal [120]. The exact destruction pathway is still unclear. Some earlier studies have suggested that PFAS molecules would first undergo decarboxylation or desulfonylation, then a sequential chain-shortening by one CF_2 as each step, which is called the “flake-off” degradation mechanism [118]. However, a recent study has revealed new evidence using carbon and fluorine nuclear magnetic resonance spectroscopic (^{13}C and ^{19}F NMR) that the final milling products does not support the previously assumed pathway [121]. This might be attributed to the extreme conditions of localized high pressure and temperature during ball milling [122], which warrant further investigations to elucidate the destruction mechanisms.

10. Conclusions and future perspectives

PFAS are persistent in the environment due to their exceptional physical and chemical properties, so it is a challenge to eliminate them effectively from various environmental matrices. Significant efforts have focused on degradation of PFAS using thermal and non-thermal approaches. However, many of these techniques are still challenged with high energy consumption, low performance in the presence of competing ions and organic constituents typically present in real environmental matrices, and the generation of greenhouse gases and harmful by-products. In addition, most thermal and nonthermal treatment technologies have been utilized at the lab scale, and their large-scale applications have not been fully investigated precisely for PFAS mineralization.

The research path for future work should be focused on the efficient utilization of PFAS remediation processes in treatment trains. For the cost-efficient treatment of PFAS, combinations of different technologies should be examined in both the lab and large scale. For example, the incorporation of UV light irradiation or adsorption with the sonication process could enhance the elimination efficacy for PFAS and co-contaminants such as natural organic matter and humic acid. Perfluoroalkyl carboxylic acids (PFCAs) could be mineralized through a sodium hydroxide–mediated defluorination pathway. PFCA decarboxylation in polar aprotic solvents Dimethyl sulfoxide (DMSO) produced reactive perfluoroalkyl ion intermediates that degraded to fluoride ions (78 to ~100%) within 24 h [123]. Existing investigations have been restricted to realizing the elimination efficacies of one process under facile conditions. Preferably, the application of various research pathways will eventually deliver different treatment processes to removing PFAS at a reduced cost under practical field conditions.

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Data will be made available on request.

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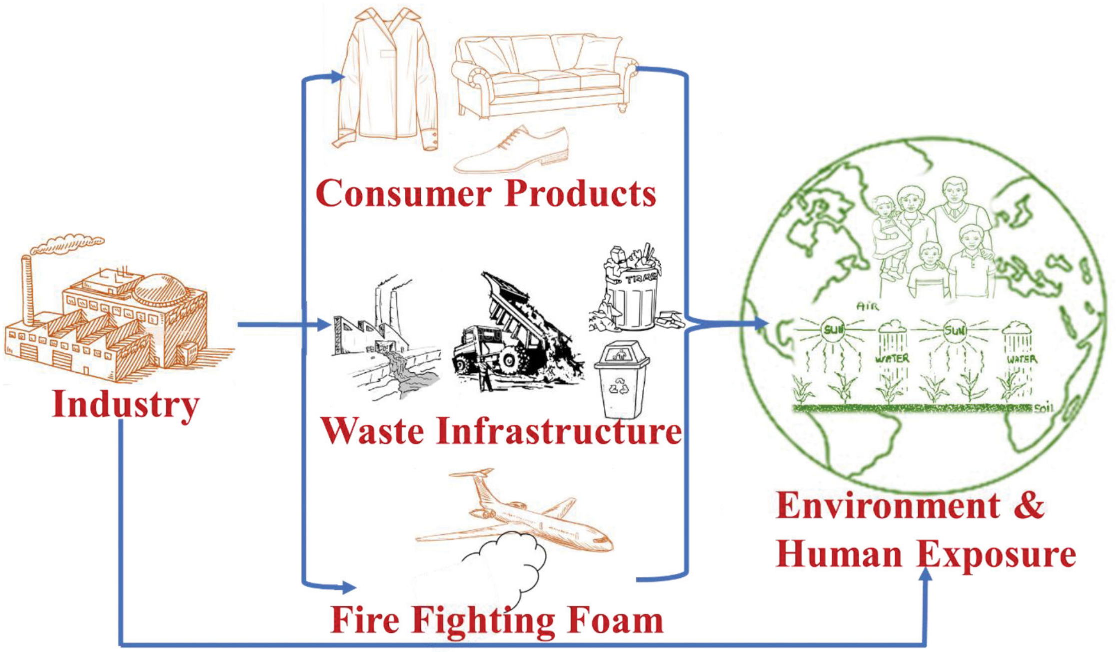

Fig. 1.
Understanding PFAS fate and transport.

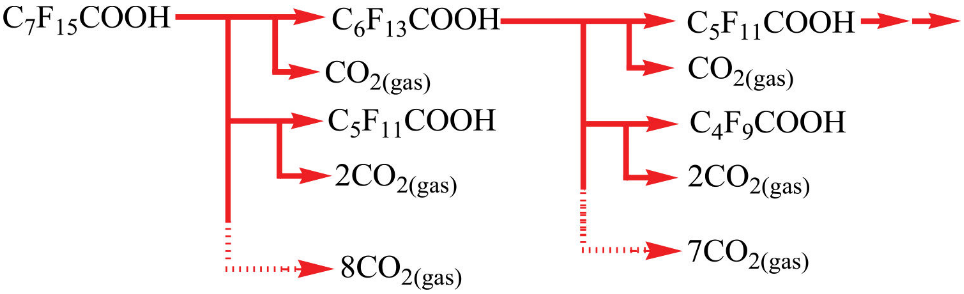

Fig. 2.
Mineralization processes of PFOA [78].

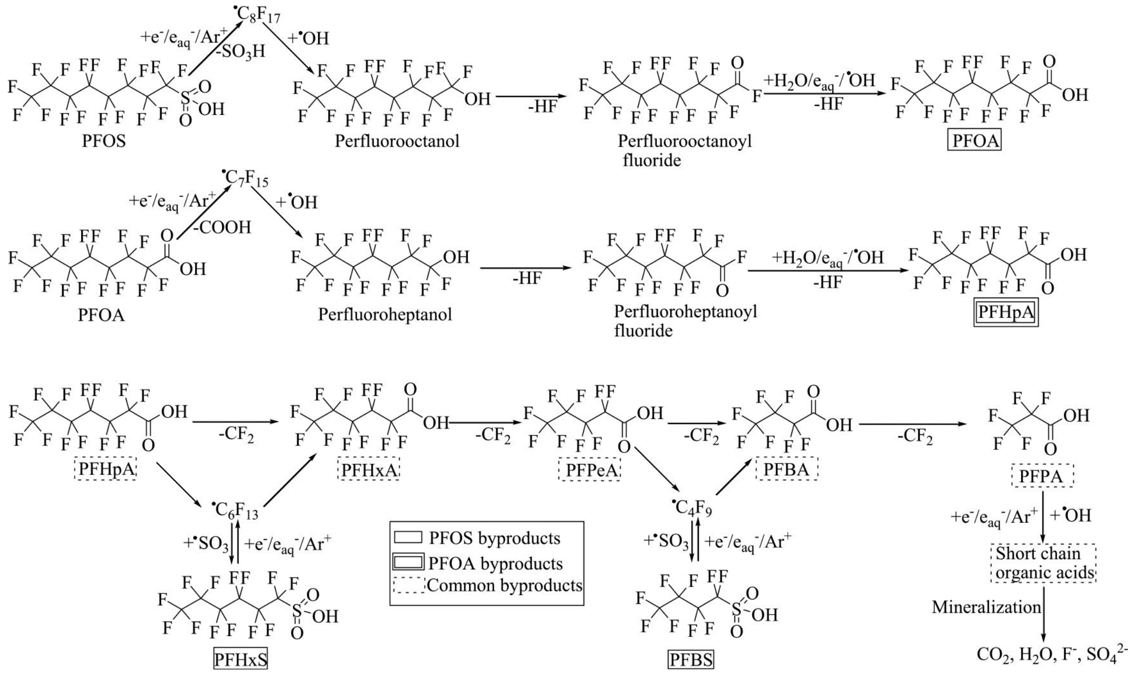

Fig. 3.

Proposed degradation pathway for PFOA and PFOS in plasma treatment [81].

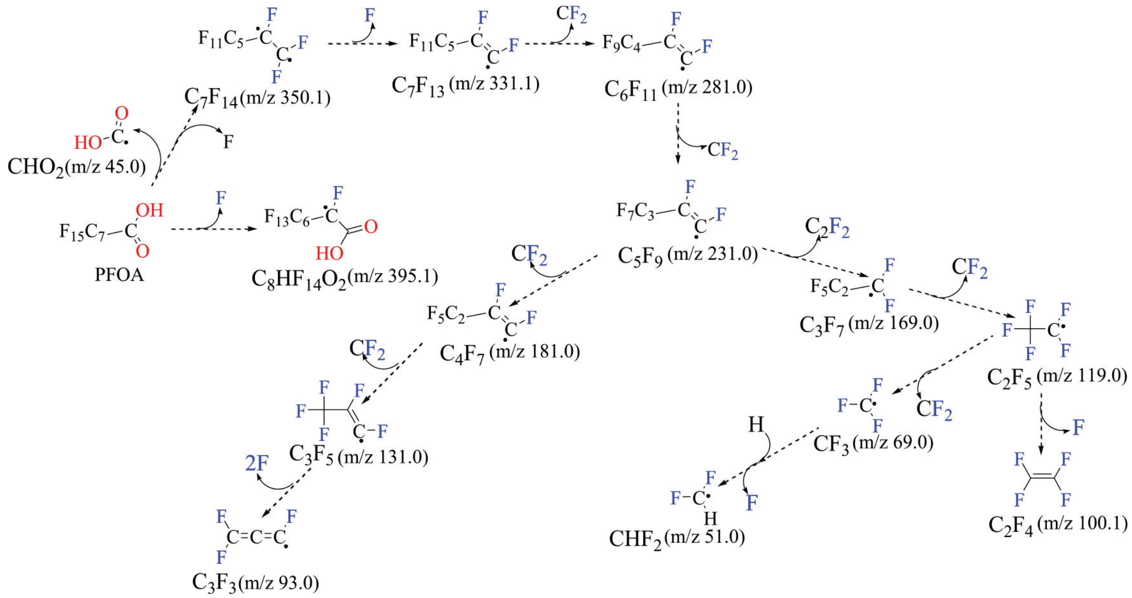

Fig. 4.

Proposed thermal decomposition pathways of PFOA [106].

Table 1

Selected sonochemical PFAS degradation technologies.

Type of solution	Type of PFAS and concentration	Atmosphere	Irradiation time (min), sonolytic frequency (kHz), and power density (W/L or W/cm^2)	Degradation rate constant (min^{-1})	Yield	Ref.
Synthetic	PFOA (C_0 = 10 ppm) and PFOS (C_0 = 10 ppm)	air	60 min	PFOA: 0.0155	63%	[37]
			200 kHz	PFOS: 0.0068	28%	
		argon		PFOA: 0.032	85%	[37]
			200 W/L	PFOS: 0.016	60%	
Landfill/groundwater	PFOA (C_0 = 100 ppb) and PFOS (C_0 = 100 ppb)	argon	120 min	PFOA: 0.021	-	[38]
			354 kHz			
			250 W/L	PFOS: 0.0094		
Synthetic	PFOA (C_0 = 30 ppb) and PFOS (C_0 = 60 ppb)	argon	180 min	PFOA: -	44%	[39]
			358 kHz	PFOS: -	39%	
			250 W/L			
AFFF concentrate	PFOS (C_0 = 65 ppb to 13,000 ppb)	argon	120 min	-	73%	[44]
			505 kHz			
			188 W/L			
Synthetic	PFOA (C_0 = 0.24 μM) and PFOS (C_0 = 0.2 μM)	argon	120 min	PFOA: 0.041	-	[46]
			358 kHz	PFOS: 0.027		
			250 W/L			
Synthetic	PFOS (C_0 = 100 μM)	argon	120 min	F^- release rate of 3.58	-	[40]
			500 kHz	μMmin^{-1}		
			8 W/cm^2			
Synthetic	PFOA (C_0 = 0.24 μM) and PFOS (C_0 = 0.2 μM)	argon	120 min	PFOA: 0.027	-	[47]
			202 kHz	PFOS: 0.013		
			250 W/L			

Table 2

Selected microwave hydrothermal treatment technologies for PFAS degradation.

Type of solution	Type of PFAS and concentration	Conditions (additives, microwave energy and temperature)	Reaction time (hr)	Removal (%)	Defluorination efficiency (F^- %)	Ref.
Synthetic	PFOA (C_0 = 105 ppm)	2.7 g/L $Na_2S_2O_8$ 70 W 90 °C	4 hr	85.7 %	31.5 %	[56]
Synthetic	PFOA (C_0 = 105 ppm)	1.19 g/L $Na_2S_2O_8$ 70 W 90 °C	4 hr	79.1%	70 %	[60]
Synthetic	PFOA (C_0 = 100 ppm)	1.19 g/L $Na_2S_2O_8$ and 0.2 g/L zero-valent iron 70 W 90 °C	2 hr	67.6 %	22.5 %	[61]

Table 3

Selected subcritical/supercritical treatment technologies for PFAS degradation.

Type of solution	Type of PFAS and concentration	Qonditions (additives and temperature)	Reaction time (hr)	Removal (%)	Defluorination efficiency (F^- %)	Ref.
Synthetic	PFOS (C_0 = 186 ppm)	54 g/L Fe 350 °C	6 hr	>99 %	51.4 %	[69]
Synthetic	PFOS (C_0 = 186 ppm)	62 g/L Zn 350 °C	6 hr	77 %	18.5 %	[69]
Synthetic	PFOS (C_0 = 186 ppm)	61 g/L Cu 350 °C	6 hr	15.3 %	6.8 %	[69]
Synthetic	PFOS (C_0 = 186 ppm)	25 g/L A1 350 °C	6 hr	6.4 %	0.05 %	[69]
Synthetic	PFOA (C_0 = 0.83 ppm)	1008 g/L Nitric Acid 50 °C	0.67 hr	80 %	-	[73]
Synthetic	PFOS (C_0 = 0.83 ppm)	1008 g/L Nitric Acid and 20% Methanol 50 °C	0.67 hr	55 %	-	[73]