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The definitive publisher version is available online at <https://doi.org/10.1016/j.psep.2020.01.005>

Advanced treatment technologies efficacies and mechanism of per- and poly-fluoroalkyl substances removal from water

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Abstract

The increasing occurrence of chemically resistant per- and poly-fluoroalkyl substances (PFASs) in the natural environment, animal tissues and even the human body poses a significant health risk. Temporal trend studies on water, sediments, bird, fish, marine mammal and the human show that the exposure of PFAS has significantly increased over the last 20–30 years. Different physical, biological and chemical treatment processes have been investigated for PFAS removal from water. However, there is a lack of detailed understating of the mechanism of removal by different methods, especially by different advanced chemical treatment processes. This article reviews PFASs removal efficacy and mechanism by the advanced chemical treatment methods from aqueous solution. Review shows that several advanced oxidation processes (e.g., electrochemical oxidation, activated persulfate oxidation, photocatalysis, UV-induced oxidation) are successful in degrading PFASs. Moreover, defluorination treatment, some thermal and non-thermal degradation processes are also found to be prominent for the degradation of PFASs with some limitations including process costs over physical treatment (e.g., sorption), production of toxic by-products and greenhouse gases. Finally, knowledge gaps concerning the advanced chemical treatment of PFASs are discussed.

Keywords: PFAS; Advanced oxidation; Reduction; Photocatalysis; Wastewater treatment

1.0 Introduction

Perfluoroalkyl and polyfluoroalkyl substances (PFAS) have a common aliphatic carbon backbone, in which hydrogen atoms have been replaced by fluorine atoms. They are a diverse class of chemicals which have some unique chemical attributes, including extremely high thermal and chemical stability owing to their highly polar and strong carbon-fluorine bonds. PFAS are primarily used in numerous industrial and consumer products such as surfactants, firefighting foams, paints, alkaline cleaners, carpets, non-stick cookware, upholstery, floor polishes, shampoos, fume suppressants, photographic films, semiconductors, food packaging, pesticide formulations, denture cleaners and masking tape.¹⁻³ Low concentrations (ng L^{-1}) of PFAS notably perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), have been found in human tissue and blood serum worldwide.⁴⁻¹²

PFAS occurring in the surface water (i.e. rivers, ponds, lakes and streams) are mainly derived from the discharge of untreated effluents, leakage from the soil, and atmospheric deposition¹³. In China, Liu et al.¹⁴ claimed that 80–90% of PFOA and PFOS contamination was caused by wastewater discharge from manufacturing and industrial effluents into surface water. By investigating the impact of two fluoropolymer manufacturing facilities in France on downstream contamination of a river, Bach et al.¹⁵ found that 14 kg PFOA, 4295 kg perfluorohexanoic acid (PFHxA) and 965 kg perfluorononanoic acid (PFNA) discharged to a river by the two facilities, which can still be detected 15 km downstream from the industrial site. Secondly, the persistent pollutants, especially PFAS, could be condensed in the soil to reach a comparatively high concentration. While in the unsaturated soil, PFAS tend to leach downward during precipitation or irrigation, and this process is a significant driver of PFAS transport from soil to surface water. In Germany, Skutlarek et al.¹⁶ reported that PFOS and PFOA ranged from no detection (n.d.) to 193 ng L^{-1} and n.d. to 3640 ng L^{-1} , respectively, which were transferred from the runoff from the

contaminated soil. Moreover, atmospheric transport can lead to measurable PFAS accumulation in surface water.¹⁷

Table 1 shows the worldwide occurrence of PFAS including PFOA, PFOS, perfluoropentanoic acid (PFPeA) and PFHxA in the surface water from different areas.¹⁸⁻²¹ Concentrations ranging from ng L^{-1} to mg L^{-1} of PFAS have been reported to be present in water samples. Notably, in Bormida River, Italy, the level of PFOA ranged from 253 to 6468 ng L^{-1} , with the mean value of 1613 ng L^{-1} and the median value of 1353 ng L^{-1} , which was higher than the others¹⁷. Also, PFOS was in a lower level compared with PFOA, with a mean value of 48.92 ng L^{-1} (ranging from < method limit of quantification (MLQ) to 150 ng L^{-1} , median at 23 ng L^{-1}) existing in Welland River, Canada and lower concentrations in other places.²² In Bohai Sea of China, PFPeA was in a wide range of <MLQ–16085 ng L^{-1} (mean value of 298 ng L^{-1} and median value of 1.25 ng L^{-1}). Similarly, PFPeA ranged from <MLQ to 150 ng L^{-1} (mean value of 45.78 ng L^{-1} and the median value of 21.5 ng L^{-1}) was reported in Welland River, Canada. Besides, PFHxA ranged from <MLQ to 5103 ng L^{-1} with a mean value of 68.6 ng L^{-1} and a median value of 1.64 ng L^{-1} was detected in Bohai Sea, China. In Welland River, Canada, PFHx varied from <MLQ to 150 ng L^{-1} with the mean value of 29.94 ng L^{-1} and the median value of 16.5 ng L^{-1} . On the other hand, compared with different areas, Songhua River (China) was less contaminated by PFAS as the concentrations of PFOA and PFOS were both below 1.0 ng L^{-1} .²³ In addition, landfill leachate also contributes to the release PFAS to wastewater treatment plants, which was estimated to be between 563 and 638 kg for 2013 in the US alone.

Different advanced treatment processes such as oxidation (with H_2O_2 , Fenton's reagent, Fenton's reagent under UV, iron and heat), UV treatment in combination with iodide, activated persulfate, iron and titanium, aqueous periodate, and subcritical water (350 °C) catalyzed by nanosized zero-valent iron, have all been tested successfully in the laboratory.²⁴⁻²⁹ All of these

methods achieved removal rates ranging from 62% to 100% of PFOS. Conventional oxidation processes were also performed using oxygen-based radicals, but they are not practically viable for the decomposition of perfluorochemicals.³⁰ Other physical separation processes such as filtration processes (nanofiltration, ultrafiltration, microfiltration and reverse osmosis processes) have also been successfully applied for the rejection of PFAS from the aqueous matrix achieving between 67% and >99% removal.³¹⁻³⁷

Other advanced treatment processes, including degradation and photodegradation of PFAS, showed significant results with 100% removal.³⁸ Remediation and treatment of PFOS and PFOA contaminated water are extremely challenging. Although there are many review articles for PFAS fate and remediation, occurrences and different strategies of PFAS remediation, there is no review focused on the degradation mechanisms of PFAS. Also, there is no comprehensive review of comparing the mechanism of PFAS degradation by the different advanced treatment system. Therefore, this paper provides a critical review of the state-of-the-art of different advanced degradation methods for the removal of PFAS from contaminated water.

2.0 Degradation mechanisms

2.1 PFAS degradation technologies

The degradation of PFAS has been carried out by different processes. **Figure 1** shows the degradation of PFAS by advanced oxidation processes (AOPs) such as oxidation, disinfection, ozonation, aeration packed towers, potassium permanganate, ultraviolet (UV) treatment, (UV/H₂O₂), chlorination (Cl₂) with and without chloramination, and chlorine dioxide processes. As shown in Figure 1, the utilities 7, 11-15, 17 and 18 introduced the oxidation and disinfection processes, which proved mostly ineffective (Figure 1). PFAA are generally resistant to oxidation, hence, the lack of removal of PFAA via these full-scale processes is not surprising. As AOPs use

the hydroxyl radicals, yet hydroxyl radicals have been shown ineffective towards PFOA and PFOS at the bench-scale.³⁹⁻⁴¹ In comparison, the degradation of some PFAA in water was found to be highly effective by using different AOPs such as photocatalytic oxidation, photochemical reduction, photochemical oxidation, thermally-induced reduction, persulfate radical, and sonochemical pyrolysis.^{24,28,29,40,42} However, most of these technologies are not employed in current drinking water treatment practices.

Figure 1

The partial removal of PFHxS (34%) and PFOS (35%) (Figure 1) was obtained by using a UV system (80 mJ cm⁻²) at Utility 13. On the other hand, the degradation of PFOS and PFOA via UV photolysis was the most effective process as demonstrated by many researchers.^{39,43-45} However, the removal of perfluoroalkyl carboxylic acids (PFCA) or the smaller chain sulfonate and perfluorobutanesulfonic acid (PFBS) by the UV system at Utility 13 was not effective.

As a result of the complete substitution of fluorine (C–F bond) for hydrogen (C–H bond) in PFOS and PFOA, such compounds resist oxidation. This is due to the presence of most electronegative element fluorine, which resists oxidation reaction to take place. Fluorine is also known that as the most potent inorganic oxidant with a reduction potential of 3.6 V.⁴⁶ Therefore, it is thermodynamically unfavourable attempting to generate the fluorine atom with any other one-electron oxidant. The utilization of the hydroxyl radicals, ozone (or O-atom), and AOPs is considered as a viable solution for recalcitrant organics by many researchers;⁴⁷⁻⁵⁰ although this is not the case for PFOS and PFOA. Subsequently, PFOS and PFOA contain no hydrogens to be removed at pH usually found in the environment. In general, hydroxyl radicals must act through a direct electron transfer to form the less thermodynamically favoured hydroxyl ions. Therefore, the

replacement of all of the organic hydrogens for fluorines in PFOS and PFOA makes these compounds inert to advanced oxidation techniques.⁴¹ A wide range of activated persulfate, subcritical water, Fenton's agent, zero-valent metal, and combinations of at least two of the above reagents have been used to improve oxidation process for overcoming these difficulties mentioned. The results of these methods are described by Espana et al.³⁸ AOPs are generally characterized by the high reactivity of the sulphate (SO_4^*) and hydroxyl radicals (OH^*) in driving oxidation processes on any compound. Highly oxidative sulphate radical anions (SO_4^*) were found to be very efficient for the degradation of PFOA to F^- and CO_2 as major products.²⁴ In the mineralization process, small amounts of shorter chain PFCA are formed, indicating that further oxidation is required to complete mineralization. Complete decomposition of PFOA at a concentration of 1.35 mM by light-activated persulfate at 50 mM $[\text{S}_2\text{O}_8]^{-2}$ and 4 h of irradiation was reported.²⁴ Further research work showed that heat-activated persulfate could also effectively decompose PFOA,²⁶ which yields F^- ions and CO_2 with ratios of (moles of F^- formed)/(moles of fluorine content in initial PFOA), and of (moles of CO_2 formed)/(moles of carbon content in initial PFOA) being 77.5% and 70.2%, respectively^{25,26}. However, these results conclusively demonstrated the mineralization of PFOA. Fujii et al.⁵¹ and Lee et al.²⁷ show correspondingly that decomposition rates of PFOA were at around 68%. Recently, it was demonstrated that sulphite under UV could degrade up to 100% of PFOA.⁵² Kingshott⁵³ also evaluated different methods for activating persulfate to treat PFOS and reported that Fenton's reagent-activated persulfate, H_2O_2 activated persulfate and heat activated persulfate, all showed >97.5% PFOS destruction. On the other hand, PFOA removal in a UV-Fenton system achieved 95% by Tang et al.⁵⁴ Other methods to improve persulfate's ability to degrade PFOA included microwave induction.⁵⁵ The degradation of PFOA could be faster at lower pH or higher concentration of persulfate, also indicated by Lee et al.⁵⁶ For PFOS removal, subcritical water (350 °C) catalyzed by zero-valent iron applied by Hori et al.²⁸ The decomposition

to carbon dioxide and fluoride ions was facilitated by the adsorption of PFOS molecules onto Fe_3O_4 precipitate followed by oxidation mechanism.

However, many photolytic oxidation/reduction methods such as UV light in combination with iodide, aqueous periodate, iron, and titanium-mediated photochemical decomposition have been attempted in laboratory studies.^{25,29,43,57-63} By these methods, the PFOA removal achieved ranged from 9%–70%. The direct irradiation with UV at 254 nm, however, showed ineffective in the removal of PFOA.⁶⁴ Bhakhri et al.⁶⁵ used four oxidizing agents (potassium ferrate, sodium persulfate, potassium permanganate and calcium hypochlorite) to oxidize POFA, which turned out to be unsuccessful. Furthermore, the treatment of the anionic HFOSA-glycinic acid, which is considered the most stable surfactant molecule, produced PFOS as reported by Schröder and Meesters.⁴¹

PFOS and PFOA alter to less toxic products, mainly fluoride ions, carbon dioxide and shorter chain PFCA by oxidation reaction processes. As a result, further treatment is not required. Chemical oxidation has the potential to destroy PFOS and PFOA in situ rather than transferring contamination to another waste stream or area indicated by Hawley et al.⁶⁶ AOPs have many advantages over conventional chemical oxidation processes (**Table 2**) including higher oxidation potential, no production of potentially carcinogenic chlorinated by-products, and no persistence of the oxidant.^{67,68} The degradation of PFOS and PFOA at the mg L^{-1} level has been unsuccessful for AOPs such as ozone, O_3/UV , $\text{O}_3/\text{H}_2\text{O}_2$, and Fenton's reagent,⁴¹ as have other oxidizing agents such as potassium ferrate, sodium persulfate, potassium permanganate and calcium hypochlorite.⁶⁵ In addition, direct UV irradiation at 254 nm did not remove PFOA.⁶⁴ To accelerate the reaction, activation at higher temperature is required.²⁶ The oxidation or UV radiation requires relatively high temperature (70–90 °C) or energy-consuming irradiation to proceed.⁵⁶ Moreover, the conditions required to destroy PFOA by the activated persulfate oxidation process partially are

difficult to apply at full-scale for in situ remediations. It is possible for this reason that the oxidation process has not yet been tested at pilot scale or full commercial scale.³⁸

The PFAS degradation has been observed experimentally. The degradation of PFAS such as PFCA ($C_nF_{2n+1}-COO^-$) undergoes two pathways upon reaction with e_{aq}^- (**Figure 2**).

Figure 2

First, two H/F exchanges occur consecutively on the α -position and yield $C_{n-1}F_{2n-1}-CH_2-COO^-$, which has high resistance for degradation. Additional C-F bond cleavage from middle $-CF_2-$ groups is possible if the fluorocarbon chain is too long. Shorter-chain PFCAs are generated from a decarboxylation mechanism shown in Figure 2b. Unstable perfluorinated alcohol ($C_nF_{2n+1}-OH$) yielded PFCAs that is subject to HF elimination.⁶⁹ The resulted acyl fluoride is hydrolyzed to release the second fluoride ion. Consequently, the shorter-chain PFCA ($C_{n-1}F_{2n-1}-COO^-$) forms and enters the next reaction cycle.³⁹ This decarboxylation-hydroxylation-elimination-hydrolysis (DHEH) pathway has been mainly deduced from previous literature;^{39,52,69,70} further studies provided insights on the stability of perfluorinated alcohol. However, DHEH indirectly was supported by few pieces of evidence. First, telomeric fluorinated alcohols $C_nF_{2n+1}-CH_2-OH$ are widely used when the perfluorinated $C_nF_{2n+1}-OH$ has been rarely reported as a bulk chemical.^{71,72} This fact may reflect the instability of $C_nF_{2n+1}-OH$. Second, a similar structure, FCH_2-OH , has only been observed spectroscopically under low temperatures in a mixture of HCOH and HF (i.e. $FCH_2-OH \leftrightarrow HCOH + HF$).⁷³ However, this equilibrium supports the mechanism of HF elimination from structures with one $-F$ and one $-OH$ on the same carbon. The defluorination of 68.6% PFOA was observed within 6 h by Song et al.,⁵² but they did not quantitate the PFOA decomposition ratio.

2.2 PFAS defluorination mechanism

PFAS defluorination was observed experimentally (Figures 2 and 3). Defluorination of trifluorinated acetates (TFA, $\text{CF}_3\text{-COO}^-$) was found to be 100%, which strongly supports this DHEH mechanism shown in Figure 2c. First, direct C–F bond cleavage TFA seems less likely because it only has three high-BDE primary C–F bonds (Figure 3f). Second, the experimental results of defluorination indicated that the previously proposed stepwise defluorination mechanism for TFA was less likely to happen.⁷⁴

Figure 3

The DHEH pathway is the most probable mechanism for PFCA chain-shortening and the accompanying F^- release, while other reaction mechanisms have not been identified. A complete defluorination would have been observed if the PFCA degradation followed the single pathway of chain-shortening through the DHEH pathway. Thus, the maximum 55% defluorination from all $n \geq 2$ $\text{C}_n\text{F}_{2n+1}\text{-COO}^-$ is attributed to other reaction pathways via H/F exchange. Assuming that only these two mechanisms apply to the simple $\text{CF}_3\text{CF}_2\text{COO}^-$ structure. At the first step, DHEH will generate two F^- and CF_3COO^- , which can be fully defluorinated in the second DHEH (defluorination = 100%). In the first step, the H/F exchange will accumulate $\text{CF}_3\text{CH}_2\text{COO}^-$ with high recalcitrance (deF% = 40%). So, after the first step, the overall 55% defluorination from $\text{CF}_3\text{CF}_2\text{COO}^-$ indicates a 75% probability for H/F exchange and a 25% probability for DHEH. However, each shorter-chain PFCA product will also undergo the two competing pathways, leading to the accumulation of H-containing structures with high recalcitrance. Hence, H/F exchange in the middle of fluoroalkyl chain is also possible for long-chain PFCAs and intermediates.

Figure 4

Degradation of PFAS by defluorination occurs from the other side of the molecule as one more $-\text{COO}^-$ terminal group enables degradation. Also, α -position H/F exchange or DHEH pathways from the second $-\text{COO}^-$ would lead to higher deF% than PFCAs (Figure 4). However, the previously proposed PFOA degradation mechanism indicated that $\text{C}_n\text{F}_{2n+1}-\text{CH}_2-\text{COO}^-$ generated from $\text{C}_n\text{F}_{2n+1}-\text{CF}_2-\text{COO}^-$ decomposes to three pieces, $\bullet\text{C}_n\text{F}_{2n+1}$, CH_2 , and $\bullet\text{COO}^-$. Therefore, the proposed mechanism does not support the result. After that, the $\bullet\text{C}_n\text{F}_{2n+1}$ and $\bullet\text{COO}^-$ recombine into the shortened $\text{C}_n\text{F}_{2n+1}-\text{COO}^-$.⁷⁴ If this happens then the degradation of $\text{CF}_3-\text{CH}_2-\text{COO}^-$ would be fast, that could cause the degradation of all $n \geq 2$ PFCAs to TFA and yield 100% defluorination. As for PFAS and FTCAs, the first reaction pathway is H/F exchange occurs in the middle of the long-chain structures on relatively weak C–F bonds (Figure 4d). The other path is the cleavage of the head groups and the formation of PFCAs following either the H/F exchange or the DHEH mechanism. The similar molecular defluorination values from the decayed portion of PFASs (59–64%) and FTCAs (44–49%) in variable lengths support this speculation. According to further investigation, the mass spectra peak areas of the parent compound and the identified degradation products F mass balance seems not yet closed. Probably this happens for varying ionization efficiency significantly for different products, which leads to inaccurate estimation of product abundances.^{75,76} The novel products generated from other reaction pathways are also not identified by the screening of suspect products from chain shortening and H/F exchange. The mechanisms for some reactions still well not defined. For example, FTCA chain shortening occurred with the $-\text{CH}_2\text{CH}_2-\text{COO}^-$ headgroup remaining. High intensities of H/F exchange structures ($\text{C}_4\text{F}_8\text{H}-\text{SO}_3^-$ and $\text{C}_3\text{F}_6\text{H}-\text{SO}_3^-$) were observed in the degradation of PFOS and PFHxS,

for that PFBS and PFPrS are highly recalcitrant. However, these results suggest that there is still unknown degradation mechanisms involved in PFAS degradation. Since this treatment strategy is not very operative to short fluorocarbon chains that are not directly linked to $-\text{COO}-$, mechanistic study on the unfavourable pathways goes beyond the focus of this study. Instead, the priority should be given to further researches should focus on the improvement of the rate and extent of the degradation of recalcitrant PFAS structures.⁷⁷

2.3 Chemical oxidation mechanism

Aqueous film-forming foams (AFFF) contain PFAS, perfluoroalkyl sulfonamide-based polyfluorinated compounds, and small amounts of PFCA. For the treatment of AFFF-contaminated groundwater and to identify terminal transformation products, heat-activated persulfate processes for chemical oxidation of AFFF have been used. For the batch experiment, 15- or 50 mL polypropylene or polystyrene were centrifuged with total solution volumes of 10 or 40 mL. Concentrated AFFF stock solutions were prepared by diluting AFFF 100-fold in ultrapure water. Oxidation and the generation of the transformation of PFAS products were evaluated under well-controlled conditions, therefore to investigate the potential for remediating AFFF contamination in groundwater with heat-activated persulfate. Fluorotelomer- and perfluoroalkyl sulfonamide-based polyfluorinated compounds were transformed to perfluorinated carboxylic acids, which experienced further degradation under acidic conditions produced after persulfate decomposed. The efficiency of the remedial process decreased for the presence of aquifer sediments. When the concentration is very high, the presence of organic solvents, such as those present in AFFF formulations, inhibited the transformation of a representative perfluorinated compound and perfluorooctanoic acid. The transformation of persulfate into perfluorooctanesulfonic acid or

perfluorohexanesulfonic acid is not possible under any conditions when it is heat-activated (**Figure 5**).

Figure 5

As from the previous studies of persulfate thermolysis with Ansul and AFFF at 85 °C, at least 95% of the added persulfate decomposed after 7.5 h (**Figure 5**).⁷⁸ During the treatment of Ansul AFFF with HO•, the pH dropped significantly, which was mainly due to the production of different acids such as perfluorohexanoic acid (PFHxA), perfluoropentanoic acid (PFPeA), and perfluorobutyric acid (PFBA). After the initial conversion of 6:2 FtTAoS to PFCAs, the concentration data were consistent with the sequential $-(CF_2)$ cleavage mechanism, as observed from previous studies, with PFHpA reaching its maximum concentration first, followed by PFHxA, PFPeA, and PFBA (**Figure 5**).^{26,79-82} Initially, the experiments performed with $S_2O_8^{2-}$ at room temperature as well as in aerobic biotransformation studies.⁸³ At the end of the treatment, short-chain PFCAs accounted for approximately 13% of the initial 6:2 FtTAoS on a molar basis. A 12% loss of 6:2 FtTAoS in heated controls containing AFFF without persulfate may have been due to sorption losses to the reactor walls. It is challenging to accurately quantify low F⁻ concentrations in the presence of high levels of sulfate and other anions; therefore, the attempt to obtain the mass balance on fluorine was unsuccessful.

After 0.5 h of the experiment in both the treatment and control reactors, PFOS concentration decreased by approximately 40% and remained stable (**Figure 6**). This initial loss of PFOS may have been as a result of sorption to the reactor walls or some other physical phenomenon related to the AFFF components. PFCA concentrations primarily increased, with a total of 150 μM of PFHxA, PFPeA, and PFBA detected after 1 h. PFCA concentrations then decreased, leaving 18 μM of PFBA after 4 h of treatment. The concentration of PFCA changes with time to oxidation of

sulfonamide-based polyfluorinated compounds PFHxSAm and PFHxSAmA.⁸⁴ Oxidation of the nonfluorinated portions of these PFAA-precursors by $\text{SO}_4^{\bullet-}$ produced PFCAs as products. These PFCAs then reacted with $\text{SO}_4^{\bullet-}$ by the consecutive chain-shortening mechanism.

Figure 6

2.4 Advanced reduction mechanism

In advanced reduction processes (ARPs), highly reactive, nonselective reducing nucleophiles or radicals, such as aqueous electrons, H^{\bullet} , and $\text{SO}_3^{\bullet-}$ are generated. Recent studies have focused on degradation PFAS and PFCAs via reduction method. In advanced reduction method, radicals are generated by utilizing sulfite, dithionite, aqueous iodide, and ferrocyanide in combination with UV, ultrasound, laser flash photolysis, or electron beam (E-beam), microwave (**Table 3**). Degradation of PFCAs mainly occurred with the hydrated electron nucleophiles.⁸⁵ The degradation initiates by the apposition of C-F bond cleavage, instead of the C–C bond.^{52,74} Carboxyl group have the inductive effect of initiating the degradation, but, fluorine has the ability to withdraw electrons.⁸⁶ Saturated carbon atoms are found in PFCAs which cannot gain more electrons. Free radicals are formed after the bond cleavage as a result of UV irradiation.^{52,74}

Table 3

2.4.1 Aqueous iodide

One of the widely studied ARPs has been using KI with UV (at 254 nm) which can decompose several PFAS. In the presence of UV light, iodide (I^-) ion can form a caged complex (I^{\bullet} , e^-) in water.⁷⁴ Initially, the capabilities of KI were limited, which resulted in the high concentration of PFCAs and PFSAs remaining in the solution.^{62,85} This was likely due to quenching and sequestration by the production of triiodide (I_3^-) from high concentrations of KI^{62,74} including

iodinated hydrocarbons, CHF_3 , and C_2F_6 ; strong greenhouse gases were also produced.⁷⁴ Further improvement of KI treatment was performed by utilizing alkaline conditions and a closed reactor, which can reduce the production of greenhouse gases.^{87,88} The decomposition of PFOA and defluorination ratio improves by increasing temperature and varying the ionic strength.

2.4.2 Dithionite and sulfite

Degradation of PFOA with dithionite ($\text{S}_2\text{O}_4^{2-}$) and sulfite (SO_3^{2-}) was not very efficient with limited success. Dithionite will form two sulfur dioxide radical anions ($2\text{SO}^{\cdot-}$) when irradiated with UV (315 nm).⁸⁹⁻⁹¹ Other products, such as H_2SO_3 , HSO_3^- , and SO_3^{2-} can be generated during this process. The UV irradiation of these product forms aquated electrons and other reductants, such as H^- and sulfite radical ($\text{SO}_3^{\cdot-}$), and can then be used to breakdown PFOA.⁹²⁻⁹⁴ While PFOA degradation seems promising using dithionite and sulfite, <10% PFOA was removed with UV light. No degradation was observed when using dithionite and sulfite with ultrasound, microwave, or E-beam.⁹¹

The degradation of PFAS using ARPs needs more research to determine better degradation parameters for dithionite and sulfite. However, this process has limited applications and has not been further optimized for PFAS degradation.⁹⁵ In contrast, KI may be applied to PFCA-contaminated wastewater. Qu et al.⁷⁴ observed about 96% PFOA degradation when using KI to destroy PFCA in wastewater from a fluorochemical plant in China.

2.5 Thermal and nonthermal degradation mechanism

Thermal treatment can also break the C–C and C–F bonds when the elevated temperature is used, and perfluoroalkyl radicals are produced at high temperature. However, similar kinds of decomposition of PFAS take place as like as photolytic or photocatalytic degradation. Various types of methods are used for thermal treatment processes such as thermal, chemical reactions,

incineration, sonochemistry, sub- or supercritical, microwave-hydrothermal, and high-voltage electric discharge.

2.5.1 Incineration and thermal chemical reactions

Incineration is one the most familiar route to destroy hazardous compounds, especially organic compounds. However, it can cause harmful emissions to the environments. In incineration, high temperatures ranging from 600 °C to 1,000 °C are used for the destruction of the compounds. Incineration technique for PFAS degradation has been successfully performed.⁹⁶⁻⁹⁸ Although the incineration of PFOS and PFOA have been completed at the same temperature range as mentioned earlier, this phenomenon may form the volatile and mobile products such as 1-H-perfluoroheptane.^{96,99} If PFAS are incinerated with other wastes additional harmful emissions, such as dioxins and furans, can be formed.^{100,101} On the one hand, during the combustion of PFOS, active greenhouse gases have been noticed, including tetrafluoromethane (CF₄) and hexafluoroethane (C₂F₆).⁹⁷ The global-warming potentials of those greenhouse gasses are 5,700 and 11,900, respectively, with long atmospheric lifetimes of 50,000 and 10,000 years, respectively.^{52,102} Remediation of these harmful by-products can be done by certain additives (e.g. calcium hydroxide).^{52,102} To fully understand the incineration effects on the PFAS and formed by-products, significant further research is required. However, heated at 30–85 °C with persulfate, PFCA and perfluoroether carboxylic acid decomposes to shorter-chain carboxylic acids, F⁻, and CO₂ under much more benign condition. Similar reactions took place as with persulfate and UV light and resulted in PFOA decomposition to nondetectable levels, with faster degradation occurring with increasing temperatures.^{79,103}

2.5.2 Sonochemical degradation mechanism

To achieve chemical reactions in a solution, sonochemistry is used with the help of an acoustic field. In the solution, bubbles are breakdown by sound waves. Hence, pyrolysis and combustion of

chemicals are observed when high vapour temperatures are produced. The pollutants in aqueous media decompose by this technique. This technique is also able to decompose PFAS. Due to pyrolysis, it decomposes at the bubble/water interface.⁴⁰ This mechanism prohibits the nucleation of cavitation bubbles in aqueous solution. These bubbles will start expanding until radial maximum, transient bubbles undergo a quasi-adiabatic compression and this energy is converted into kinetic energy of the trapped molecules. Thus, the collapsing bubbles caused high temperatures (average 5000 K).^{104,105} The collapsing bubble wall strikes by the hot vapour, which generates heat from the vapour. However, this heat is shifted to the bubble surface, reaching temperatures of about 800 K.^{106,107} The H* and OH* radicals are formed due to pyrolysis of hot water vapour in the collapsing bubbles., As a result, it will react with chemicals in the bubble gas-phase. Although it will decompose due to pyrolysis and combustion reactions.^{38,108} The PFOS decomposes up to 28% by ultrasonic treatment for 1 h under an air atmosphere has been reported by Moriwaki et al.⁴⁰ PFOA was produced during the sonochemical reaction. The authors attributed PFOA formation during the reaction to oxidation after dissociation of the SO₃⁻ group, which was oxidized to SO₄⁻² by sonication. Nevertheless, by the repetition of the COO⁻ dissociation, the produced PFOA will undertake the perfluorocarbon chain short. The oxidation of the generated ions or radicals of the perfluorocarbon also shows the effect on reducing the perfluorocarbon chain.⁴⁰ Recent studies¹⁰⁹ have shown that when the bubble interfaces are lightly populated the PFAS adsorption to acoustically cavitating interfaces is increased. The degradation studies in groundwater³⁰ have shown that the decomposition rates are not significantly affected by organic content due to the preferential adsorption of PFAS to the bubble water interface.

PFOS and PFOA have been shown to sonochemically decompose due to pyrolytic reactions at the bubble/water interface,¹¹⁰ as these create incinerator level temperatures just for a concise time (ns). Ultrasonic degradation was carried out in dilute aqueous (< 1 μM) solutions of

perfluorochemicals including PFOS and PFOA, which are not representative of field concentrations. Extensive research is required before it can be applied in the field. Research needs include studies of the variables affecting the effect on sonolytic degradation rate, developing efficient and reliable methods to estimate the fraction of total surfactant molecules adsorbed to transiently cavitating bubbles, understanding of physical processes that govern sonochemical kinetics of fluorinated chemicals and how these processes are affected by acoustic frequency.³⁸

2.5.3 Sub- or supercritical treatment

Treatment methods using sub- or supercritical water can be environmentally benign. The temperature range for subcritical water is 100 °C to 350 °C, and a certain pressure is sustained to hold a liquid state. In comparison, supercritical water temperatures reach > 350 °C and pressures > 22.1 MPa.¹¹¹ At a certain temperature and pressure sub- and supercritical water plays an important role such as degrading hazardous compounds, together with high diffusivity and low viscosity. Decomposition of PFAS is increased when Iron is introduced to combine with sub- or supercritical water. The use of metal can increase the PFOS degradation efficiency in sub or supercritical treatment system in the order of Al < Cu < Zn << Fe, while the redox potential of each metal could be ordered as Cu < Fe < Zn < Al.^{28,112} The PFOS degradation efficiency order of metal ion and redox potential of metals suggests that metal surface plays a vital role rather than redox potential.²⁸ The decomposition of PFAS is increasing with increasing the surface area iron. This phenomenon is also valid for zero-valent iron.¹¹³⁻¹¹⁵ Compared with subcritical water, PFAS degradation was enhanced under supercritical conditions. Hori et al.¹¹³ observed increased consumption of PFHxS under supercritical conditions (94.8% PFHxA decomposed) compared with subcritical conditions (83.6% PFHxS decomposed), when Fe powder was added. However, more CF₃H was produced under supercritical conditions.¹¹³⁻¹¹⁵

2.5.4 Microwave-hydrothermal treatment

Persulfate can be used in combination with microwave hydrothermal treatment to decompose PFOA and will form sulfate radicals with heat, similar to persulfate and UV.⁵⁵ At 90 °C, PFOA was decomposed to non-detectable levels after 6 h, and at 60 °C, the reaction took twice as long to achieve the same PFOA removal.⁵⁵ Although microwave-hydrothermal treatment with persulfate is quick, it requires low pH to form more sulfate radicals.⁵⁶ Also, the pH will drop quickly due to the formation of more protons. Persulfate activated by microwave-hydrothermal treatment was improved with the addition of zero-valent iron powder and inhibited by the addition of chloride ions. ZVI acted as a source of ferrous ions and led to faster activation of persulfate. Within 1 h at 90 °C, about 60% PFOA was degraded (15% fluoride yield).²⁷ While PFOA degradation efficiency increased with ZVI, high concentrations of ZVI (14.4–18 mM) resulted in less PFOA degradation due to the release of ferrous ions that competed with PFOA for sulfate radicals. Chloride ions were also observed to inhibit PFOA degradation rate.¹¹⁶ Microwave-hydrothermal treatment is more cost-efficient when compared with other thermal treatment processes and can save up to 50% in energy consumption. Higher decomposition rates, enhanced kinetics, and rapid and homogeneous heating have also been observed.^{117,118}

2.5.5 High-voltage electric discharge

High-voltage electric discharge reactors can generate strong electric fields, and highly reactive species, such as hydroxyl radicals, oxygen radicals, ozone, and hydrogen radicals.¹¹⁹ This method can be cost-efficient, depending on the time of reaction and energy utilization in the system¹²⁰. Recently, A DC electrohydraulic plasma discharge reactor was used for PFOA and PFOS degradation by high-voltage electric discharge, which generated oxygen gas bubbles and high temperature (~2,000K).¹²¹⁻¹²⁴ Therefore, PFOA and PFOS molecules can adsorb onto the gas-liquid interface in high concentration.¹²² This process can generate positive collided and which can react

with the anionic forms of PFOS and PFOA. Therefore, decarboxylation degradation or C–C bond cleavage of those PFAS can take place.¹²³ Other gaseous fluorocarbons also produced including CHF₃, C₂F₆, and C₂HF₅. Shorter-chain perfluorocarboxylates, fluoride ions, or sulfate ions, were also found. Recently, Hayashi et al.¹²⁴ also performed the degradation of large-scale PFOS using DC electrohydraulic plasma discharge reactor.

However, studies using thermal and nonthermal processes for PFAS decomposition have been successful in many cases with some limitations. The limitation is the production of toxic by-products and greenhouse gases. Moreover, these methods are also relatively expensive than AOPs and physical removal processes. The cost efficiency of other methods for PFAS removal is still unknown, especially when dealing with PFAS mixture and co-contaminants.¹²⁵

3.0 Future outlook

For the removal of PFAS from the aqueous solution, different remediation technologies have been developed. However, the majority of research work has been conducted at laboratory scale with very few field applications. The main concerns that need to be addressed to apply new technologies for the removal of PFAS are usually related to high energy input requirements, high capital cost at full scale in situ remediation projects, and meager removal rates under different conditions.

Among different PFAS remediation technologies reported in the literature, PFAS removal by activated carbon is commonly used.^{38,126} Many other adsorbents that have been tested for removing PFAS at laboratory scale include carbon nanotubes,¹²⁷⁻¹³⁰ powdered activated carbon¹³¹⁻¹³⁵, commercial resins^{131,132}, maize straw-derived ash¹²⁷, polymers¹³¹, chitosan¹³⁶, alumina¹⁰², silica¹³¹, goethite⁶⁰, organo-clay¹³⁷, montmorillonite¹³⁸, where > 90% removal can be achieved. The presence of a significant amount of PFAS in landfill leachate is well documented in different parts of the world.¹³⁹ Recent studies demonstrate that PFAS can undergo abiotic¹⁴⁰ and biological

hydrolysis with an estimated half-life range of 8-100 years.^{140,141} Therefore, the degradation of PFAS under landfill conditions needs to be further studied.

Among different advanced degradation technologies used for PFAS removal, sonochemical decomposition requires extensive research work before it can be implemented in the field, and air-sparged hydro cyclone technology has shown several limitations including limited efficiency.³⁸

Future research should focus on the following:

- Numerous advanced oxidation/reduction processes are investigated in detail, but so far most of those methods are tested in the laboratory not in real wastewater treatment plants. Hence further research should focus on more commercial-scale wastewater treatment plants.
- Practical applications of photocatalytic and catalytic degradation methods require developing appropriate immobilization methods, so that photocatalysts are trapped, remain effective for long-term functioning, and are capable of being regenerated.
- Further study is needed to determine the degradation products or by-products from PFAS, in order to assist understanding degradation mechanism and the potential toxicity of degradation products.
- Research should be carried out for the development of novel advanced oxidation/reduction technologies, which do not need further use of chemicals to obtain the best cost-efficient and clean treatment option.
- Relatively new technology such as vacuum UV, electrochemical, sonolysis, and use of ionizing radiation can be applied for the removal of PFAS.

4.0 Conclusions

Different advanced remediation processes by oxidation or reduction techniques can remove PFAS from the liquid streams and have shown encouraging results. Different advanced chemical methods

produce various by-products through different reaction mechanisms. However, the majority of the treatment system has only been tested at laboratory scale, and the industrial application was rarely conducted. Consequently, industrial-scale applications are essential and the focus to be carried out in future research efforts in combating PFAS contamination in the environment.

Conflicts of interest

There are no conflicts of interest to declare.

References

1. E. Kissa, *Fluorinated surfactants and repellents*, CRC Press, 2001.
2. D. Brooke, A. Footitt and T. Nwaogu, Environmental risk evaluation report: Perfluorooctanesulphonate (PFOS), *Environ. Agency*, 2004, 1.
3. M. F. Rahman, S. Peldszus and W. B. Anderson, Behaviour and fate of perfluoroalkyl and polyfluoroalkyl substances (PFASs) in drinking water treatment: a review, *Water Res.* 2014, **50**, 318-340.
4. K. Kannan, S. Corsolini, J. Falandysz, G. Fillmann, K. S. Kumar, B. G. Loganathan, M. A. Mohd, J. Olivero, N. V. Wouwe, J. H. Yang and K. M. Aldous, Perfluorooctanesulfonate and Related Fluorochemicals in Human Blood from Several Countries, *Environ. Sci. Technol.* 2004, **38**, 4489-4495.
5. A. Kärrman, I. Ericson, B. van Bavel, P. O. Darnerud, M. Aune, A. Glynn, S. Lignell and G. Lindström, Exposure of perfluorinated chemicals through lactation: levels of matched human milk and serum and a temporal trend, 1996–2004, in Sweden, *Environ. Health Perspect.* 2006, **115**, 226-230.

6. R. Monroy, K. Morrison, K. Teo, S. Atkinson, C. Kubwabo, B. Stewart and W. G. Foster, Serum levels of perfluoroalkyl compounds in human maternal and umbilical cord blood samples, *Environ. Res.* 2008, **108**, 56-62.
7. Y. Pan, Y. Shi, J. Wang, Y. Cai and Y. Wu, Concentrations of perfluorinated compounds in human blood from twelve cities in China, *Environ. Toxicol. Chem.* 2010, **29**, 2695-2701.
8. M. Llorca, M. Farré, Y. Picó, M. L. Teijón, J. G. Álvarez and D. Barceló, Infant exposure of perfluorinated compounds: Levels in breast milk and commercial baby food, *Environ. Int.* 2010, **36**, 584-592.
9. A. M. Ingelido, V. Marra, A. Abballe, S. Valentini, N. Iacovella, P. Barbieri, M. G. Porpora, A. d. Domenico and E. D. Felip, Perfluorooctanesulfonate and perfluorooctanoic acid exposures of the Italian general population, *Chemosphere*, 2010, **80**, 1125-1130.
10. W. Liu, L. Xu, X. Li, Y. H. Jin, K. Sasaki, N. Saito, I. Sato and S. Tsuda, Human Nails Analysis as Biomarker of Exposure to Perfluoroalkyl Compounds, *Environ. Sci. Technol.* 2011, **45**, 8144-8150.
11. S. M. Bartell, A. M. Calafat, C. Lyu, K. Kato, P. B. Ryan and K. Steenland, Rate of decline in serum PFOA concentrations after granular activated carbon filtration at two public water systems in Ohio and West Virginia, *Environ. Health Perspect.* 2009, **118**, 222-228.
12. E. A. Emmett, F. S. Shofer, H. Zhang, D. Freeman, C. Desai and L. M. Shaw, Community exposure to perfluorooctanoate: relationships between serum concentrations and exposure sources, *J. Occup. Environ. Medicine/American Col. Occupat. Environ. Medicine.* 2006, **48**, 759.
13. L. Ahrens and M. Bundschuh, Fate and effects of poly- and perfluoroalkyl substances in the aquatic environment: a review, *Environ. Toxicol. Chem.* 2014, **33**, 1921-1929.

14. Z. Liu, Y. Lu, P. Wang, T. Wang, S. Liu, A. C. Johnson, A. J. Sweetman and Y. Baninla, Pollution pathways and release estimation of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) in central and eastern China, *Sci. Total Environ.* 2017, **580**, 1247-1256.
15. C. Bach, X. Dauchy, V. Boiteux, A. Colin, J. Hemard, V. Sagres, C. Rosin and J. F. Munoz, The impact of two fluoropolymer manufacturing facilities on downstream contamination of a river and drinking water resources with per- and polyfluoroalkyl substances, *Environ. Sci. Pollut. Res.* 2017, **24**, 4916-4925.
16. M. Exner and H. Färber, Perfluorinated surfactants in surface and drinking waters (9 pp), *Environ. Sci. Pollut. Res.* 2006, **13**, 299-307.
17. S. Valsecchi, M. Rusconi, M. Mazzoni, G. Viviano, R. Pagnotta, C. Zaghi, G. Serrini and S. Polesello, Occurrence and sources of perfluoroalkyl acids in Italian river basins, *Chemosphere*, 2015, **129**, 126-134.
18. M. Chen, Q. Wang, G. Shan, L. Zhu, L. Yang and M. Liu, Occurrence, partitioning and bioaccumulation of emerging and legacy per- and polyfluoroalkyl substances in Taihu Lake, China, *Sci. Total Environ.* 2018, **634**, 251-259.
19. M. Shao, G. Ding, J. Zhang, L. Wei, H. Xue, N. Zhang, Y. Li, G. Chen and Y. Sun, Occurrence and distribution of perfluoroalkyl substances (PFASs) in surface water and bottom water of the Shuangtaizi Estuary, China, *Environ. Pollut.* 2016, **216**, 675-681.
20. G. Ding, H. Xue, Z. Yao, Y. Wang, L. Ge, J. Zhang and F. Cui, Occurrence and distribution of perfluoroalkyl substances (PFASs) in the water dissolved phase and suspended particulate matter of the Dalian Bay, China, *Chemosphere*, 2018, **200**, 116-123.
21. H. Chen, J. Han, C. Zhang, J. Cheng, R. Sun, X. Wang, G. Han, W. Yang and X. He, Occurrence and seasonal variations of per- and polyfluoroalkyl substances (PFASs) including

- fluorinated alternatives in rivers, drain outlets and the receiving Bohai Sea of China, *Environ. Pollut.* 2017, **231**, 1223-1231.
22. L. A. D'Agostino and S. A. Mabury, Certain Perfluoroalkyl and Polyfluoroalkyl Substances Associated with Aqueous Film Forming Foam Are Widespread in Canadian Surface Waters, *Environ. Sci. Technol.* 2017, **51**, 13603-13613.
23. W. Dong, B. Liu, Y. Song, H. Zhang, J. Li and X. Cui, Occurrence and Partition of Perfluorinated Compounds (PFCs) in Water and Sediment from the Songhua River, China, *Arch. Environ. Contam. Toxicol.* 2018, **74**, 492-501.
24. H. Hori, A. Yamamoto, E. Hayakawa, S. Taniyasu, N. Yamashita, S. Kutsuna, H. Kiatagawa and R. Arakawa, Efficient Decomposition of Environmentally Persistent Perfluorocarboxylic Acids by Use of Persulfate as a Photochemical Oxidant, *Environ. Sci. Technol.* 2005, **39**, 2383-2388.
25. M. H. Cao, B. B. Wang, H. S. Yu, L. L. Wang, S. H. Yuan and J. Chen, Photochemical decomposition of perfluorooctanoic acid in aqueous periodate with VUV and UV light irradiation, *J. Hazard. Mater.* 2010, **179**, 1143-1146.
26. H. Hori, Y. Nagaoka, M. Murayama and S. Kutsuna, Efficient Decomposition of Perfluorocarboxylic Acids and Alternative Fluorochemical Surfactants in Hot Water, *Environ. Sci. Technol.* 2008, **42**, 7438-7443.
27. Y.-C. Lee, S.-L. Lo, P.-T. Chiueh, Y.-H. Liou and M. L. Chen, Microwave-hydrothermal decomposition of perfluorooctanoic acid in water by iron-activated persulfate oxidation, *Water Res.* 2010, **44**, 886-892.
28. H. Hori, Y. Nagaoka, A. Yamamoto, T. Sano, N. Yamashita, S. Taniyasu, S. Kutsuna, I. Osaka and R. Arakawa, Efficient Decomposition of Environmentally Persistent

Perfluorooctanesulfonate and Related Fluorochemicals Using Zerovalent Iron in Subcritical Water, *Environ. Sci. Technol.* 2006, **40**, 1049-1054.

29. H. Hori, A. Yamamoto, K. Koike, S. Kutsuna, I. Osaka and R. Arakawa, Photochemical decomposition of environmentally persistent short-chain perfluorocarboxylic acids in water mediated by iron(II)/(III) redox reactions, *Chemosphere*, 2007, **68**, 572-578.
30. J. Cheng, C. D. Vecitis, H. Park, B. T. Mader and M. R. Hoffmann, Sonochemical Degradation of Perfluorooctane Sulfonate (PFOS) and Perfluorooctanoate (PFOA) in Landfill Groundwater: Environmental Matrix Effects, *Environ. Sci. Technol.* 2008, **42**, 8057-8063.
31. C. Y. Tang, Q. S. Fu, A. P. Robertson, C. S. Criddle and J. O. Leckie, Use of Reverse Osmosis Membranes to Remove Perfluorooctane Sulfonate (PFOS) from Semiconductor Wastewater, *Environ. Sci. Technol.* 2006, **40**, 7343-7349.
32. C. Y. Tang, Q. S. Fu, C. S. Criddle and J. O. Leckie, Effect of Flux (Transmembrane Pressure) and Membrane Properties on Fouling and Rejection of Reverse Osmosis and Nanofiltration Membranes Treating Perfluorooctane Sulfonate Containing Wastewater, *Environ. Sci. Technol.* 2007, **41**, 2008-2014.
33. R. Rattanaoudom, PhD dissertation Environmental Engineering and Management Inter-University, 2011.
34. E. Steinle-Darling and M. Reinhard, Nanofiltration for Trace Organic Contaminant Removal: Structure, Solution, and Membrane Fouling Effects on the Rejection of Perfluorochemicals, *Environ. Sci. Technol.* 2008, **42**, 5292-5297.
35. T. Wang, C. Zhao, P. Li, Y. Li and J. Wang, Fabrication of novel poly(m-phenylene isophthalamide) hollow fiber nanofiltration membrane for effective removal of trace amount perfluorooctane sulfonate from water, *J. Membrane Sci.* 2015, **477**, 74-85.

36. X. Hang, X. Chen, J. Luo, W. Cao and Y. Wan, Removal and recovery of perfluorooctanoate from wastewater by nanofiltration, *Sep. Purif. Technol.* 2015, **145**, 120-129.
37. T. D. Appleman, E. R. V. Dickenson, C. Bellona and C. P. Higgins, Nanofiltration and granular activated carbon treatment of perfluoroalkyl acids, *J. Hazard. Mater.* 2013, **260**, 740-746.
38. V. A. A. Espana, M. Mallavarapu and R. Naidu, Treatment technologies for aqueous perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA): A critical review with an emphasis on field testing, *Environ. Technol. Innov.* 2015, **4**, 168-181.
39. H. Hori, E. Hayakawa, H. Einaga, S. Kutsuna, K. Koike, T. Ibusuki, H. Kiatagawa and R. Arakawa, Decomposition of environmentally persistent perfluorooctanoic acid in water by photochemical approaches, *Environ. Sci. Technol.* 2004, **38**, 6118-6124.
40. H. Moriwaki, Y. Takagi, M. Tanaka, K. Tsuruho, K. Okitsu and Y. Maeda, Sonochemical Decomposition of Perfluorooctane Sulfonate and Perfluorooctanoic Acid, *Environ. Sci. Technol.* 2005, **39**, 3388-3392.
41. H. F. Schröder and R. J. W. Meesters, Stability of fluorinated surfactants in advanced oxidation processes—A follow up of degradation products using flow injection–mass spectrometry, liquid chromatography–mass spectrometry and liquid chromatography–multiple stage mass spectrometry, *J. Chromatograph. A* 2005, **1082**, 110-119.
42. J. D. LaZerte, L. J. Hals, T. S. Reid and G. H. Smith, Pyrolyses of the Salts of the Perfluoro Carboxylic Acids¹, *J. American Chem. Soc.* 1953, **75**, 4525-4528.
43. J. Chen, P.-y. Zhang and J. Liu, Photodegradation of perfluorooctanoic acid by 185 nm vacuum ultraviolet light, *J. Environ. Sci.* 2007, **19**, 387-390.
44. J. Chen and P. Zhang, Photodegradation of perfluorooctanoic acid in water under irradiation of 254 nm and 185 nm light by use of persulfate, *Water Sci. Technol.* 2006, **54**, 317-325.

45. T. Yamamoto, Y. Noma, S.-i. Sakai and Y. Shibata, Photodegradation of Perfluorooctane Sulfonate by UV Irradiation in Water and Alkaline 2-Propanol, *Environ. Sci. Technol.* 2007, **41**, 5660-5665.
46. P. Wardman, Reduction potentials of one-electron couples involving free radicals in aqueous solution, *J. Phy. Chem. Ref. Data* 1989, **18**, 1637-1755.
47. T. Oppenlander, Photochemical Purification of Water and Air Treatment. *Journal*, 2003.
48. M. Pera-Titus, V. García-Molina, M. A. Baños, J. Giménez and S. Esplugas, Degradation of chlorophenols by means of advanced oxidation processes: a general review, *Appl. Catal. B Environ.* 2004, **47**, 219-256.
49. R. Andreozzi, V. Caprio, A. Insola and R. Marotta, Advanced oxidation processes (AOP) for water purification and recovery, *Catal.Today* 1999, **53**, 51-59.
50. O. Legrini, E. Oliveros and A. M. Braun, Photochemical processes for water treatment, *Chem. Rev.* 1993, **93**, 671-698.
51. S. Fujii, C. Polprasert, S. Tanaka, N. P. Hong Lien and Y. Qiu, New POPs in the water environment: distribution, bioaccumulation and treatment of perfluorinated compounds – a review paper, *J. Water Suppl.: Res. Technol. Aqua* 2007, **56**, 313-326.
52. Z. Song, H. Tang, N. Wang and L. Zhu, Reductive defluorination of perfluorooctanoic acid by hydrated electrons in a sulfite-mediated UV photochemical system, *J. Hazard. Mater.* 2013, **262**, 332-338.
53. L. M. Kingshott, Centre of Environmental Policy, Imperial College London, 2008.
54. H. Tang, Q. Xiang, M. Lei, J. Yan, L. Zhu and J. Zou, Efficient degradation of perfluorooctanoic acid by UV–Fenton process, *Chem. Eng. J.* 2012, **184**, 156-162.

55. Y.-C. Lee, S.-L. Lo, P.-T. Chiueh and D.-G. Chang, Efficient decomposition of perfluorocarboxylic acids in aqueous solution using microwave-induced persulfate, *Water Res.* 2009, **43**, 2811-2816.
56. Y.-C. Lee, S.-L. Lo, J. Kuo and Y.-L. Lin, Persulfate oxidation of perfluorooctanoic acid under the temperatures of 20–40°C, *Chem. Eng. J.* 2012, **198-199**, 27-32.
57. C. Jing, P.-y. ZHANG and L. Jian, Photodegradation of perfluorooctanoic acid by 185 nm vacuum ultraviolet light, *J. Environ. Sci.* 2007, **19**, 387-390.
58. Y. Wang, P. Zhang, G. Pan and H. Chen, Ferric ion mediated photochemical decomposition of perfluorooctanoic acid (PFOA) by 254nm UV light, *J. Hazard. Mater.* 2008, **160**, 181-186.
59. Y. Wang, P. Y. Zhang, G. Pan and H. Chen, Photochemical degradation of environmentally persistent perfluorooctanoic acid (PFOA) in the presence of Fe(III), *Chinese Chem. Lett.* 2008, **19**, 371-374.
60. C. Y. Tang, Q. Shiang Fu, D. Gao, C. S. Criddle and J. O. Leckie, Effect of solution chemistry on the adsorption of perfluorooctane sulfonate onto mineral surfaces, *Water Res.* 2010, **44**, 2654-2662.
61. H. Park, Photolysis of aqueous perfluorooctanoate and perfluorooctane sulfonate, *Revue Roumaine de Chimie*, 2010, **55**, 611-619.
62. H. Park, C. D. Vecitis, J. Cheng, N. F. Dalleska, B. T. Mader and M. R. Hoffmann, Reductive degradation of perfluoroalkyl compounds with aquated electrons generated from iodide photolysis at 254 nm, *Photochem. Photobiol. Sci.* 2011, **10**, 1945-1953.
63. C. R. Estrellan, C. Salim and H. Hinode, Photocatalytic decomposition of perfluorooctanoic acid by iron and niobium co-doped titanium dioxide, *J. Hazard. Mater.* 2010, **179**, 79-83.
64. Y. Qiu, Study on treatment technologies for perfluorochemicals in wastewater, Repository, 2007.

65. K. R. Roberts and T. M. Finelli, Removal of PFOA from water using UV treatment, chemical oxidation, & adsorption by activated carbon & zeolites, Digitalcommons. 2012.
66. E. L. Hawley, Remediation Technologies for Perfluorinated Compounds (PFCs), Including Perfluorooctane Sulfonate (PFOS) and Perfluorooctanoic Acid (PFOA), CSWAB ORG. 2012.
67. A. B. C. Alvares, C. Diaper and S. A. Parsons, Partial Oxidation by Ozone to Remove Recalcitrance from Wastewaters - a Review, *Environ. Technol.* 2001, **22**, 409-427.
68. B. Langlais, D. A. Reckhow and D. R. Brink, Ozone in water treatment, *Appl. Eng.* 1991, **558**.
69. K. Nohara, M. Toma, S. Kutsuna, K. Takeuchi and T. Ibusuki, Cl atom-initiated oxidation of three homologous methyl perfluoroalkyl ethers, *Environ. Sci. Technol.* 2001, **35**, 114-120.
70. Y. Gu, W. Dong, C. Luo and T. Liu, Efficient reductive decomposition of perfluorooctanesulfonate in a high photon flux UV/sulfite system, *Environ. Sci. Technol.* 2016, **50**, 10554-10561.
71. M. Vandamme, L. a. Bouchard, A. Gilbert, M. Keita and J.-F. o. Paquin, Direct esterification of carboxylic acids with perfluorinated alcohols mediated by XtalFluor-E, *Org. Lett.* 2016, **18**, 6468-6471.
72. G. Yuan, H. Peng, C. Huang and J. Hu, Ubiquitous occurrence of fluorotelomer alcohols in eco-friendly paper-made food-contact materials and their implication for human exposure, *Environ. Sci. Technol.* 2016, **50**, 942-950.
73. R. Suenram, F. Lovas and H. Pickett, Fluoromethanol: Synthesis, microwave spectrum, and dipole moment, *J. Mol. Spectros.* 1986, **119**, 446-455.
74. Y. Qu, C. Zhang, F. Li, J. Chen and Q. Zhou, Photo-reductive defluorination of perfluorooctanoic acid in water, *Water Res.* 2010, **44**, 2939-2947.

75. J. Liu, D. J. Van Hoomissen, T. Liu, A. Maizel, X. Huo, S. R. Fernández, C. Ren, X. Xiao, Y. Fang and C. E. Schaefer, Reductive defluorination of branched per-and polyfluoroalkyl substances with cobalt complex catalysts, *Environ. Sci. Technol. Lett.* 2018, **5**, 289-294.
76. S. Park, C. de Perre and L. S. Lee, Alternate reductants with VB12 to transform C8 and C6 perfluoroalkyl sulfonates: Limitations and insights into isomer-specific transformation rates, products and pathways, *Environ. Sci. Technol.*, 2017, **51**, 13869-13877.
77. M. J. Bentel, Y. Yu, L. Xu, Z. Li, B. M. Wong, Y. Men and J. Liu, Defluorination of Per- and Polyfluoroalkyl Substances (PFASs) with Hydrated Electrons: Structural Dependence and Implications to PFAS Remediation and Management, *Environ. Sci. Technol.*, 2019.
78. R. L. Johnson, P. G. Tratnyek and R. O. B. Johnson, Persulfate persistence under thermal activation conditions, *Environ. Sci. Technol.*, 2008, **42**, 9350-9356.
79. C. Liu, C. Higgins, F. Wang and K. Shih, Effect of temperature on oxidative transformation of perfluorooctanoic acid (PFOA) by persulfate activation in water, *Sep. Purif. Technol.* 2012, **91**, 46-51.
80. S. Park, L. S. Lee, V. F. Medina, A. Zull and S. Waisner, Heat-activated persulfate oxidation of PFOA, 6: 2 fluorotelomer sulfonate, and PFOS under conditions suitable for in-situ groundwater remediation, *Chemosphere*, 2016, **145**, 376-383.
81. Y. Qian, X. Guo, Y. Zhang, Y. Peng, P. Sun, C.-H. Huang, J. Niu, X. Zhou and J. C. Crittenden, Perfluorooctanoic acid degradation using UV–persulfate process: modeling of the degradation and chlorate formation, *Environ. Sci. Technol.*, 2015, **50**, 772-781.
82. T. A. Bruton and D. L. Sedlak, Treatment of Aqueous Film-Forming Foam by Heat-Activated Persulfate Under Conditions Representative of In Situ Chemical Oxidation, *Environ. Sci. Technol.*, 2017, **51**, 13878-13885.

83. K. C. Harding-Marjanovic, E. F. Houtz, S. Yi, J. A. Field, D. L. Sedlak and L. Alvarez-Cohen, Aerobic biotransformation of fluorotelomer thioether amido sulfonate (Lodyne) in AFFF-amended microcosms, *Environ. Sci. Technol.*, 2015, **49**, 7666-7674.
84. E. F. Houtz, C. P. Higgins, J. A. Field and D. L. Sedlak, Persistence of perfluoroalkyl acid precursors in AFFF-impacted groundwater and soil, *Environ. Sci. Technol.*, 2013, **47**, 8187-8195.
85. H. Park, C. D. Vecitis, J. Cheng, W. Choi, B. T. Mader and M. R. Hoffmann, Reductive defluorination of aqueous perfluorinated alkyl surfactants: effects of ionic headgroup and chain length, *J. Phy. Chem. A*. 2009, **113**, 690-696.
86. C. Blondel, P. Cacciani, C. Delsart and R. Trainham, High-resolution determination of the electron affinity of fluorine and bromine using crossed ion and laser beams, *Phy. Rev. A*. 1989, **40**, 3698.
87. Y. Qu, C.-J. Zhang, P. Chen, Q. Zhou and W.-X. Zhang, Effect of initial solution pH on photo-induced reductive decomposition of perfluorooctanoic acid, *Chemosphere*, 2014, **107**, 218-223.
88. C. Zhang, Y. Qu, X. Zhao and Q. Zhou, Photoinduced Reductive Decomposition of Perfluorooctanoic Acid in Water: Effect of Temperature and Ionic Strength, *CLEAN – Soil Air Water*. 2015, **43**, 223-228.
89. S. G. MAYHEW, The redox potential of dithionite and SO^{-2} from equilibrium reactions with flavodoxins, methyl viologen and hydrogen plus hydrogenase, *European J. Biochem.* 1978, **85**, 535-547.
90. S. Makarov, Novel trends in chemistry of sulfur-containing reductants, *Uspekhi Khimii*, 2001, **70**, 1005.

91. B. P. Vellanki, B. Batchelor and A. Abdel-Wahab, Advanced Reduction Processes: A New Class of Treatment Processes, *Environ. Eng. Sci.* 2013, **30**, 264-271.
92. M. Fischer and P. Warneck, Photodecomposition and photooxidation of hydrogen sulfite in aqueous solution, *J. Phy. Chem.* 1996, **100**, 15111-15117.
93. R. Lian, D. A. Oulianov, R. A. Crowell, I. A. Shkrob, X. Chen and S. E. Bradforth, Electron photodetachment from aqueous anions. 3. Dynamics of geminate pairs derived from photoexcitation of mono-vs polyatomic anions, *J. Phys. Chem. A.* 2006, **110**, 9071-9078.
94. X. Li, J. Ma, G. Liu, J. Fang, S. Yue, Y. Guan, L. Chen and X. Liu, Efficient reductive dechlorination of monochloroacetic acid by sulfite/UV process, *Environ. Sci. Technol.*, 2012, **46**, 7342-7349.
95. L. Huang, W. Dong and H. Hou, Investigation of the reactivity of hydrated electron toward perfluorinated carboxylates by laser flash photolysis, *Chem. Phy. Lett.* 2007, **436**, 124-128.
96. P. J. Krusic, A. A. Marchione and D. C. Roe, Gas-phase NMR studies of the thermolysis of perfluorooctanoic acid, *J. Fluorine Chem.* 2005, **126**, 1510-1516.
97. T. Yamada, P. H. Taylor, R. C. Buck, M. A. Kaiser and R. J. Giraud, Thermal degradation of fluorotelomer treated articles and related materials, *Chemosphere*, 2005, **61**, 974-984.
98. P. Taylor, T. Yamada, R. Striebich, J. Graham and R. Giraud, Investigation of waste incineration of fluorotelomer-based polymers as a potential source of PFOA in the environment, *Chemosphere*, 2014, **110**, 17-22.
99. P. J. Krusic and D. C. Roe, Gas-Phase NMR Technique for Studying the Thermolysis of Materials: Thermal Decomposition of Ammonium Perfluorooctanoate, *Anal. Chem.* 2004, **76**, 3800-3803.

100. K. Tuppurainen, I. Halonen, P. Ruokojärvi, J. Tarhanen and J. Ruuskanen, Formation of PCDDs and PCDFs in municipal waste incineration and its inhibition mechanisms: a review, *Chemosphere*, 1998, **36**, 1493-1511.
101. G. McKay, Dioxin characterisation, formation and minimisation during municipal solid waste (MSW) incineration, *Chem. Eng. J.* 2002, **86**, 343-368.
102. F. Wang and K. Shih, Adsorption of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) on alumina: Influence of solution pH and cations, *Water Res.* 2011, **45**, 2925-2930.
103. Y.-C. Lee, S.-L. Lo, J. Kuo and Y.-L. Lin, Persulfate oxidation of perfluorooctanoic acid under the temperatures of 20–40 C, *Chem. Eng. J.* 2012, **198**, 27-32.
104. Y. T. Didenko, W. B. McNamara and K. S. Suslick, Hot Spot Conditions during Cavitation in Water, *J. American Chem. Soc.* 1999, **121**, 5817-5818.
105. E. Ciawi, J. Rae, M. Ashokkumar and F. Grieser, Determination of Temperatures within Acoustically Generated Bubbles in Aqueous Solutions at Different Ultrasound Frequencies, *J. Phy. Chem. B.* 2006, **110**, 13656-13660.
106. M. Ashokkumar and F. Grieser, A Comparison between Multibubble Sonoluminescence Intensity and the Temperature within Cavitation Bubbles, *J. American Chem. Soc.* 2005, **127**, 5326-5327.
107. N. C. Eddingsaas and K. S. Suslick, Evidence for a Plasma Core during Multibubble Sonoluminescence in Sulfuric Acid, *J. American Chem. Soc.* 2007, **129**, 3838-3839.
108. H.-M. Hung and M. R. Hoffmann, Kinetics and Mechanism of the Sonolytic Degradation of Chlorinated Hydrocarbons: Frequency Effects, *J. Phys. Chem. A.* 1999, **103**, 2734-2739.

109. C. D. Vecitis, H. Park, J. Cheng, B. T. Mader and M. R. Hoffmann, Enhancement of Perfluorooctanoate and Perfluorooctanesulfonate Activity at Acoustic Cavitation Bubble Interfaces, *J. Phy. Chem. C*. 2008, **112**, 16850-16857.
110. T. Y. Campbell, California Institute of Technology, 2010.
111. P. G. Jessop and W. Leitner, Supercritical Fluids as Media for Chemical Reactions, *Chem. Syn. Supercrit. Fluid*. 1999, 1-36.
112. H. Hori, M. Murayama, T. Sano and S. Kutsuna, Decomposition of Perfluorinated Ion-Exchange Membrane to Fluoride Ions Using Zerovalent Metals in Subcritical Water, *Indust. Eng. Chem. Res.* 2010, **49**, 464-471.
113. H. Hori, Y. Nagaoka, T. Sano and S. Kutsuna, Iron-induced decomposition of perfluorohexanesulfonate in sub-and supercritical water, *Chemosphere*, 2008, **70**, 800-806.
114. H. Hori, Y. Noda, A. Takahashi and T. Sakamoto, Decomposition of perfluorinated ionic liquid anions to fluoride ions in subcritical and supercritical water with iron-based reducing agents, *Indust. Eng. Chem. Res.* 2013, **52**, 13622-13628.
115. H. Hori, H. Saito, H. Sakai, T. Kitahara and T. Sakamoto, Efficient decomposition of a new fluorochemical surfactant: Perfluoroalkane disulfonate to fluoride ions in subcritical and supercritical water, *Chemosphere*, 2015, **129**, 27-32.
116. Y. Lee, S. Lo, J. Kuo and C. Hsieh, Decomposition of perfluorooctanoic acid by microwaveactivated persulfate: Effects of temperature, pH, and chloride ions, *Front. Environ. Sci. Eng.* 2012, **6**, 17-25.
117. M. Park, S. Komarneni and R. Roy, Microwave-hydrothermal decomposition of chlorinated organic compounds, *Materials Letters*, 2000, **43**, 259-263.
118. J. R. Jones, P. B. Langham and S.-Y. Lu, Microwave-enhanced tritium-hydrogen exchange: application to radioactive waste reduction, *Green Chem.* 2002, **4**, 464-466.

119. B. R. Locke, M. Sato, P. Sunka, M. R. Hoffmann and J. S. Chang, Electrohydraulic Discharge and Nonthermal Plasma for Water Treatment, *Indust. Eng. Chem. Res.* 2006, **45**, 882-905.
120. M. Magureanu, D. Piroi, N. B. Mandache, V. David, A. Medvedovici and V. I. Parvulescu, Degradation of pharmaceutical compound pentoxifylline in water by non-thermal plasma treatment, *Water Res.* 2010, **44**, 3445-3453.
121. K. Yasuoka, K. Sasaki and R. Hayashi, An energy-efficient process for decomposing perfluorooctanoic and perfluorooctane sulfonic acids using dc plasmas generated within gas bubbles, *Plasma Source. Sci. Technol.* 2011, **20**, 034009.
122. Y. Matsuya, N. Takeuchi and K. Yasuoka, Relationship Between Reaction Rate of Perfluorocarboxylic Acid Decomposition at a Plasma–Liquid Interface and Adsorbed Amount, *Electrical Engin. Japan*, 2014, **188**, 1-8.
123. N. Takeuchi, Y. Kitagawa, A. Kosugi, K. Tachibana, H. Obo and K. Yasuoka, Plasma–liquid interfacial reaction in decomposition of perfluoro surfactants, *Journal of Physics D: Appl. Physic.* 2013, **47**, 045203.
124. R. Hayashi, H. Obo, N. Takeuchi and K. Yasuoka, Decomposition of Perfluorinated Compounds in Water by DC Plasma within Oxygen Bubbles, *Electrical Eng. Japan*, 2015, **190**, 9-16.
125. N. N. Mahamuni and Y. G. Adewuyi, Advanced oxidation processes (AOPs) involving ultrasound for waste water treatment: A review with emphasis on cost estimation, *Ultrason. Sonochem.* 2010, **17**, 990-1003.
126. D. Kriens and K. Kessler, Investigation of perfluorochemical (PFC) contamination in Minnesota Phase One, 2006.

127. X. Chen, X. Xia, X. Wang, J. Qiao and H. Chen, A comparative study on sorption of perfluorooctane sulfonate (PFOS) by chars, ash and carbon nanotubes, *Chemosphere*, 2011, **83**, 1313-1319.
128. S. Deng, Q. Zhang, Y. Nie, H. Wei, B. Wang, J. Huang, G. Yu and B. Xing, Sorption mechanisms of perfluorinated compounds on carbon nanotubes, *Environ. Pollut.* 2012, **168**, 138-144.
129. S. Deng, Y. Bei, X. Lu, Z. Du, B. Wang, Y. Wang, J. Huang and G. Yu, Effect of co-existing organic compounds on adsorption of perfluorinated compounds onto carbon nanotubes, *Front. Environ. Sci. Eng.* 2015, **9**, 784-792.
130. Y. Bei, S. Deng, Z. Du, B. Wang, J. Huang and G. Yu, Adsorption of perfluorooctane sulfonate on carbon nanotubes: influence of pH and competitive ions, *Water Sci. Technol.* 2014, **69**, 1489-1495.
131. S. T. M. L. D. Senevirathna, S. Tanaka, S. Fujii, C. Kunacheva, H. Harada, B. H. A. K. T. Ariyadasa and B. R. Shivakoti, Adsorption of perfluorooctane sulfonate (n-PFOS) onto non ion-exchange polymers and granular activated carbon: Batch and column test, *Desalination*, 2010, **260**, 29-33.
132. Q. Yu, R. Zhang, S. Deng, J. Huang and G. Yu, Sorption of perfluorooctane sulfonate and perfluorooctanoate on activated carbons and resin: Kinetic and isotherm study, *Water Res.* 2009, **43**, 1150-1158.
133. J. Yu and J. Hu, Adsorption of Perfluorinated Compounds onto Activated Carbon and Activated Sludge, *J. Environ. Eng.* 2011, **137**, 945-951.
134. M. C. Hansen, M. H. Børresen, M. Schlabach and G. Cornelissen, Sorption of perfluorinated compounds from contaminated water to activated carbon, *J. Soils Sediment.* 2010, **10**, 179-185.

135. Y. Qu, C. Zhang, F. Li, X. Bo, G. Liu and Q. Zhou, Equilibrium and kinetics study on the adsorption of perfluorooctanoic acid from aqueous solution onto powdered activated carbon, *J. Hazard. Mater.* 2009, **169**, 146-152.
136. Q. Zhang, S. Deng, G. Yu and J. Huang, Removal of perfluorooctane sulfonate from aqueous solution by crosslinked chitosan beads: Sorption kinetics and uptake mechanism, *Bioresour. Technol.* 2011, **102**, 2265-2271.
137. P. Das, V. Kambala, M. Mallavarapu and R. Naidu, Remediation of perfluorooctane sulfonate in contaminated soils by modified clay adsorbent—a risk-based approach, *Water Air Soil Pollut.* 2013, **224**, 1714.
138. Q. Zhou, S. Deng, Q. Yu, Q. Zhang, G. Yu, J. Huang and H. He, Sorption of perfluorooctane sulfonate on organo-montmorillonites, *Chemosphere*, 2010, **78**, 688-694.
139. S. N. S. Ismail and L. A. Manaf, The challenge of future landfill: A case study of Malaysia, *J. Toxicol.* 2013, **5**, 2400-2407.
140. J. W. Washington and T. M. Jenkins, Abiotic Hydrolysis of Fluorotelomer-Based Polymers as a Source of Perfluorocarboxylates at the Global Scale, *Environ. Sci. Technol.*, 2015, **49**, 14129-14135.
141. K. Rankin, H. Lee, P. J. Tseng and S. A. Mabury, Investigating the Biodegradability of a Fluorotelomer-Based Acrylate Polymer in a Soil–Plant Microcosm by Indirect and Direct Analysis, *Environ. Sci. Technol.*, 2014, **48**, 12783-12790.