



## **Final Draft of the original manuscript**

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**Persulfate-based degradation of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) in aqueous solution: Review on influences, mechanisms and prospective.**  
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## 1 **1. Introduction**

2 Per- and poly-fluoroalkyl substances (PFAS) are a series of synthetic organics with a wide range  
3 of industrial and consumer applications [1]. These perfluorinated organics are characterized by unique  
4 properties, including superior surface-tension-lowering properties and resistance to thermal and  
5 chemical degradation [1, 2]. PFOA and PFOS are highlighted as the most studied and frequently found  
6 PFAS in various environmental matrices [3]. It is evident that PFOA and PFOS are persistent,  
7 bio-accumulative and ubiquitously distributed in aquatic environments [4-6]. The wide distribution  
8 constitutes a considerable threat to ecological security [7-10] and human health [11]. A comprehensive  
9 summary of current exposure fate, and potential health effects of contaminants in polar bears from the  
10 circumpolar Arctic reported that PFOS acted as one of the main pollutants in selected polar bears [12].  
11 Moreover, the human health risks of PFOA and PFOS have gained increasing concern during the past  
12 decade [13-16]. Bioaccumulation of PFOA and PFOS in human bodies could be ascribed to food and  
13 drinking water [14]. PFAS concentrations were summarized based on various food items, including  
14 vegetables, dairy products, beverages, eggs, meat products, fish, and shellfish, indicating that the  
15 dietary PFAS exposure was mostly through fish and shellfish consumption [17]. Similar phenomena  
16 were observed in an investigation of five different categories of typical South Korean seafood [18]. As  
17 a result, the elimination of PFOA and PFOS in the aqueous environment has become urgent.

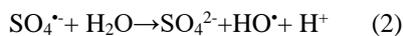
18 There have been numerous attempts at PFOA and PFOS removal from aqueous solution, including  
19 adsorption [19-23], coagulation [24], reverse osmosis [25, 26], thermal treatment [22, 27], sonolysis  
20 [28-30], electron beam [31], photocatalysis [32], advanced oxidation/reduction [33] and so on.  
21 Adsorption, coagulation and reverse osmosis could not decompose PFOA and PFOS and currently  
22 require further treatments of hazardous solid wastes or concentrated wastewater, which are expensive

1 and difficult. In addition, thermal treatment, sonolysis, electron beam and photocatalysis require  
2 specific equipment or harsh reaction conditions. Among these options, Advanced Oxidation Processes  
3 (AOPs) for water treatment processes are characterized by occurring at room temperature, and driven  
4 by the in-situ generation of a powerful oxidizing agent, such as hydroxyl radicals, at a sufficient  
5 concentration for organic decomposition in aqueous environment [33, 34]. In recent years, persulfate  
6 has attracted great attention as an alternative to  $\text{H}_2\text{O}_2$  for AOPs due to its high redox potential ( $\text{SO}_4^{\cdot-}$ ,  
7 2.5V~3.1V) and longer lifetime than  $\cdot\text{OH}$  [35-38]. Persulfate-based (including peroxymonosulfate (PMS)  
8 and peroxydisulfate (PDS)) oxidation is easy to operate in both ex-situ and in-situ treatments and could  
9 be performed with various activation methods according to initial conditions [39]. There has been a  
10 series of studies concerning on persulfate-based degradation of PFOA and PFOS with various  
11 activation methods [40-43]. Because of their strong C-F bonds (116 kcal/mol) [40], the decomposition  
12 of PFOA and PFOS is more complicated than that of other organic contaminants in persulfate-based  
13 processes. Although there have been several reviews involving PFAS removal, persulfate-based  
14 oxidation has only been briefly mentioned and discussed in passing as acting as one of numerous  
15 techniques [44, 45]. The influences, mechanisms and potential of persulfate oxidation, and the details  
16 of PFOA and PFOS decomposition in persulfate-based processes, have not been integrally reviewed. In  
17 addition, practical feasibility and environmental implications of byproducts have not been discussed in  
18 these reviews. This review has following objectives: (1) to summarize the application and mechanisms  
19 of present persulfate activation methods in PFOA and PFOS decomposition; (2) to summarize, analyze  
20 and compare the factors influencing the removal efficiency; (3) to summarize the detailed degradation  
21 mechanisms of PFOA and PFOS and analyze the economic feasibility and practical considerations of  
22 persulfate oxidation; (4) to identify knowledge gaps and research required in the near future.

## 2. Persulfate activation methods for PFOA and PFOS degradation

### 2.1. Heat activation

Persulfate forms two sulfate radicals through scission of the peroxide bond resulting from absorption of heat energy (Eq. (1)) [46]. Thermal energy input can cause fission of the O-O bond in persulfate, resulting in sulfate radicals [46]. The activation energies for the reaction of persulfate are different in neutral, basic and acidic conditions based on previous studies [47]. Some sulfate radicals can react with H<sub>2</sub>O to form hydroxyl radicals via Eq.(2) [48]. The reaction of sulfate radicals with water is quite slow in most reaction systems with a reaction rate of below  $2 \times 10^{-3} \text{ s}^{-1}$  [48]. But the reaction (Eq.(2)) proceeds quickly at higher temperature, indicating that temperature could significantly accelerate its reaction rate [49].



Heat activated persulfate oxidation was frequently used in PFOA and PFOS degradation due to convenient operation [50-52]. A complete defluorination of 0.1 mM PFOA was observed after 18 h using persulfate activated by heat (100 mM Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and T = 70 °C) [53]. To investigate the potential of heat-activated persulfate for remediating aqueous film-forming foam contamination in groundwater, an in situ chemical oxidation trial was conducted [54]. It was observed that fluorotelomer- and perfluoroalkyl sulfonamide-based polyfluorinated compounds were transformed to perfluorinated carboxylic acids [54]. In particular, perfluorinated carboxylic acids could be degraded further with time [54]. Various activation methods including heat, ultraviolet, Fe<sup>2+</sup> and ultrasound were compared for PFOS removal using persulfate oxidation, indicating that the highest defluorination efficiency was achieved by heat activation (PFOS: 0.186 mM; K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>: 18.5 mM; pH: 7.0) [55].

## 2.2. Microwave activation

Microwave (MW) radiation has gained a great deal of attention owing to the molecular-level heating, which leads to homogeneous and quick thermal reactions [56]. Concerning the mechanism of microwave radiation, it has been generally assumed thermal and non-thermal effects in microwave radiation [57]. Compared with heating with an electric oven, microwave energy was reported to probably induce molecular motion by the rotation of dipoles and migration of ions, resulting in non-thermal effect which could increase the removal to some extent [56]. The microwave-hydrothermal treatment was found to accelerate the decomposition rates of the chlorinated compounds about 4-6 times faster than the hydrothermal treatment itself ( $C_0=25\text{mM}$ ,  $T=150^\circ\text{C}$  and  $190^\circ\text{C}$ ,  $C_{\text{NaOH}}=0.1\text{ M}$  and  $2.5\text{M}$ )[58]. The phenomenon was mainly attributed to non-thermal effects of microwave. Additionally, microwave was applied to activate persulfate for removal of organic pollutants [43, 59, 60]. On one hand, the thermal effects of microwave could cause fission of the O-O bond in persulfate [61]. On the other hand, the non-thermal effects of microwave was reported to probably induce molecular motion by the rotation of dipoles and migration of ions, which was believed to accelerate the fission of the O-O bond in persulfate and cause C-C bond cleavage [43].

The microwave-hydrothermal activated persulfate decomposition was effective for PFOA and the C2-C7 perfluoroalkyl groups [59, 60]. As for sewage sludge containing PFOA, the degradation products of PFOA were below quantification limits in all sludge samples after microwave heating-assisted persulfate oxidation [61]. In addition, microwave was employed to assist the decomposition of PFOA using iron-activated persulfate oxidation, resulting in 67.6% PFOA removal and 22.5% defluorination efficiency [43]. An adequate amount of energy is provided by microwave treatment to cleave C-C bonds without causing depolymerisation and the microwave-hydrothermal treatment can lead to efficient

1 energy conversion and significant savings (50%) in energy consumption [43]. The microwave  
2 enhancement could be probably contributed to heat activation, C-C bond cleavage and mass transfer  
3 enhancement [43].

### 4 **2.3. Ultraviolet activation**

5 Ultraviolet irradiation, an effective method of water disinfection, can be considered as a form of  
6 energy [62]. Persulfate can be activated via ultraviolet light forming sulfate radicals (Eq. (3)) [46]. The  
7 ultraviolet energy breaks the O-O bond, similar to heat-activated persulfate, and a quantum yield of unity  
8 has been proven for acidic, basic, and neutral conditions [63]. Quantum yield is an important factor for  
9 characterizing the activation of persulfate and the ultraviolet wavelength has significant influence on  
10 the quantum yields [39]. In general, 254 nm is usually used as the radiation wavelength for persulfate  
11 [39].

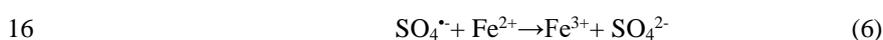
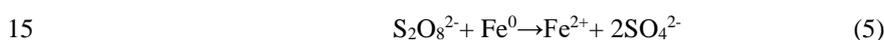
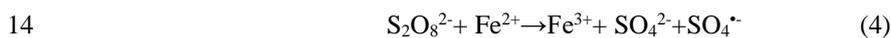


13 Ultraviolet activated persulfate oxidation has been widely applied for the degradation of various  
14 organic pollutants including PFOS and PFOA [64-66]. A comparison was carried out between GenX  
15 (hexafluoropropylene oxide dimer acid, a PFOA substitute) and PFOA using ultraviolet activated  
16 persulfate oxidation [66]. The results indicated that <5% GenX was oxidized after 3 h in ultraviolet  
17 activated persulfate system, which was much lower than ~27% for PFOA [66]. Meanwhile, it was noted  
18 that only <10% PFOA was oxidized after 3 h in single ultraviolet irradiation. The molecular structure of  
19 PFOA could be effectively cleaved by ultraviolet activated persulfate oxidation, while the side CF<sub>3</sub>- at  
20 the α-carbon probably acts as an effective barrier that prevents GenX from being cleaved by SO<sub>4</sub><sup>•-</sup> or  
21 •OH [66]. The destruction of PFOA using ultraviolet and persulfate were investigated to figure out the  
22 potential influences and a first-principles kinetic model was built to simulate PFOA destruction in

1 various matrixes [67]. Similarly, PFOS was effectively defluorinated in the ultraviolet /  $K_2S_2O_8$  system  
 2 with an apparent rate constant of  $0.162\text{ h}^{-1}$  [55]. Additionally, PFOA was jointly decomposed through  
 3 185 nm ultraviolet light photolysis and initiation of sulfate radicals, mainly due to the strong absorption  
 4 of PFOA from deep UV-region to 220 nm [65].

#### 5 **2.4. Iron activation**

6 Iron, the most widely studied metal, is an effective activator, relatively non-toxic, environmentally  
 7 friendly, and more cost effective than other transition metals [68]. Ferrous iron ( $Fe^{2+}$ ) and zero-valent  
 8 iron (ZVI) are both capable to activate persulfate to form the sulfate radical via the pathway of Eq. 4 and  
 9 Eq. 5. [69]. The activation of persulfate through dissolved  $Fe^{2+}$  requires lower activation energy (i.e.,  
 10  $14.8\text{ kcal}\cdot\text{mol}^{-1}$ ) compared to other activation techniques [35]. Insufficient iron concentration causes  
 11 inefficient persulfate usage, while too much  $Fe^{2+}$  results in the iron scavenging the sulfate radical via Eq.  
 12 5 [70]. Therefore, the ability of  $Fe^{2+}$  activated persulfate process is limited by the fast conversion of  
 13  $Fe^{2+}$  to  $Fe^{3+}$  after persulfate activation [35].



17 Though iron activated persulfate oxidation has been widely utilized to degrade some organic  
 18 contaminants [46, 69, 71], only a few studies have focused on PFOS and PFOA removal based on iron  
 19 activation. It was observed that introducing ZVI into the PFOA solution with persulfate addition would  
 20 lead to a synergetic effect with heat activation that accelerated the PFOA decomposition rate, and  
 21 reduced the reaction time [43]. Lower the activation energy of persulfate resulted from ferrous ions  
 22 formation [43]. PFOS was effectively defluorinated in the  $Fe^{2+}$  /  $K_2S_2O_8$  system and the apparent rate

1 constant was  $0.131 \text{ h}^{-1}$  [55]. It was interesting that  $\text{Fe}^{2+}$  activated persulfate decreased the transport of  
2 perfluoroalkyl acids in one-dimensional porous media columns, while permanganate and catalyzed  
3 hydrogen peroxide increased the transport of perfluoroalkyl acids [72]. Furthermore, iron has the  
4 potential for the modification of some catalysts. Iron-modified diatomite was synthesized to enhance the  
5 efficiency of PFOA decomposition in a hydrogen peroxide and persulfate system, achieving a removal  
6 rate of 83% [73].

## 7 **2.5. Ultrasound activation**

8 Ultrasound irradiation is characterized by extremely high temperatures (5000 K) inside the bubble  
9 or near the interphase and  $\bullet\text{OH}$  generation [74-78]. Pyrolysis induced by high temperatures is evidently  
10 capable to decompose organics in aqueous solution [79]. Chen et al. [28, 29] investigated the  
11 sonochemical degradation of PFOS and PFOA in groundwater, achieving effective removal even in the  
12 natural matrix. Simultaneously, the high temperatures near the interphase are effective and efficient for  
13 persulfate activation [78]. Persulfate can be activated via ultrasound forming sulfate radicals (Eq. (7))  
14 [80]. Therefore, the degradation mechanism of the sono-activated persulfate system is considered as the  
15 synergistic effects of thermal decomposition and free radical-induced reactions [81]. Besides, it is  
16 evident that ultrasound generates violent turbulence, which enhances the mass transfer in the solution  
17 [82]. The mass transfer enhancement is reasonably beneficial for accelerating the relevant reactions.



19 Up to now, sono-activated persulfate oxidation has been put into use to some PFOS and PFOA  
20 degradation [55, 80, 83]. It was found that the apparent rate constant of  $\text{SO}_4^{2-}$  in the ultrasound /  $\text{K}_2\text{S}_2\text{O}_8$   
21 system was  $0.026 \text{ h}^{-1}$  for PFOS removal [55]. When 10 mM persulfate was used, 51.2% of initial  
22 ammonium perfluorooctanoate ( $46.4 \mu\text{M}$ ) was decomposed and the defluorination ratio reached 11.15%

1 within 120 min reaction time [80]. Furthermore, a research was conducted to determine the effectiveness  
2 of ultrasonic irradiation and sodium persulfate oxidation of water contaminated with three  
3 perfluorosulfonates [83]. A combination of 25 mM  $\text{Na}_2\text{S}_2\text{O}_8$  and 120 minutes of ultrasonic irradiation  
4 (100W, 20 kHz) was found to cause greater defluorination in both PFOS and PFBS than with just one  
5 treatment process [83].

## 6 **2.6. Others**

7 As well as above-mentioned methods, there were some other activation methods that applied in  
8 persulfate oxidation of PFOS and PFOA. Under relatively low temperatures of 25-45°C, carbon activated  
9 persulfate oxidation of PFOA was evaluated for degradation enhancement, resulting in a high PFOA  
10 removal rate [42]. Similar phenomenon was found along with a chemisorption process [84]. It was  
11 found that 10-40% of the PFOA was removed at powdered activated carbon concentrations between  
12 200 and 1000 mg/L and an initial PFOA concentration of 0.5  $\mu\text{M}$  [84]. Moreover, electron beam  
13 technology has been used to treat refractory compounds as a radical-based advanced oxidation process  
14 [40]. Electron beam activated persulfate was applied for the PFOS degradation, achieving a removal rate  
15 of 79.8% with 5.0 mM  $\text{Na}_2\text{S}_2\text{O}_8$  and 100 kGy electron beam [40]. In spite of aqueous solution,  
16 mechanochemical destruction using persulfate was applied for the disposal of solid waste containing  
17 F53B ( $\text{C}_8\text{ClF}_{16}\text{O}_4\text{SK}$ , a PFOS alternative) [85]. F-53B removal rate and the defluorination ratio reached  
18 88% and 54% after 8 h of milling with 60 g balls at the best mass ratio [85]. Even so, some other  
19 activation methods (e.g. electrochemical activation and nano-carbon materials) which are not applied to  
20 treat PFOA and PFOS yet.

## 21 **2.7 Comparison of representative methods**

22 The comparison of mentioned activation methods was demonstrated in Table 1. It was obvious

1 that homogeneous / heterogeneous activations were both explored based on various mechanisms. The  
2 majority of homogeneous methods were dependent on energy consumption, which played a vital role in  
3 their economic feasibility. In spite of cost consideration, some energy-dependent methods (ultraviolet  
4 [67], ultrasound [83] and electron beam [40]) provide non-radical degradation paths, which are  
5 beneficial for PFOS and PFOA removal. Although persulfate-based degradation of PFOS and PFOA  
6 has attracted wide attention as an emerging alternative of traditional AOPs [44], few practical attempts  
7 are carried out in large scale projects. By now, several studies are found to simulate the scavenging and  
8 inhibiting effects of real PFAS contaminated matrixes. It was reported that the heat-activated persulfate  
9 oxidation efficiency decreased in the presence of natural aquifer solids [54, 86]. Even so, heat-activated  
10 persulfate could be employed in a treatment-train approach to reduce the contaminant mass in source  
11 zones as a complement to pump-and-treat remediation of PFAS [86]. The transport, sorption and fate of  
12 PFAS (including PFOA and PFOS) in porous medias were investigated to simulate in situ chemical  
13 oxidation of aqueous film-forming foam-impacted sites [72]. Overall, the knowledge of practical  
14 application is far from abundance and there is still a long way to go in this field.

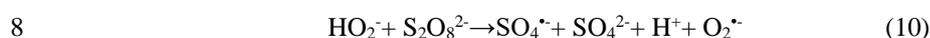
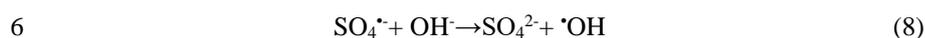
15 *Table 1*

### 16 **3. Influences of operational factors on the removal efficiency**

#### 17 **3.1. pH**

18 Generally, the pH value plays an important role in the degradation of contaminants in  $\text{SO}_4^{2-}$ -based  
19 systems [87]. The influences of pH on the degradation of PFOS and PFOA in the activated persulfate  
20 system have been frequently investigated. In fact, different results were presented based various  
21 experiments (Table 2), indicating different optimal pH values is in acidic [59] and alkaline [73] ranges,  
22 respectively. It was obvious that majority of the selected studies considered the acid pH as the optimal pH.

1 Higher PFOA removal was observed in at lower pHs in these studies and the mechanisms were ascribed  
 2 to acid catalyzation [88]. Similar phenomenon was found in a PFOS degradation study using various  
 3 activated methods [55]. Under alkaline conditions, sulfate radicals may react with OH<sup>-</sup> to form more  
 4 hydroxyl radicals (<sup>•</sup>OH) (Eq. (8)) [59]. It is obvious that SO<sub>4</sub><sup>•-</sup> has higher redox potential (2.5V~3.1V)  
 5 and longer lifetime than <sup>•</sup>OH [35].



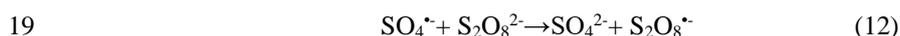
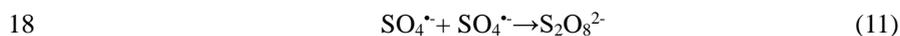
9 *Table 2*

10 Nevertheless, pH presented less influences on PFOA degradation when compared to temperature  
 11 [51]. The degradation of PFOA certainly showed an increasing trend at higher initial pH values (pH=9.2)  
 12 [51]. It was reported that low pH may enhance a radical-radical interaction, instead of radical-pollutant  
 13 reactions [89]. Similar phenomenon was found in a heterogeneous activation process. Homogenous  
 14 generation of superoxide radical anions (O<sub>2</sub><sup>•-</sup>, E<sup>0</sup>=-0.33V) and sulfate radicals by persulfate with  
 15 dissolved Fe<sup>2+</sup> ions at pH 12 for the decomposition of PFOA was not as effective as their heterogeneous  
 16 generation by persulfate with Fe-modified diatomite [73]. The enhancement of degradation in alkaline  
 17 conditions could be attributed to the radical creative reactions (Eq. (9-10)) [73]. In addition, the effects  
 18 of pH on heterogeneous activators cannot be ignored. Activated carbon was positively charged at pH <  
 19 pHPZC, and negatively charged at pH > pHPZC [42]. Overall, there is still a controversy about the  
 20 influences of pH condition on the degradation of PFOA and PFOS by persulfate-based oxidation.

### 21 **3.2. Initial persulfate dosage**

22 The initial persulfate concentration has a significant impact on the removal of organic pollutants in

1 the persulfate oxidation system. Most studies have reported that the removal rate increased with  
 2 increasing concentration of persulfate (Table 3). In a microwave-hydrothermal activated persulfate study,  
 3 the PFOA decomposition rate increased with increasing  $S_2O_8^{2-}$  doses especially at low dosage levels  
 4 (0-20 mM) [59]. The PFOA defluorination rate also kept increasing with an increment of persulfate dose  
 5 (0-50 mM) [59]. In the presence of ZVI, the similar phenomenon was observed at lower doses of  
 6 persulfate (0-10 mM) [43]. As for heat activation, the pseudo-first-order rate constants for PFOA  
 7 decomposition increased with the increasing persulfate concentration (0-50 mM), indicating that higher  
 8 persulfate concentration accelerated the oxidation process [50]. Furthermore, the enhancement of  
 9 degradation with increasing persulfate concentration was found in other activation systems, such as  
 10 activated carbon [42] and ultraviolet [90]. These results suggest that more sulfate radicals are produced  
 11 with increasing persulfate concentration, leading to more quickly degradation of PFOA. With one  
 12 exception, Hori et al. [91] found the photochemical reactivity increased when the initial concentration of  
 13  $S_2O_8^{2-}$  was increased from 0 mM to 26.8 mM, but no further increase in the PFOA decomposition rate  
 14 was observed with further increase in the initial concentration of  $S_2O_8^{2-}$ . It is evident that there is a limit  
 15 in the persulfate concentration enhancement for pollutant removal [92]. It is believed that the  
 16 recombination of excess  $SO_4^{\bullet-}$  radicals (Eq. (11)) and the reaction between  $SO_4^{\bullet-}$  and excess  $S_2O_8^{2-}$  (Eq.  
 17 (12)) are predominantly responsible for the phenomenon [91, 93].



20 *Table 3*

### 21 3.3. Temperature

22 Reaction temperature is a crucial variable for aqueous viscosity [94] and mass transfer coefficients

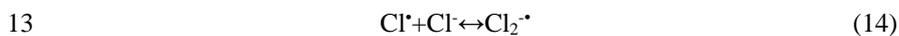
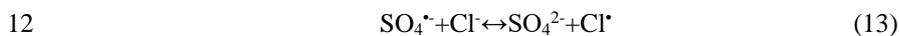
[95]. Meanwhile, higher temperature is beneficial for persulfate activation compared with the ambient temperature range [88]. Even at relatively low temperatures (20-40 °C), persulfate could be effectively activated to decompose PFOA [96]. The temperature influences have been noticed by a series of studies (Table 4). Generally, increasing temperature had a positive effect on PFOA and PFOS decomposition in the persulfate based system due to the acceleration of  $\text{SO}_4^{\bullet-}$  formation [50, 55]. With the reaction temperature increased from 25 to 85 °C, the fitting  $k$  of pseudo-first-order kinetic model increased from  $0.12 \times 10^{-2} \text{ h}^{-1}$  to  $9.15 \times 10^{-2} \text{ h}^{-1}$  [51]. Elevated temperature could effectively promote the PFOA decomposition and accelerated to reach a steady-state condition within a shorter reaction time when activated carbon was introduced to the persulfate oxidation system [42]. Nevertheless, Lee et al. [43, 60] found only 15.1% of PFOA in aqueous solution was decomposed rapidly within 30 min and no significant further decomposition was observed with time. The phenomenon could be attributed to the rapid release of a large quantity of radical oxidants in a short period and the exhaustion of the remaining persulfate ions [43, 60]. Besides, temperature may be vital for the performance of porous heterogeneous activators (e.g. activated carbon) due to its significant influence on adsorption processes [42]. For instance, PFOA adsorption onto activated carbon is an endothermic reaction and elevated temperatures accelerates the adsorption process [42]. The accelerated adsorption process may be beneficial for the PFOA/PFOS removal. Overall, increasing temperature has a positive effect on PFOA and PFOS degradation in a certain range.

*Table 4*

### 3.4. Coexisting ions and organic matters

There have been concerns about the effects of coexisting ions and organic matters on the PFOA and PFOS degradation efficiency of the persulfate based system due to their widely distribution in natural

1 water bodies [41, 60, 90]. Among the coexisting ions, Cl<sup>-</sup> attracted predominant attention probably due  
2 to its significant inhibition on PFOA decomposition [60, 67, 86]. It was noticed that K<sub>obs</sub> of PFOA  
3 decreased from 0.38 h<sup>-1</sup> to 0.14 h<sup>-1</sup> when chloride concentration increased from 0 M to 0.15 M [60]. The  
4 chemical reaction mechanism could be explained by Eq (13)-(15) [60]. PFOA removal decreased  
5 significantly at initial Cl<sup>-</sup> concentrations of 10-500 mM, with PFOA transformation accounting for just  
6 6% and 3% of initial PFOA at initial Cl<sup>-</sup> concentrations of 100 and 500 mM, respectively [86]. In  
7 addition, it was found that ClO<sub>3</sub><sup>-</sup> was generated in the presence of Cl<sup>-</sup> during the persulfate oxidation  
8 experiment [67]. Accordingly, Cl<sup>-</sup> must first produce ClO<sub>3</sub><sup>-</sup> before PFOA could be degraded [67]. Apart  
9 from Cl<sup>-</sup>, HCO<sub>3</sub><sup>-</sup> also showed a negative effect on PFOA degradation mainly due to the competition of  
10 carbonate species to react with SO<sub>4</sub><sup>•-</sup> [67]. Other coexisting inorganic ions have been rarely reported by  
11 now.



15 Meanwhile, coexisting organic matters cannot be ignored on account of their wide distribution in  
16 wastewater and natural waters [41, 90]. Humic acid is the main component of natural organic matters in  
17 various aqueous matrixes [97]. It is evident that humic acid is an oxidant consumer and a competitor  
18 with PFOA for SO<sub>4</sub><sup>•-</sup> [90]. In fact, humic acid can act as scavengers of SO<sub>4</sub><sup>•-</sup> and <sup>•</sup>OH with a  
19 significantly high rate constant and inhibition of PFOA degradation [90]. To explore the presence of  
20 dissolved gasoline components on persulfate oxidation of PFOA, the addition of ethylbenzene at  
21 almost 40 times the molar level of PFOA did not significantly affect PFOA oxidation rates [41]. On the  
22 whole, no positive effect is detected, and the influence of coexisting organic matters on PFOA

1 degradation depends on the type and concentration.

## 2 **4. Reaction mechanisms and pathways**

### 3 **4.1 The pathway of PFOS degradation**

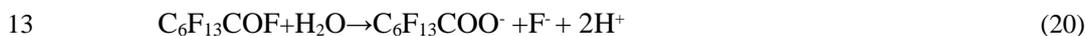
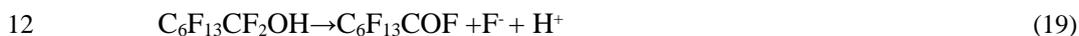
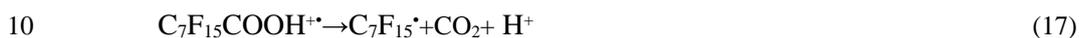
4 There were a series of studies in connection with the persulfate-based reaction mechanisms and  
5 pathways of PFOS and PFOA in the past decade. It was found that the first oxidative attack of PFOS by  
6 permanganate could occur at the C-S and C-C bonds [98]. Similarly, it is evident that the oxidation  
7 potential of  $\text{SO}_4^{\cdot-}$  is 2.5 eV-3.1 eV, lower than that of the C-F bond (3.6 eV) [35]. Therefore, the first  
8 oxidative attack of PFOS by  $\text{SO}_4^{\cdot-}$  could be deduced to occur at the C-S bonds [40, 55]. There was a  
9 consensus that PFOS could be converted to PFOA with a series of reactions as demonstrated in Fig.1  
10 [40, 55]. With the attack of  $\text{SO}_4^{\cdot-}$ , PFOS was converted to an unstable radical ( $\text{C}_8\text{F}_{17}^{\cdot}$ ) with an  
11 intermediate of  $\text{C}_8\text{F}_{17}\text{SO}_3^{\cdot}$ . In the subsequent reactions,  $\cdot\text{OH}$  could play a vital role for the formation of  
12  $\text{C}_8\text{F}_{17}\text{OH}$ , though it cannot induce the direct decomposition of PFOS [99]. And then,  $\text{C}_7\text{F}_{15}\text{COF}$  was  
13 formed with one HF unit missing due to the unstable alcohol form of  $\text{C}_n\text{F}_{2n+1}\text{OH}$  ( $\text{C}_8\text{F}_{17}\text{OH}$  in this step)  
14 [100]. After that,  $\text{C}_7\text{F}_{15}\text{COF}$  was converted to PFOA with an intermediate of  $\text{C}_7\text{F}_{15}\text{CF}(\text{OH})\text{O}^{\cdot}$  [40].  
15 During the process, another HF was eliminated with  $\cdot\text{OH}$  involvement [88]. The mechanisms for  
16 further decomposition of PFOS could be considered as same as that of PFOA, which will be discussed  
17 in the following.

18 *Fig.1*

### 19 **4.2 The pathway of PFOA degradation**

20 As for PFOA decomposition, the defluorination ratio is much lower than the corresponding PFOA  
21 degradation ratio, indicating that PFOA is not totally transformed into fluoride ions [60]. The reaction  
22 intermediates of PFOA were identified in the HPLC-MS spectra and several short-chain perfluoroalkyl

1 carboxylates (C2-C6) were the dominating byproducts [42, 43, 60]. The generated perfluoroalkyl  
 2 carboxylates were PFHpA (C<sub>6</sub>F<sub>13</sub>COOH), PFHeA (C<sub>5</sub>F<sub>11</sub>COOH), PFPeA (C<sub>4</sub>F<sub>9</sub>COOH), PFBA  
 3 (C<sub>3</sub>F<sub>7</sub>COOH) and PFPrA (C<sub>2</sub>F<sub>5</sub>COOH) [86, 88]. There were a series of reactions unveiling the  
 4 mechanisms of PFOA defluorination, with one CF<sub>2</sub> unit missing in each round (Fig.2) [40, 53, 88]. The  
 5 first round with one CF<sub>2</sub> unit missing could be evidently explained by Eq (16)-(20) [40, 88].  
 6 Decarboxylation and the unstable alcohol form were the predominant mechanisms as analyzed above.  
 7 Similar reactions were believed to occur continuously with sufficient sulfate radicals and hydroxyl  
 8 radicals until complete decomposition [88].



14 *Fig.2*

### 15 4.3 Environmental implications of proposed byproducts

16 To investigate the potential risks of byproducts from persulfate oxidation of PFOS and PFOA, rate  
 17 constants [67] and bioconcentration factors [101] of short-chain (C1-C6) perfluoroalkyl carboxylic  
 18 acids (PFCAs) were collected and compared (Table 5). It was observed that the rate constants increased  
 19 with a decrease in chain-length, which is consistent with a previous study about PFCAs decay by  
 20 electrochemical oxidation [67, 102]. In addition, the decomposition efficiency increased from 67.2%  
 21 (PFHpA) to 77.9% (TFA) and the defluorination efficiency increased from 23.2% (PFHpA) to 65.2%  
 22 (TFA) [59]. The existing data indicates that the decomposition efficiency and defluorination efficiency

1 increased with a decrease in chain-length for PFCA degradation with persulfate treatment [59].  
2 Therefore, it could be concluded that the byproducts could be effectively degraded with sufficient  $\text{SO}_4^{\cdot-}$   
3 supply. As for plant uptake characteristics, bioconcentration factors (BCFs) could be employed to  
4 reflect the plant availability of PFAS in aquatic macrophytes [101], which was consistent with a  
5 previous study [103]. As a whole, it was obvious that long-chain PFCA exhibited the higher BCFs  
6 compared with short-chain PFCA, indicating that short-chain PFCA presented lower plant availability.  
7 Undoubtedly, low plant availability of pollutants is beneficial for ecological security. Therefore, the  
8 byproducts of PFOS and PFOA degradation can be characterized by higher reaction rate with  $\text{SO}_4^{\cdot-}$ ,  
9 higher decomposition and defluorination efficiency, and lower plant availability compared with PFOS  
10 and PFOA.

11 *Table 5*

## 12 **5. Practical implications**

### 13 **5.1 Economic evaluation**

14 Economic feasibility is a crucial condition for a technique development from lab scale to practical  
15 application. Due to few available practical applications, we focused on the cost estimation of published  
16 laboratory studies. According to previous studies, energy and chemical costs were considered, while  
17 pumps, equipment, process control, analytical sampling, and labor were excluded [45, 104]. The energy  
18 cost was calculated using the electric energy per order (EE/O) parameter, which represents the energy  
19 in kWh needed to degrade a contaminant by an order of magnitude in a unit volume ( $1 \text{ m}^3$ ) of  
20 contaminated water [45, 104]. Chemical cost was based on the chemical demand ( $\text{kg}/\text{m}^3$ ), which was  
21 obtained from optimum concentrations [45, 104]. In addition,  $t_{90}$  means the required time to degrade  
22 90% of contaminant and  $k$  is the rate constant. The energy cost was calculated based on the US average

1 electricity rate (US \$0.09/kWh) and the chemical price was obtained from Alibaba [45, 105]. Total cost  
2 was presented for two methods based on per ton water and per gram PFAS, respectively.

3 Based on limited previous lab-scale studies with detailed energy input and chemical cost, several  
4 comments were outlined according to Table 6.

5 a) Costs of low-concentration treatments were notably higher than those of high-concentration  
6 treatments.

7 b) Energy cost rather than chemical cost took a dominating share of the total cost.

8 c) Heat activation achieved greater PFOS degradation efficiency than other activation  
9 methods.

10 d) Chemical activation (e.g.  $\text{Fe}^{2+}$ ) presented the lowest cost among the existing activation methods  
11 due to the low energy expense.

12 *Table 6*

13 It should be noted that there was still a huge gap between this cost estimation and full-scale  
14 application. Infrastructure, operation and labor management are vital factors in an actual project. By  
15 now, there is no sufficient data to assess the cost details of persulfate oxidation for PFOS and PFOA  
16 degradation.

17 **5.2 Practical consideration**

18 Undoubtedly, persulfate-based oxidation is a promising technique for PFOS and PFOA  
19 degradation due to its outstanding advantages, such as high redox potential, convenient storage and  
20 transportation, longevity and non-selective degradation [78]. More practical attempts are urgently  
21 needed to promote the development of persulfate-based techniques. Persulfate-based oxidation needs to  
22 be reasonably applied into practical projects according to the specific circumstances. A series of vital

1 factors should be taken into consideration before or during the future field attempts.

2 a) Cost estimation. Field application cost commonly consists of energy consumption, chemical  
3 expenditure, infrastructure, equipment, labor and so on, which is definitely more complicated than lab  
4 studies [45, 104]. Project budget can be employed to outline the entire necessary expenditures in a real  
5 project.

6 b) Persulfate dose. Pollutant dose, coexisting ions and organic matters, mixing uniformity,  
7 temperature, and pH should be taken into consideration in the estimation of persulfate dose, rather than  
8 simple calculation of pollutant mass balance. Water quality investigation needs to be finished and  
9 simulation manipulation trials are necessary for actual persulfate dose confirmation. Generally, extra  
10 dose based on the calculated dose is indispensable due to less guaranteed mixing uniformity and  
11 impurities.

12 c) Applicability. Persulfate oxidation could not be applied everywhere polluted by PFOS or PFOA.  
13 The technological choice usually depends on technical cost and technical maturity. If the concentration  
14 of PFOS or PFOA is extremely low, the economic feasibility of persulfate oxidation would be  
15 uncompetitive compared with other techniques. If persulfate oxidation acts as a phase in a multiple  
16 process, it may be effective for PFOS and PFOA removal.

17 d) Activation method. As we know, the activation method depends on technical cost and  
18 application scenarios. For PFOS and PFOA removal from underground water, chemical activation (e.g.  
19  $\text{Fe}^{2+}$ ) may perform better than energy activation (e.g. ultrasound, heat and ultraviolet) due to the cost  
20 and mixing uniformity consideration. As for wastewater plant, energy activation is competitive based  
21 on its high efficiency and controlled conditions.

## 22 **6. Knowledge gaps and research needs**

1           Although persulfate-based PFOS and PFOA decomposition is a promising approach for effective  
2 degradation, there is still a long way to go for practical application. The research of persulfate-based  
3 PFOS and PFOA decomposition is not abundant and more detailed studies are needed in the near future.  
4 Based on the literature review and our research experience, several suggestions about knowledge gaps  
5 and research needs are provided as follows.

6           a) The oxidation process is time consuming and the removal rate is still not satisfied. The  
7 decomposition process of PFOA was reported to take over 6 h [67] and PFOS needed even more time,  
8 much longer than other organic pollutants using persulfate oxidation [39, 106]. More efficient  
9 approaches (e.g. catalysts) are urgently needed to accelerate the reaction process and enhance the  
10 decomposition rate of PFOS and PFOA in the persulfate-based system. Some synergistic techniques,  
11 such as plasma, ultrasound and so on, are potential for enhancing decomposition.

12           b) The coexisting ions are not sufficiently analyzed. Until now, only a few coexisting ions  
13 including  $\text{Cl}^-$  and  $\text{HCO}_3^-$  were investigated. There are numerous types of ions in wastewater and natural  
14 waters and the influences cannot be ignored. More coexisting ions ( $\text{NO}_3^-$ ,  $\text{HPO}_4^{2-}$ , ) should be  
15 concerned as well as the ion products. The influences of coexisting ions on the priority of relevant  
16 reactions are beneficial for understanding the mechanisms in real conditions.

17           c) The coexisting organic matters have not been covered due to the component complexity of  
18 wastewater and natural waters. Apart from humic acid, other organics probably compete with PFOS  
19 and PFOA for reactive radicals and the underlying mechanisms are valuable for large-scale practical  
20 application. However, the relevant information is very limited. In spite of humic acid, some other  
21 coexisting organics could be taken into consideration. The coexisting organics may affect PFOS and  
22 PFOA decomposition through competition of reactive radicals.

1 d) The ion accumulation would be observed due to the unavoidable formation of  $F^-$  and  $SO_4^{2-}$ . The  
2 influence of these ion products on the reaction processes is unclear, especially when the concentrations  
3 increase to certain levels. The influences of  $F^-$  and  $SO_4^{2-}$  accumulation on reaction processes need to be  
4 explored. Multi-angle investigations are necessary for further understanding the interaction  
5 mechanisms. Novel approaches need to be proposed for controlling salt accumulation. In addition, The  
6 emission of  $F^-$  and  $SO_4^{2-}$  into natural waters is restricted due to a series of national water quality  
7 standards.

8 e) The majority of previous studies are focused on lab-scale investigations rather than pilot-scale  
9 and full-scale studies. Actual aqueous circumstance is more complicated than lab conditions. More  
10 practical attempts (e.g., pilot-scale and full-scale studies) are urgently needed to promote the  
11 development of persulfate-based techniques for actual water purification.

12 f) There are rare studies focused on the cost evaluation and optimization of persulfate-based PFOS  
13 and PFOA decomposition. The collaborative optimization of variables can not be found in the present  
14 literatures. Meanwhile, the economic consideration should never be ignored when large-scale  
15 application is carried forward. Optimization models should be introduced to analyze the variables of  
16 PFOS and PFOA degradation. In this way, optimal removal efficiency is obtained in the selected  
17 variable range. In addition, the economic cost of persulfate oxidation should be considered and  
18 compared with other treatments.

## 19 **7. Summary and conclusions**

20 This review has presented the current development of persulfate-based degradation of PFOS and  
21 PFOA. Persulfate activation methods, including heat, microwave, iron, ultrasound and others, are  
22 summarized for enhanced removal of PFOS and PFOA. The operational factors influencing the

1 removal efficiency, including pH, initial persulfate dosage, temperature, coexisting inorganic anions  
2 and organic matters, are analyzed to give detailed information for further studies. There is still a  
3 controversy about the influences of pH condition on PFOA and PFOS degradation using persulfate-based  
4 processes. As for initial persulfate dosages, there is a limit in persulfate concentration enhancement for  
5 PFOS and PFOA removal. The recombination of excess  $\text{SO}_4^{\cdot-}$  radicals and the reaction between  $\text{SO}_4^{\cdot-}$   
6 and excess  $\text{S}_2\text{O}_8^{2-}$  are mainly responsible for the limit. Similarly, increasing temperature has a positive  
7 effect on PFOA and PFOS decomposition in a certain range. Apart from  $\text{Cl}^-$  and  $\text{HCO}_3^-$ , other coexisting  
8 inorganic ions have been rarely reported by now. As for coexisting organic matters, their influence on  
9 PFOA degradation depends on the types and concentrations of these organic matters. The  
10 persulfate-based reaction mechanisms and pathways of PFOS and PFOA are also reviewed. PFOS  
11 can be converted to PFOA with a series of reactions. For PFOA defluorination, there are several  
12 reactions unveiling the mechanisms, with one  $\text{CF}_2$  unit missing each round and similar reactions are  
13 believed to occur continuously with sufficient sulfate radicals and hydroxyl radicals. Decarboxylation  
14 and the unstable alcohol form of  $\text{C}_n\text{F}_{2n+1}\text{OH}$  are the predominant mechanisms of PFOS and PFOA  
15 defluorination. Although there are several important knowledge gaps for further applications, persulfate  
16 oxidation is undoubtedly a promising alternative for PFOS and PFOA removal.

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1 **Table 1** Comparison of selected activation methods.

Activation methods	Homogeneous/heterogeneous	PFOS/PFOA	Energy dependency	Mechanisms	Practical attempt	Ref.
Heat	Homogeneous	PFOS, PFOA	Yes	Radical	Yes	[41, 54, 86]
Microwave	Homogeneous	PFOA	Yes	Radical	No	[60]
Ultraviolet	Homogeneous	PFOA	Yes	Radical, non-radical	No	[67]
Iron	Heterogeneous (Fe <sup>0</sup> ) Homogeneous (Fe <sup>2+</sup> )	PFOA	No	Radical	Yes	[72]
Ultrasound	Homogeneous	PFOS, PFOA	Yes	Radical, non-radical	No	[83]
Activated carbon	Heterogeneous	PFOA	No	Radical	No	[42]
Electron beam	Homogeneous	PFOS	Yes	Radical, non-radical	No	[40]

2

1 **Table 2** Comparison of pH effects in activated persulfate oxidation literatures.

Analytes	Initial pH range	Optimal pH	Activation methods	Ref.
PFOA	2.0, 3.6, 8.8, 11.5	2.0	Microwave-hydrothermal	[59]
PFOA	2.5, 6.6, 8.8, 10.5	2.5	Microwave-hydrothermal	[60]
PFOA	2.5, 3.6, 7.1, 11.0	2.5	Relatively low temperatures	[96]
PFOA	2.5, 3.8, 7.1, 11.0	2.5	Activated carbon	[42]
PFOA	3.0, 9.0, 12.0	12.0	Iron-modified diatomite	[73]
PFOA	2.0, 2.5, 2.9	2.0	Heat	[88]
PFOA	1.0, 2.0, 3.0, 6.0, 8.0	1.0	Heat	[86]
PFOA	2.5, 4.1, 5.3, 7.1, 9.2	9.2	Heat	[51]
PFOS	3.0, 6.0, 11.0	3.0	Ultraviolet, ultrasound, heat, Fe <sup>2+</sup>	[55]

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1 **Table 3** Optimal persulfate dosages in activated persulfate oxidation literatures.

Analytes	Dosage range (mM)	Initial analyte concentration ( $\mu\text{M}$ )	Optimal dosage (mM)	Activation methods	Ref.
PFOA	0-50	1350	26.8	Xenon-mercury lamp	[91]
PFOA	0-50	253.8	50.0	Microwave-hydrothermal	[59]
PFOA	0-50	3.74	50.0	Heat	[50]
PFOA	0, 1.0, 5.0, 10.0	240.7	10.0	Microwave-hydrothermal and ZVI	[43]
PFOA	0-200	241.5	200	Relatively low temperatures	[96]
PFOA	0-10	0.50	10.0	Heat	[51]
PFOA	6.03, 12.06, 24.12, 36.18, 60.3	120.6	60.3	Activated carbon	[42]
PFOA	4.2, 8.4, 21, 42, 84	0.242	84.0	Heat	[41]
PFOA	0.5, 1.0, 2.0, 4.0	20	4.0	Heat	[88]
PFOA	0.021, 0.084, 0.21, 0.42	15.3	0.42	Ultraviolet	[90]
PFOA	0.042, 0.42, 0.84	0.0003	0.84	Microwave-hydrothermal	[61]
PFOS	3.70, 9.25, 18.52, 27.78, 37.04, 46.30	185.87	46.30	Heat	[55]
PFOA	5, 10, 15, 20, 25, 30	150	25	Ultraviolet	[67]

1 **Table 4** Comparison of temperature effects in activated persulfate oxidation literatures.

Analytes	Temperature range (°C)	Optimal temperature (°C)	Activation methods	Ref.
PFOA	20, 50, 70	70	Heat	[50]
PFOA	25, 60, 90, 130	90	Microwave-hydrothermal	[43]
PFOA	25, 60, 90, 130	90	Microwave-hydrothermal	[60]
PFOA	20, 30, 40	40	Relatively low temperatures	[96]
PFOA	25, 85	85	Heat	[51]
PFOA	25, 35, 40, 45	45	Activated carbon	[42]
PFOA	20, 30, 40, 50, 60	60	Heat	[41]
PFOA	25, 35, 40, 50	50	Heat	[88]
PFOA	20, 50, 70	70	Heat	[53]
PFOA	20, 50, 70	70	Microwave-hydrothermal	[61]

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1 **Table 5** Comparison of C1-C6 PFCAs, PFOA and PFOS (<sup>a</sup> k - reaction rate constant with SO<sub>4</sub><sup>-</sup> [67];  
 2 <sup>b</sup>DC and DF mean decomposition efficiency and defluorination efficiency [59]; <sup>c</sup>Data was from Pi et al  
 3 [101]; - means no mention).

PFAS	Abbreviation	<sup>a</sup> k (M <sup>-1</sup> ·s <sup>-1</sup> ) with SO <sub>4</sub> <sup>-</sup>	<sup>b</sup> DC %	<sup>b</sup> DF %	<sup>c</sup> BCFs (L/kg)	
					<i>Echinodorus horemanii</i>	<i>Eichhornia crassipes</i>
C <sub>8</sub> F <sub>17</sub> SO <sub>3</sub> H	PFOS	-	-	-	86.8±6.5	89.8±6.9
C <sub>7</sub> F <sub>15</sub> COOH	PFOA	2.59×10 <sup>5</sup>	-	-	43.0±2.7	27.5±2.9
C <sub>6</sub> F <sub>13</sub> COOH	PFHpA	2.68×10 <sup>5</sup>	67.2	23.2	24.5±1.8	25.2±1.5
C <sub>5</sub> F <sub>11</sub> COOH	PFHxA	7.02×10 <sup>5</sup>	67.5	25.6	29.4±1.9	24.9±1.8
C <sub>4</sub> F <sub>9</sub> COOH	PFPeA	1.26×10 <sup>6</sup>	70.9	37.8	13.7±1.1	26.0±2.2
C <sub>3</sub> F <sub>7</sub> COOH	PFBS	1.05×10 <sup>7</sup>	74.5	44.8	29.5±2.0	18.8±1.3
C <sub>2</sub> F <sub>5</sub> COOH	PFPrA	9.31×10 <sup>7</sup>	76.4	57.5	-	-
CF <sub>3</sub> COOH	TFA	-	77.9	65.2	-	-

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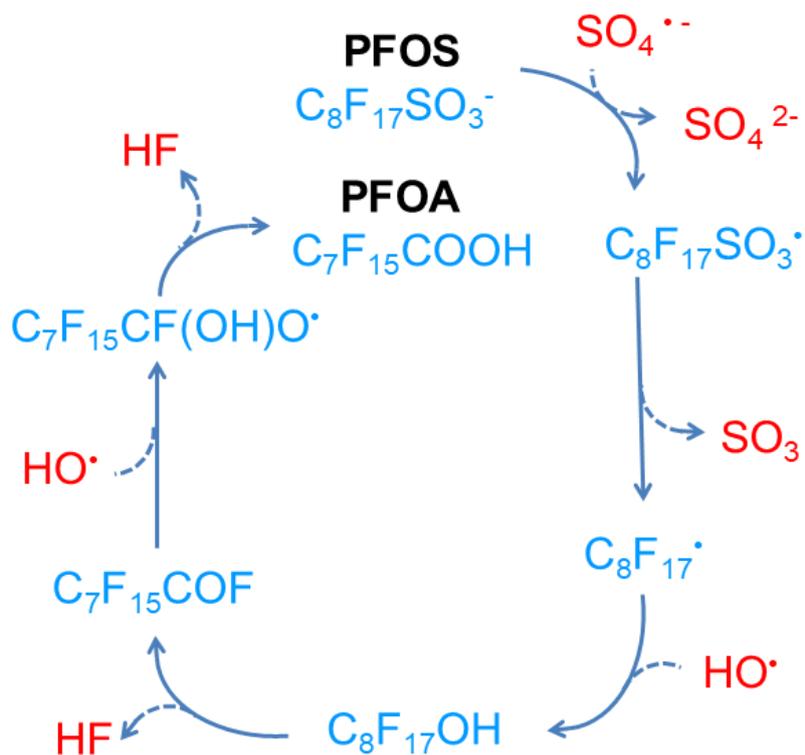
1 **Table 6** Cost estimation of persulfate-based literatures for PFOS and PFOA decomposition.

PFAS	Activation method	C <sub>Initial</sub> (mg/L)	k (min <sup>-1</sup> )	t <sub>90</sub> (min)	EE/O (kWh/m <sup>3</sup> )	Energy cost (\$/m <sup>3</sup> )	Chemical cost (\$/m <sup>3</sup> )	Total cost		Ref.
								Water volume \$/m <sup>3</sup>	PFAS dose \$/g	
PFOA	Heat	2.1	1.70×10 <sup>-3</sup>	1355	44226	3980	4.76	3985	1898	[51]
PFOA	Heat	0.1	3.17×10 <sup>-3</sup>	727	21204	1908	10.0	1918	19180	[41]
PFOA	Microwave and Iron	100	1.47×10 <sup>-2</sup>	157	9595	864	0.09	864	8.64	[43]
PFOA	Microwave hydrothermal	105.17	1.12×10 <sup>-2</sup>	206	8178	736	0.9	737	7.01	[59]
PFOA	Microwave	105.17	1.37×10 <sup>-2</sup>	168	4653	419	0.9	420	3.99	[60]
PFOS	Heat	100	4.17×10 <sup>-4</sup>	5524	64447	5800	8.5	5809	58.09	[55]
PFOS	Ultrasound	100	8.33×10 <sup>-5</sup>	27654	396374	35673	8.5	35682	3568	[55]
PFOS	Ultraviolet	100	3.00×10 <sup>-4</sup>	7679	38395	3456	8.5	3465	34.65	[55]
PFOS	Fe <sup>2+</sup>	100	2.17×10 <sup>-4</sup>	10616	-	-	8.5	8.5	0.085	[55]

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## 1 Figure captions:



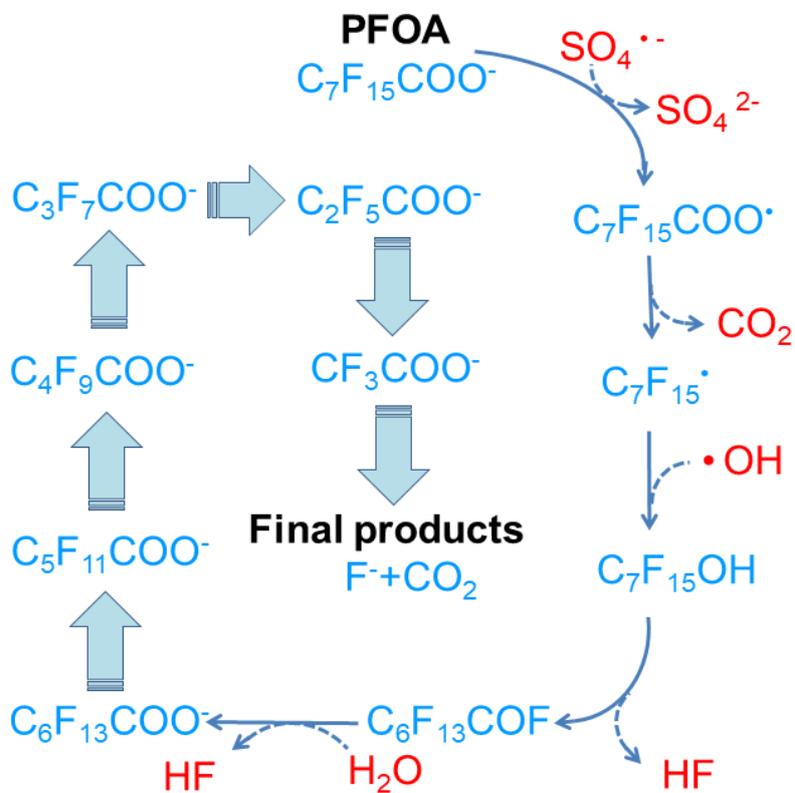
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Fig.1. Proposed mechanisms for the conversion of PFOS to PFOA in the persulfate-based system [40, 55].

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Fig.2. Proposed pathway for PFOA decomposition in the persulfate-based system [40, 53, 88].