

## Challenging the contamination of per- and polyfluoroalkyl substances in water: advanced oxidation or reduction?



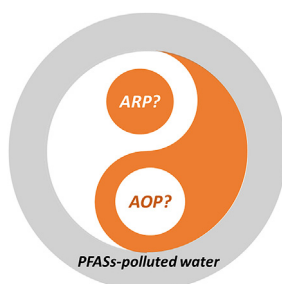
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### HIGHLIGHTS

- Recent advances on PFASs degradation in both AOPs and ARPs are reviewed.
- Fundamentals and impacting parameters of both AOPs and ARPs are summarized.
- The degradation pathways of typical PFASs in both AOPs and ARPs systems are reviewed.
- Limitations and prospects of the current PFASs degradation systems are proposed.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Nowadays, the increasing discharge of persistent per- and polyfluoroalkyl substances (PFASs) caused serious environmental issues. In addition to advanced oxidation processes (AOPs), advanced reduction processes (ARPs) based on reducing radicals, e.g., hydrated electron and superoxide anions have attracted great attentions as promising methods for remediation of PFASs pollution. This review, based on 128 cited references, provides a critical overview on the performance of different AOPs and ARPs. The unique properties of reactive species, e.g.,  $\text{SO}_4^{\cdot-}$  and  $e_{aq}^-$  and their generation mechanisms in different systems were discussed. Moreover, the efficiencies of different systems were further compared from several aspects, e.g., PFASs decomposition rate, reaction time and energy consumption. More specially, for some model compounds of PFASs, such as perfluorooctanoic acid, perfluorooctane sulfonate and perfluoroalkyl ether carboxylic acids, we systematically discussed their degradation and defluorination pathways in both AOPs and ARPs. The reported literatures showed that the degradation pathways of these PFASs are closely related to their head groups in either AOPs or ARPs. Finally, some key conclusions were summarized, and the implications of the state-of-the-art knowledge on practical PFASs remediation in water treatments were summarized and the future priority research directions were proposed.

### 1. Introduction

Poly- and perfluoroalkyl substances (PFASs) are a series of anthropogenic chemicals that have been extensively used since the 1940s [1,2]. Most of the PFASs consist of either a partially or fully fluorinated

alkyl-chain tails and an ionic head [3]. Owing to the innate chemical and thermal stability of the C–F bond and the hydrophobic/oleophobic properties [4,5], PFASs have been widely used in various industrial and consumer products, including non-stick cookware, carpets, up-holsteries, food packaging and fire-fighting foams, etc. [6,7]. Nowadays, there are

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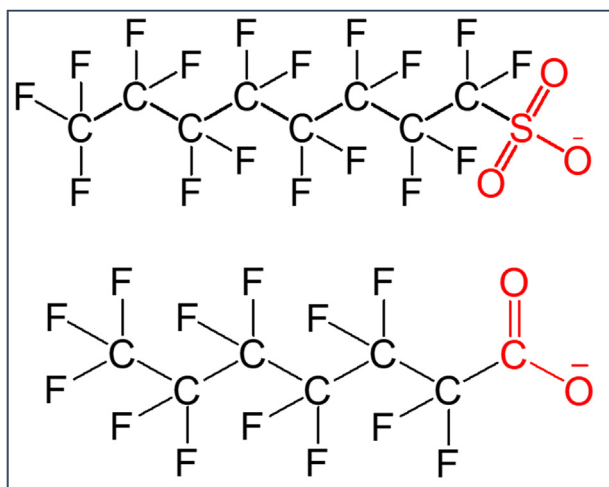


Fig. 1. The molecular structures of PFOA and PFOS.

~5000 PFASs-related chemicals, which have been synthesized and pervaded almost every aspects of our lives [8]. Moreover, there are also many PFASs with unknown chemical structures. The mass production and usage have caused serious PFASs pollution for surface water, ground water and soil around the world [9–11]. One of the important PFASs sources is electrochemical fluoropolymers industry, which produced a large amount of PFASs-containing wastewater [12,13], and discharged directly into the environment before PFASs pollution was regulated. Besides, firefighting foams as well as other consumer and industrial products contribute to the contamination of PFASs in the environment [14]. Other natural processes, e.g., the conversion of fluoromeric telomers and fluorosulfonamide under sunlight irradiation, are also the important sources for perfluorocarboxylic acids (PFCAs) in the environment, accounting for up to 5% [15,16]. It was reported that PFASs could enter human body through drinking water and food chain [17], which would further threat to human health and induce various diseases, including cancer, renal damage, and endocrine disruption [18–22]. Among PFASs, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) are the two most commonly detected PFASs in the environment. In 2009 and 2019, PFOS and PFOA were listed into the Stockholm Convention's Category 2B control list, respectively [23]. Moreover, the United States, European Union and Australia have also set up the advisory limit for PFOS and PFOA in drinking water. Accordingly, in this review, PFOA and PFOS are also the primary focus, and their chemical structures are presented in Fig. 1.

The high resistance and toxicity of PFASs have attracted worldwide attention, and numerous strategies for PFASs removal from aqueous solution have been attempted, e.g., physical adsorption [24], reverse

osmosis (RO) [25], thermal treatment [26], sonochemical destruction [27], electrochemistry [28], plasma reactors [29], photocatalysis [7] and advanced oxidation/reduction etc. [30,31]. Although some advanced functional adsorbents [32,33] and RO membranes [34] can concentrate PFASs, further treatments for the concentrated wastewater are required. While, for thermal treatment, sonochemical destruction, electrochemistry and plasma reactors, special equipment and harsh reaction conditions should be constructed. Furthermore, in photocatalytic systems, the corrosion resistance and light absorption ability of the photocatalysts are the key factors for actual application of these techniques [35]. Although some photocatalysts have been demonstrated to be efficient for PFASs degradation, the stability and fouling resistance of the system cannot be guaranteed [36,37].

Among these techniques, the efficiency of advanced oxidation and reduction processes (AOPs and ARPs) have been demonstrated for the treatment of various contaminants [38,39], which are generally driven by the generation of some strong oxidants or reductants by *in-situ* or *ex-situ* activation, such as hydroxyl radicals ( $\bullet\text{OH}$ ), sulfate radicals ( $\text{SO}_4^{\bullet-}$ ), hydrated electrons ( $e_{\text{aq}}^-$ ) and carbon dioxide anion radicals ( $\text{CO}_2^{\bullet-}$ ) [40]. Recently,  $\text{H}_2\text{O}_2$  and peroxydisulfate (PDS) based AOPs have been systematically studied due to the simple operation in either *in-situ* or *ex-situ* treatments, and various activation methods regarding to the degradation of PFASs were also investigated [41]. However, due to the strong C–F bonds (485 kJ/mol) and the high electron density around F atom, the decomposition of PFOA and PFOS in both  $\bullet\text{OH}$  and  $\text{SO}_4^{\bullet-}$  based systems is more complicated than other organic contaminants [42]. On the other hand,  $e_{\text{aq}}^-$  based ARPs by using sulfite, iodide ions and indole derivatives as the electron donors were also developed [25,43,44]. As one of the most active reductive species ( $-2.9$  eV vs NHE),  $e_{\text{aq}}^-$  is demonstrated to be able to break the C–F bond directly [45,46]. Nevertheless, both the coexisting species in water, such as  $\text{H}^+$ ,  $\text{O}_2$ , natural organic matter (NOM) and the molecular structure of  $e_{\text{aq}}^-$  source materials could affect the decomposition of PFASs [47,48]. In addition to  $e_{\text{aq}}^-$ , the PFASs decomposition processes using other typical reductive species, including  $\text{H}\bullet$  and  $\text{CO}_2^{\bullet-}$  were also investigated depending on the used activation methods and the source chemicals [49,50]. Although a variety of AOPs and ARPs were developed to degrade PFASs, PFASs exhibit different reactivities in different systems due to the structural differences and the special properties of PFASs in redox reactions. However, most current studies only consider the PFASs decomposition by oxidation and reduction reaction separately. Even some review articles have summarized the PFASs decomposition in either ARPs or AOPs but rarely compared them under different reaction conditions [30,42]. Therefore, it is of great significance to systematically compare the different redox systems reported in recent years, as well as to select appropriate treatment schemes for various PFASs pollution problems.

This paper reviewed the recent breakthrough for PFASs novel destruction in both AOPs and ARPs. Additionally, the mechanisms of

**Table 1**  
Photooxidative studies for the degradation of PFASs under different PDS activation systems.

Activation method	Compound	Concentration ( $\mu\text{M}$ )	Decomposition reaction-rate constant ( $\text{h}^{-1}$ )	Defluorination (%)	Energy input	Chemical consumption	Ref.
UV	PFOA	29.6	0.25	73.8%	200W Xe	PDS 6.4–50.0 mM	[87]
UV	PFOS	186	0.162	19.32%	15W Hg*2	PDS 18.5 mM	[66]
UV	PFBA	50	0.43	39.6%	1000W Hg	PDS 4 g/L	[88]
Fe-zedites/UV	PFOS	20	0.10	69%	20W Hg	Fe-BEA35 0.5 g/L	[74]
$\text{In}_2\text{O}_3/\text{UV}$	PFOA	120.7	0.2543	94.2%	320W Xe	$\text{In}_2\text{O}_3$ 0.05 g/L	[89]
US	PFOS	186	0.026	5.82%	100W	PDS 18.5 mM	[66]
HT	PFOA	374	1.36	77.5%	80 °C	PDS 10.0–50.0 mM	[73]
HT	PFOA	0.242	0.123	69%	50 °C	PDS 60–84 mM	[78]
HT	PFOS	186	0.233	25.71%	–	PDS 18.5 mM	[66]
$\text{Fe}^{2+}$	PFOS	186	0.131	13.88%	–	PDS 18.5 mM $\text{Fe}^{3+}$ 3 mM	[66]
Fe/PAC/HT	PFOA	0.5	–	10–40%	80 °C	PAC 200–1000 mg/L	[67]
ZVI/MW/HT	PFOA	240.7	0.88	62.6%	90 °C	PDS 5 mM, ZVI 0.09–0.9 mmol	[68]

UV: ultraviolet, US: ultrasound, HT: hydrothermal, PAC: powdered activated carbon, ZVI: zero-valent iron, MW: microwave, Xe: xenon lamps, Hg: mercury lamps.

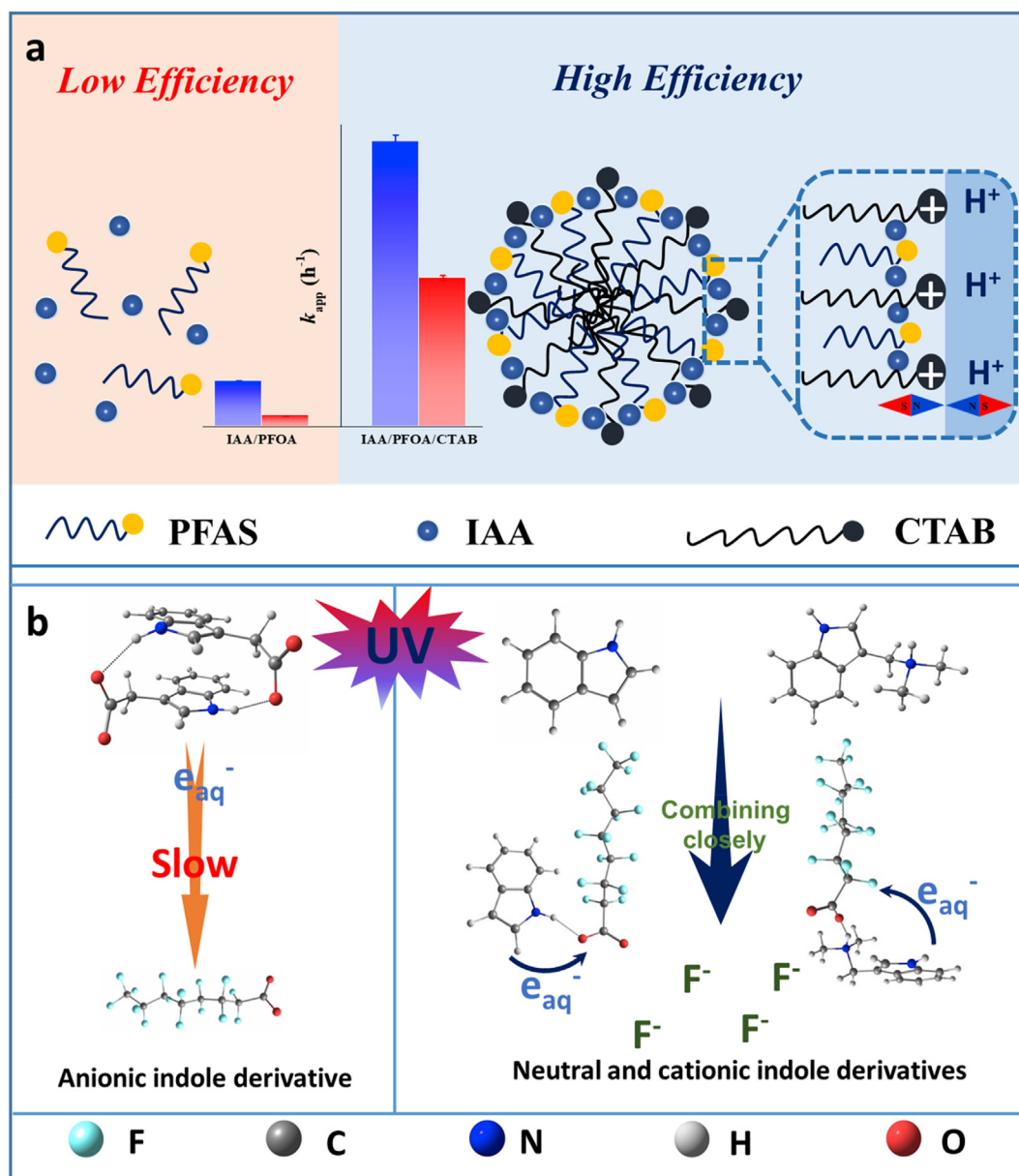


Fig. 2. Schematic diagram of the PFOA degradation mechanism in (a) CTAB/3-IAA/PFOA and (b) indole/PFOA systems.

PFASs degradation and defluorination, as well as the principles of various AOPs and ARPs, were also summarized and compared. On this basis, the challenges that remain for these technologies were discussed, and future research directions were proposed. This review would be important to outline the significant issues that need further attention in order to promote the research of AOPs and ARPs for PFASs destruction.

## 2. AOPs for PFASs decomposition

AOPs are a class of novel technologies by using different activation methods to generate  $\bullet OH$ ,  $SO_4^{\bullet -}$  and other reactive oxidative species (ROS) for degrading pollutants [51,52]. Nowadays, various activation techniques, e.g., photolysis [53], radiolysis [54], pyrolysis [55], sonolysis [56] and transition metal activation [57] with the assistance of source chemicals, e.g.,  $O_3$ ,  $H_2O_2$ , PDS and peroxymonosulfate (PMS) are reported for effective decomposition of many contaminants. Herein, we mainly focus on the effect of different activation methods on PFASs degradation efficiency. Moreover, the influence from various

environmental factors and transformation mechanisms in different systems are also summarized and analyzed.

### 2.1. Iron activation

Iron (Fe), is the most widely existing transition metal in the natural environment [58]. Due to the polyvalent property, it can exhibit different species under different redox states, thus iron can act as an effective activator for  $H_2O_2$ , PDS and PMS etc. In the traditional Fenton system, ferrous iron ( $Fe^{2+}$ ) was used to activate  $H_2O_2$  to generate  $\bullet OH$  for the treatment of various organic pollutants [59], while the  $\bullet OH$  produced in Fenton system cannot attack PFASs directly [60,61]. In order to enhance the PFASs degradation, UV-assisted Fenton system was developed by Tang et al. [62]. Compared to the bulk Fenton system, both PFOA degradation and defluorination efficiencies were significantly improved, and a two-stage PFOA degradation mechanism was proposed. In the first stage, strong oxidant ( $\bullet OH$ ) could contribute to the fast defluorination and degradation of PFOA with the assistance of UV light, while as  $H_2O_2$

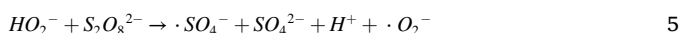
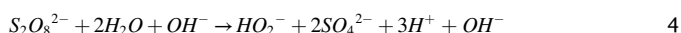
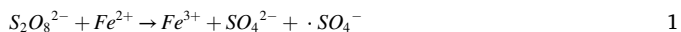
**Table 2**  
Photoreductive studies for the degradation of PFASs under different  $e_{aq}^-$  generating systems.

$e_{aq}^-$ generating system	Compound	Concentration ( $\mu$ M)	Reaction time (h)	Decomposition reaction-rate constant ( $h^{-1}$ )	Defluorination (%)	Energy input	Chemical consumption	Ref.
KI/UV	PFOA	24	2.5	0.174	–	8W Hg	KI 10 mM	[3]
	PFOS	20		0.39				
KI/UV	PFOA	25	14	0.438	98%	15W Hg	KI 0.1–0.8 mM	[43]
KI/UV	PFOA	25	6	0.885	–	15W Hg	KI 0.25 mmol/L	[48]
KI/HA/UV	PFOS	30	8	0.50	97.9%	14W Hg	KI 0.3 mM, HA 1.0 mg/L	[104]
$SO_3^{2-}$ /UV	PFOA	20	24	–	88.5%	10W Hg	$Na_2SO_3$ 10.0 mmol/L	[95]
$SO_3^{2-}$ /UV	PFOS	37.2	4	0.87	68.5%	10W Hg	$Na_2SO_3$ 20 mM	[45]
Indole/UV	PFOA	24	8	0.67	74.78%	36W Hg	Indole 1 mM	[47]
IAA/UV	PFOS	20	10	–	71%	36W Hg	IAA 1 mM	[113]
IAA/CTAB/UV	PFOA	24	2.5	1.67	90%	500W Hg	IAA 1 mM, CTAB 0.14 mM	[114]
IAA/organoclay/UV	PFOA	24	10	0.5873	90.1%	36W Hg	IAA 1 mM, organoclay 2.2 g/L	[112]
EDTA/UV	PFOS	10	10	0.113	51.19%	14W Hg	EDTA 0–2 mM	[98]
$Fe^{II}NTA$ /UV	PFOS	10	10	0.081	29.5%	14W Hg	$Fe^{2+}$ 0.3 mM, NTA 2 mM	[120]

UV: ultraviolet, HA: humic acids, IAA: 3-indoleacetic acid, CTAB: cetyltrimethyl ammonium bromide, EDTA: ethylene diamine tetraacetic acid, NTA: nitrilotriacetic acid, Hg: mercury lamps.

was completely consumed,  $Fe^{3+}$  could induce further defluorination. Although bulk Fenton system could not oxidize PFASs directly, other PFASs such as perfluorosulfonamides could be directly oxidized by  $\bullet OH$  and converted into PFCAs [16]. In addition to the degradation techniques, Fenton system was also studied to assist coagulation, and PFOA could be removed by simultaneous precipitation of dissolved organic matter and PFOA in solution [63].

Recent studies also demonstrated that Fe could activate PDS to produce  $SO_4^{\bullet -}$  and directly oxidize PFASs. The pathway for the activation of PDS by  $Fe^{2+}$  was summarized in Eqs. 1–3 [64,65]. Yang et al. [66] found that PFOS could be effectively defluorinated in  $Fe^{2+}/K_2S_2O_8$  system with the reaction rate constant of  $0.131 h^{-1}$ . To further improve PFOA degradation efficiency, iron-modified activated carbon (Fe/AC) was synthesized, which could initially enrich PFOA on the surface of Fe/AC, and the degradation efficiency for Fe/AC + PDS was much higher than bulk PDS system [67]. Simultaneously, with the addition of Fe/AC, the activation energies ( $E_a$ ) of PFOA degradation and defluorination were also significantly reduced due to the coordinative binding between Fe and PFOA, implying that lower reaction temperature and shorter reaction time were needed in Fe/AC + PDS system [67]. In addition, zero-valent iron (ZVI) was also studied to degrade PFOA with PDS addition, which would lead to the synergetic effect with heat activation, thus accelerating the PFOA decomposition and reducing the reaction time [68]. Moreover, iron modified diatomite was also synthesized to activate PDS and  $H_2O_2$  [69]. However, in the system, a different degradation mechanism was proposed, and the generated  $O_2^{\bullet -}$  under alkaline conditions (Eqs. (4) and (5)) played the dominant role in PFOA degradation process.



## 2.2. Heat activation

Thermal activation is also a common approach for producing  $SO_4^{\bullet -}$ , which has been used to degrade different antibiotics and pesticides (Eqs. (6) and (7)) [70,71]. Specially, since geothermal energy is an important

earth resource, it can be used to *in-situ* activate PDS without external heating [72]. Nowadays, there are many researchers focusing on the PFOA degradation by thermal activation of PDS. Hori et al. [73] found that the addition of PDS in 80 °C hot water could led to efficient PFOA decomposition, and  $F^-$  and  $CO_2$  were detected as the major degradation products in the aqueous and gas phases, respectively. Moreover, some short-chain PFCAs and H-perfluoroalkanes were also detected during the reaction. Furthermore, it was reported that the presence of powdered activated carbon (PAC) could enhance PFOA decomposition efficiency in the thermal activated PDS system by concentrating PFOA on PAC surface and reducing the activation energy for the reaction between  $SO_4^{\bullet -}$  and PFOA via surface covalent bonding between PFOA and PAC [67]. Moreover, the addition of PAC also extended the reaction pH from acidic to neutral pH condition, attributing to the fact that PAC catalyzed the generation of  $SO_4^{\bullet -}$ , which further react with the transformation products to produce covalently bound PFOA. In addition to PAC, zeolite can also act as a micro-reactor in the thermal activated PDS system [74]. Similar to PAC, zeolite can effectively adsorb PFOA from aqueous solution and then decrease the activation energy for the generation of  $SO_4^{\bullet -}$ . More importantly, after six adsorption/degradation cycles, zeolite still maintain the insignificant decline for PFOA degradation performance. Besides, microwave and iron assisted PFOA decomposition was also studied in the thermal activation system [68]. In this study, the introduced ZVI and PDS leading the synergetic effect that greatly accelerated the PFOA decomposition rate. ZVI could not only react with PFOA, but also reduce the activation energy for generation of  $SO_4^{\bullet -}$  at lower reaction temperature. Thermal activated PDS systems were also studied to enhance the recovery of PFASs from the impacted soils [75]. In this system, the formed  $SO_4^{\bullet -}$  and  $\bullet OH$  could convert cationic and zwitterionic PFASs into anionic PFASs, which can be more easily eluted from the polluted soils. Recently, geothermal energy activated PDS was also used in several practical groundwater remediation cases [76,77]. Park et al. [78] used heat-activated PDS to oxidize of PFOA, 6:2 fluorotelomer sulfonate (6:2 FTSA), and PFOS under conditions suitable for *in-situ* groundwater remediation. In this system, by injecting PDS to groundwater directly, efficient PFOA, 6:2 FTSA and PFOS oxidative degradation was obtained. Furthermore, Thomas et al. [76] directly treated aqueous film-forming foam (AFFF) polluted groundwater near a fire site by *in-situ* PDS oxidation. In the system, the biggest advantage is that geothermal energy could be used directly, thus effectively reducing the energy consumption. However, there are still some disadvantages for using heat-activated PDS to treat PFAS-impacted sites. Firstly, the production of short-chain PFCAs is undesirable since they migrate underground more easily and are difficult to treat with adsorption techniques [79]. On the other hand,

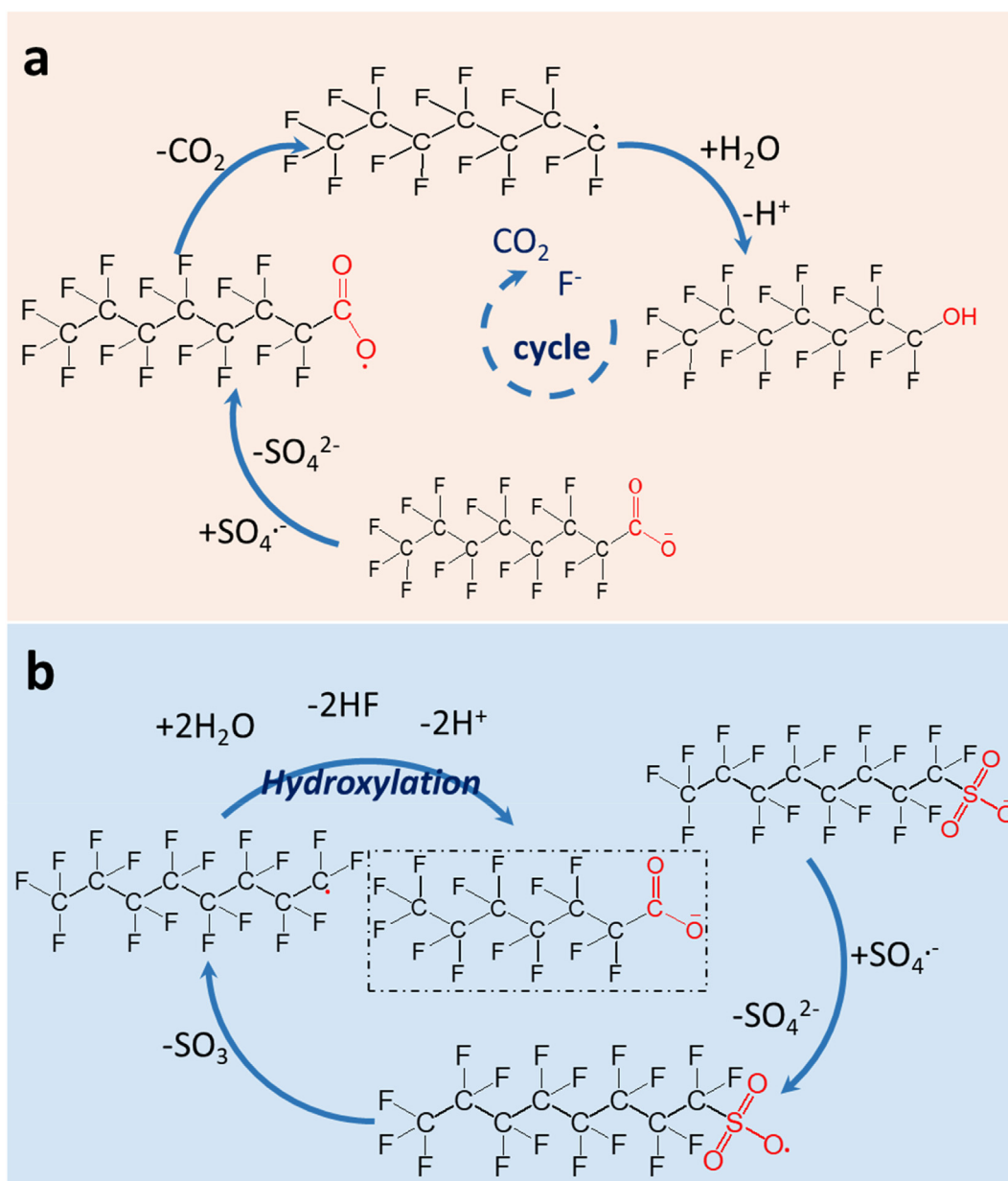


Fig. 3. Schematic diagram of the (a) PFOA and (b) PFOS degradation mechanism in AOPs.

chemical oxidation could produce  $\text{ClO}_3^-$  through scavenging reactions with  $\text{Cl}^-$  in the solution, and the liberation of  $\text{F}^-$  from PFASs under acidic conditions may produce potentially hazardous levels of HF [80].



### 2.3. Ultraviolet (UV) activation

Due to the low wavelength and high energy, UV irradiation is often used for water disinfection [81], photo-exciting photocatalysts [82], activating  $\text{H}_2\text{O}_2$  and PDS etc [83,84]. Similar to the heat-activating PDS system, UV light could also break the O–O bond of PDS to produce two  $\text{SO}_4^{\cdot -}$ , and the generation process of  $\text{SO}_4^{\cdot -}$  is presented in Eq. (8). Recently, different UV/PDS based systems were widely investigated owing to the extremely high efficiency for the production of  $\text{SO}_4^{\cdot -}$  in removing environmental pollutants [85]. Owing to the high UV–visible light absorption

efficiency, PDS could be rapidly converted into  $\text{SO}_4^{\cdot -}$  under UV irradiation, which would further result highly efficient PFASs decomposition [42,86]. For example, Hori et al. [87] used a 200 W mercury lamp to activate PDS, and a large amount of  $\text{SO}_4^{\cdot -}$  was produced, resulting in the completed PFOA degradation within 4 h. Recently, Wang et al. [88] further investigated the efficiency of UV/PDS system for the decomposition of perfluorobutyric acid (PFBA) at pH 2. As expected, 50  $\mu\text{M}$  PFBA could be fully degraded during 5 h under the irradiation of 1000 W mercury lamp. Moreover, both  $\text{SO}_4^{\cdot -}$  and  $\cdot \text{OH}$  are demonstrated to be responsible for the PFBA degradation process. In addition to direct activation, some catalysts were synthesized to promote the generation of  $\text{SO}_4^{\cdot -}$  in the UV/PDS system. Yuan et al. [89] developed a heterogeneous  $\text{In}_2\text{O}_3/\text{PDS}$  photocatalytic system, and the outstanding PFOA degradation efficiency was achieved under UV light irradiation. In this system, the synergistic effect of direct hole oxidation and *in-situ* generated radicals, especially surface radicals would attribute to the PFOA defluorination process. Moreover, some other photocatalysts including  $\text{MnFe}_2\text{O}_4/\text{mSiO}_2$  [90], oxygen-vacancy-rich  $\text{In}_2\text{O}_3$  and  $\text{TiO}_2$  were also developed [91,92],

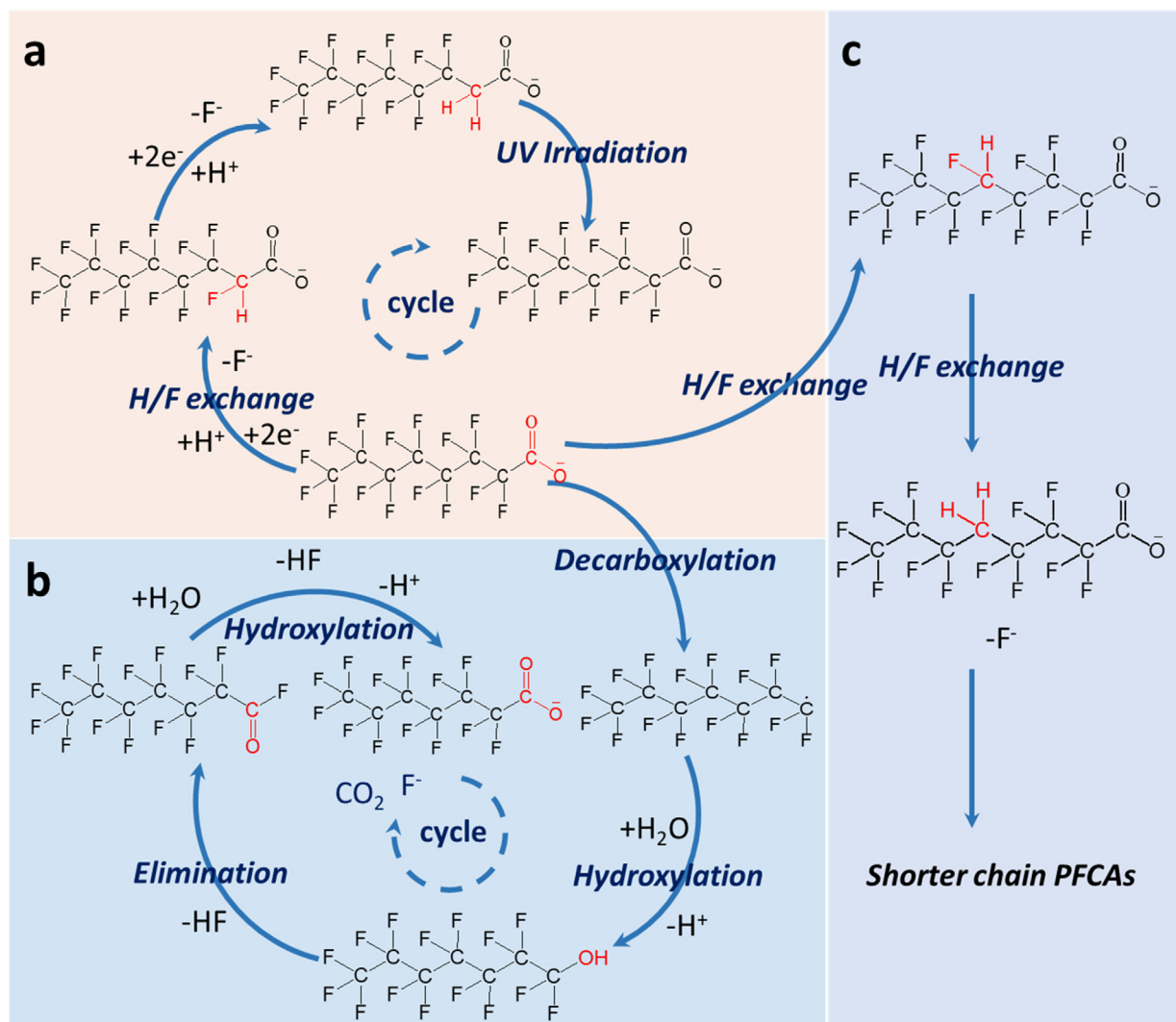


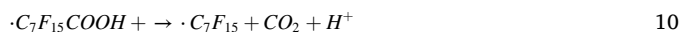
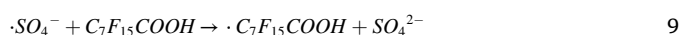
Fig. 4. Schematic diagram of the PFOA degradation mechanism in hydrated electron basing system.

and the promoted PFOA degradation was observed in these systems. In general, UV-activated PDS techniques are similar to thermally activated PDS methods, and the disadvantages of thermally activated PDS systems also exist in UV-activated systems.



#### 2.4. PFAS degradation mechanism in PDS based systems

Overall,  $SO_4^{\cdot -}$  induced PFOA degradation process is summarized in two steps as shown in Eqs. 9–13. Firstly, the generated  $SO_4^{\cdot -}$  induces the dissociation of the ionic head of PFOA, resulting in the formation of unstable perfluoroalkyl radicals, which is then hydrolyzed to  $C_7F_{15}OH$ . Subsequently, the formed unstable  $C_7F_{15}OH$  can eliminate two HF to generate  $C_6F_{13}COOH$  [31,79]. Through a similar degradation mechanism, the shortened PFCAs can be further degraded by losing  $CF_2$  unit and mineralizing to  $CO_2$  and  $F^-$ , resulting in the generation of progressively shorter PFCAs.



The efficiencies of different PDS based systems are further compared from the aspects of decomposition reaction rate, reaction time and energy consumption as shown in Table 1. It is obvious that different activation methods were explored based on various mechanisms, and most of these systems are dependent on energy consumption, which plays a critical role for economic feasibility. Although PDS based PFASs degradation had attached wide attentions as an emerging alternative for traditional AOPs, few systems were attempted in practical treatment of PFASs. By now, several studies were conducted to simulate the scavenging and inhibition effects of real PFASs contaminated water matrices on the degradation process. However, most studies showed decreased PFASs degradation efficiency under natural conditions [76]. Conclusively, for PDS based systems, there is still a long way to go in the practical application for PFASs remediations.

### 3. ARPs for PFASs decomposition

ARPs mainly use the reductive active species including  $e_{aq}^-$ , active hydrogen atom, carbon dioxide anion radical and superoxide anion radical to degrade pollutants [49,50,93,94]. In these systems,  $e_{aq}^-$  basing

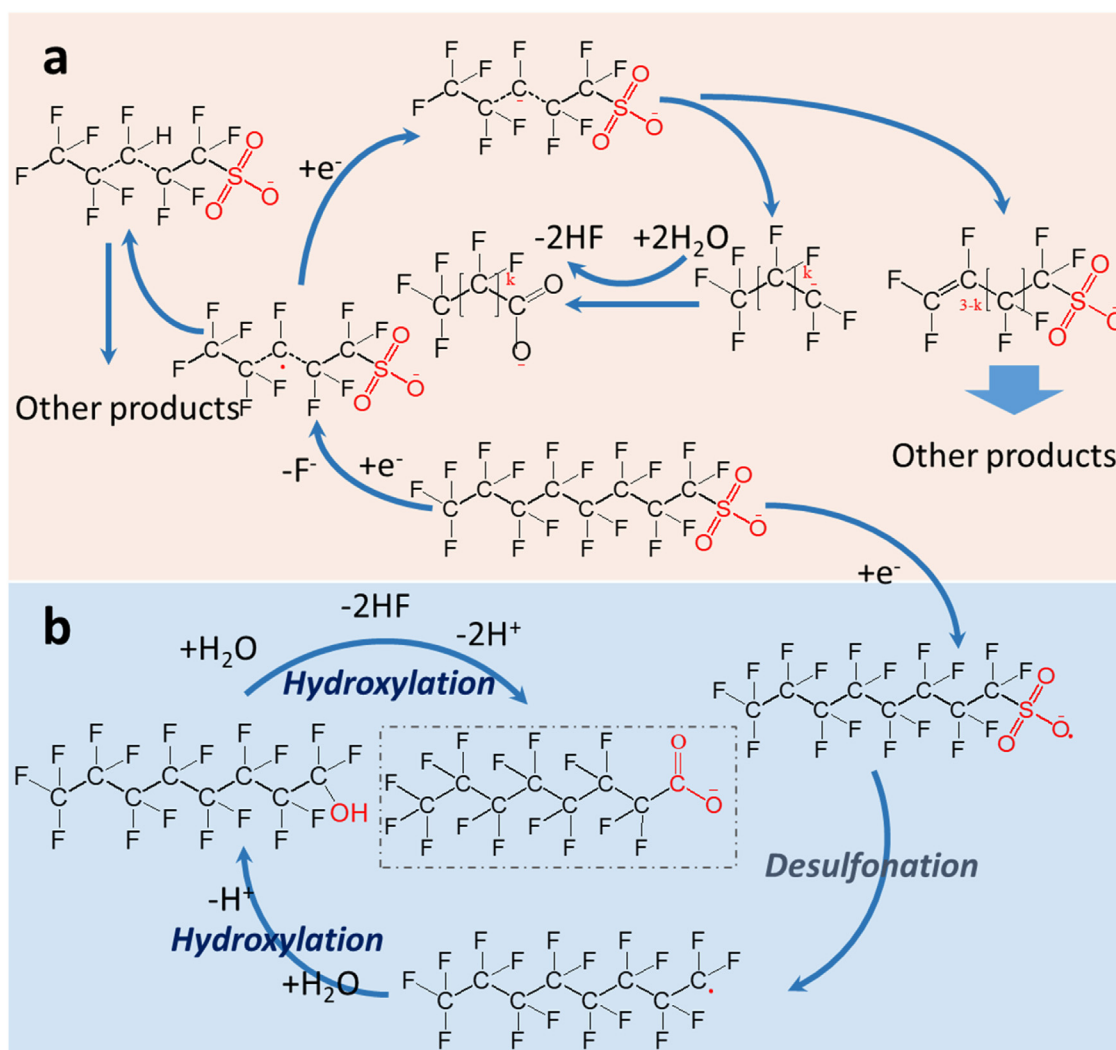


Fig. 5. Schematic diagram of PFOS degradation mechanism in hydrated electron basing system.

techniques were extensively investigated due to the extremely negative standard reduction potential of  $-2.9$  eV vs NHE. Different  $e_{aq}^-$  source materials, e.g., sulfite ( $SO_3^{2-}$ ) [95], iodide ( $I^-$ ) [43], indole derivatives [44] and hydroxyphenylacetic acids (HPAs) [96] were attempted to degrade PFASs under UV irradiation. However, due to the highly reductive reactivity, the produced  $e_{aq}^-$  may be consumed under ambient conditions through two mechanisms. Firstly, the generated  $e_{aq}^-$  could react with  $H^+$  to produce the active hydrogen atom ( $H\bullet$ ), subsequently, the produced  $H\bullet$  can further consume  $e_{aq}^-$  to form  $H_2$  (Eqs. (14) and (15)). Secondly, the generated  $e_{aq}^-$  could react with the present dissolved oxygen to generate superoxide anion radical ( $O_2^{\bullet-}$ ), which may further combine with proton or react with  $e_{aq}^-$  as shown in Eqs. 16–19 [97].

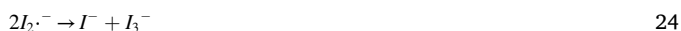


Moreover, some natural small molecular acids and photocatalysts with strong photo-reducibility were also investigated in different systems for generating  $H\bullet$ , carbon dioxide anion radical and  $O_2^{\bullet-}$  to degrade PFASs [49,98]. In this review, we summarized the reported ARPs for PFASs treatments in different systems. In particular, the unique properties of these  $e_{aq}^-$  based systems, the performances and degradation mechanisms are systematically reviewed and discussed. Moreover, the influence from various environmental factors and the transformation pathways for different systems are also discussed.

### 3.1. UV/iodide systems

The photochemistry process of iodide has been concerned since 1960s [99]. Previous studies have demonstrated that the UV irradiation of iodide could produce excited iodide ( $I\bullet \cdot H_2O^{\bullet*}$ ) (Eq. (20)) [100,101]. The generated  $I\bullet \cdot H_2O^{\bullet*}$  could then be converted to  $e_{aq}^-$  as presented in Eq. (21), accompanied by the generation of  $I\bullet$  and water molecule. Finally,  $I\bullet$  would further undergo a series of transformations (Eqs. 22–27).

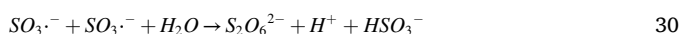




In the study from Park et al. [3], they systematically studied the effects of chain length and ionic headgroup species on the degradation and defluorination of PFASs by using different PFCAs and perfluorinated sulfonic acids (PFASs) as model compounds. And the results demonstrated that the ionic headgroup, either carboxylate or sulfonate could significantly affect the degradation kinetics and mechanism of PFASs by  $e_{aq}^-$ . Both the PFASs reduction kinetics and the F index (F index =  $-[F]_{\text{products}}/[PFASs]_{\text{degraded}}$ ) increase linearly with the increase of chain length, suggesting the multiple reaction sites across the fluorocarbon tail. Furthermore, Qu et al. [43] investigated the PFOA degradation mechanism in UV/KI system. Through products analysis and  $O^{18}$  isotopic labeling experiment, two major PFOA defluorination pathways were proposed. Firstly, direct cleavage of C–F bonds occurs via nucleophilic attack by  $e_{aq}^-$ . Secondly, the stepwise removal of  $CF_2$  by UV irradiation and hydrolysis induces further degradation. Moreover, the UV/KI system was used to treat PFOA-containing wastewaters from a teflon-manufacturing plant. As expected, more than 96% PFOA was effectively removed after 12 h. The results showed that the decomposition of PFOA in the UV/KI system was obviously dependent on the pH condition [48], as the initial pH increased from 5 to 10, the PFOA degradation rate constant increased about 48 times. Further study indicated that the presence of natural organic matter (NOM) could enhance the photoreductive degradation of PFOS in UV/KI system [102]. Several factors associated with NOM could attribute to the increased PFOS decomposition: a) NOM enhances the effective generation of  $e_{aq}^-$  due to the reduction of  $I_2$ , HIO,  $IO_3^-$  and  $I_3^-$  to  $I^-$ ; b) the quinones functional groups of NOM could act as the electron shuttles, enhancing the electron transfer efficiency; c) the weak association of both  $I^-$  and PFOS with NOM increases the reaction probability. Although the UV/KI system exhibits high degradation activity for various PFASs, there are still several aspects limiting its application. Firstly, the generated  $e_{aq}^-$  in the UV/KI system are easily quenched by the dissolved oxygen and proton, thus highly efficient PFASs degradation could only be obtained under anaerobic and alkaline conditions. Secondly, the additional iodide in the system could increase the toxicity and even enhance the production of iodized disinfection by-products. Therefore, whether this technique could be applied to PFASs remediation in practice remains controversial.

### 3.2. UV/sulfite systems

The UV/sulfite system is another most widely studied  $e_{aq}^-$  based systems. As early as 1920s, the photoionization reaction of sulfite was already reported [103]. Due to the  $pK_a$  of 7.21 for  $HSO_3^-$ , at alkaline pH, the major sulfite species is  $SO_3^{2-}$  rather than  $HSO_3^-$ . Under UV irradiation,  $SO_3^{2-}$  is converted to  $SO_3^{\cdot-}$  together with  $e_{aq}^-$  (Eq. (28)), and the generated  $SO_3^{\cdot-}$  could be subsequently self-quenched to produce  $S_2O_6^{2-}$  (Eqs. (29) and (30)), which would further convert to  $SO_4^{2-}$ . Therefore, for efficiently reductive destruction of PFASs, the UV/sulfite system must be operated under alkaline conditions.



Recently, several studies have been reported for the degradation of PFASs by UV/sulfite system. Song et al. [95] demonstrated that in  $N_2$ -saturated aqueous solution more than 80% defluorination ratio could be obtained within 24 h reaction. By using  $NO_2^-$  and  $NO_3^-$  as quenching agents,  $e_{aq}^-$  was proven as the active species responsible for the decomposition of PFOA. In further study, Gu et al. [45] used UV/sulfite system to degrade PFOS, and similar phenomenon was observed. By identifying the generated intermediates and theoretical calculations, two possible PFOS transformation pathways were proposed. On the one hand, the PFOS degradation occurs from the cleavage of C–S bond, inducing the generation of PFOA, which would be further degraded. On the other hand, once an external electron is attached to PFOS anion, it would tend to localize in the region over the middle C atoms of PFOS due to the lower dissociation energy, inducing the generation of shorter chain PFASs. In this study, the researchers also assessed the toxicity caused by sulfite through luminescent bacteria toxicity test. Since the sulfite is likely oxidized by  $O_2$  to form sulfate, the generation of sulfate significantly decreased the toxicity of the system.

In addition to PFOA and PFOS, the structure-reactivity relationships of PFASs and perfluoroalkyl ether carboxylic acids (PFECAs) were further revealed in the following researches. Bentel et al. [104] systematically studied the degradation and defluorination of PFASs with different chain lengths and functional groups in the UV/sulfite system. As reported, the PFASs with different chain lengths showed similar degradation and defluorination trends, while trifluoroacetate showed significantly slower degradation rate and higher defluorination rate, which could be attributed to the distinct degradation mechanism (more discussion shown below). However, for PFASs ( $C_nF_{2n+1}SO_3^-$ ), both degradation and defluorination decreased with the shortening of chain length. While, compared to PFCAs, the presence of  $-CH_2CH_2-$  in fluorotelomer carboxylic acids (FTCAs) resulted in significant persistence and dependence on  $C_nF_{2n+1}$  length. Significant FTCAs degradation was obtained only when  $n > 5$ , while negligible degradation was observed for  $n < 5$ . In addition to these PFASs, the degradation of some PFECAs was also discussed in the UV/sulfite system [105]. The rate and extent of PFECA degradation depended on both branching extent and chain length of oxygen-segregated fluoroalkyl moieties (the detailed degradation mechanism is discussed below). Moreover, the effect of pH on PFCA degradation showed that as pH increased from 9.5 to 12.3, the substantially enhanced degradation rate and extent of PFCA defluorination were obtained [106]. The results of degradation kinetics and transformation products indicated that at pH 12, the  $e_{aq}^-$  cleaved the strong C–F bonds that could not occur at pH 9.5. What's more, the high pH value also significantly favored the preferred decarboxylation pathway toward a deep defluorination. Recently, the aqueous film-forming foam (AFFF) containing PFASs mixture was also treated directly by the UV/sulfite system [107]. As expected, the reactivity varied widely among PFASs, but reaction rates observed for individual PFASs in AFFF are similar to the rates observed in single-solute experiments. The long-chain PFASs and PFCAs were readily degraded, while other structures for notably short chain PFASs and fluorotelomer sulfonic acids (FTSs) were more recalcitrant. In this system, the final defluorination ratio could reach up to 53% of the total F content in AFFF.

To further enhance the degradation and defluorination efficiency of the resistant PFASs, some coupled techniques were developed. By integrating thermally activated PDS and UV/sulfite systems, some FTCAs and FTSAs, which could not be completely defluorinated in UV/sulfite system, were firstly oxidized to PFCAs before reductive defluorination [108]. Moreover, the UV/KI and UV/sulfite systems were also combined together [109]. In the new system, the addition of iodide significantly accelerated the reductive degradation of both PFASs and PFCAs. In UV/sulfite + KI system, the rapid scavenging of reactive iodine species by  $SO_3^{2-}$  extended the lifetime of  $e_{aq}^-$  8 times longer than that in bulk UV/KI system. Moreover, the addition of KI also substantially enhanced  $SO_3^{2-}$  utilization, leading to >90% overall defluorination ratio. Compared to UV/KI system, the UV/sulfite system does not produce toxic substances,



while the reaction still needs anaerobic and alkaline conditions to achieve high efficiency.

### 3.3. UV/indole systems

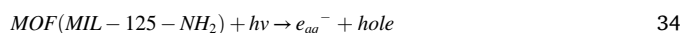
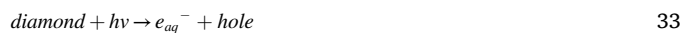
In order to expand the application of  $e_{aq}^-$  based techniques for PFASs degradation, indole and its derivatives (e.g., 3-indole-acetic acid (3-IAA)) were explored for PFASs degradation [47,93]. In these systems, indole derivatives were used as the  $e_{aq}^-$  source chemicals, and prior studies demonstrated that under UV irradiation, these compounds also produce large amount of  $e_{aq}^-$  (Eq. (31)).



In the study of Tian et al. [110], organic modified montmorillonite mineral was used as the reaction matrix. Attributing to the protection effect on  $e_{aq}^-$  by the presence of organic montmorillonite, the reductive degradation of PFASs was dramatically enhanced under ambient conditions [44]. Furthermore, different organic modification materials, including cetyl trimethyl ammonium bromide (CTAB), dodecyl trimethyl ammonium bromide, trimethyl phenyl ammonium bromide, poly-4-vinylpyridine-co-styrene and 12-aminolauric acid were used to modify montmorillonite [110,111]. The organic montmorillonite exhibited excellent adsorption capability for both 3-IAA and PFASs, creating a confinement for ensuring the reduction reaction. Under UV irradiation,  $e_{aq}^-$  and indole cationic radicals are simultaneously generated from indole and indole derivatives. Consequently, cationic radicals can be stabilized by the negatively charged layer of the montmorillonite, which would inhibit the recombination reaction between  $e_{aq}^-$  and indole cationic radicals, contributing to the higher  $e_{aq}^-$  utilization. More interestingly, the organic modification also protects  $e_{aq}^-$  from quenching by oxygen and proton via creating an anaerobic condition in the space of montmorillonite. Further studies showed that the organic modification can effectively prevent the interference from a variety of environmental factors, e.g., nitrate and sulfate [44]. Moreover, the actual efficiency of this organic montmorillonite system was also proven by PFASs-containing industrial wastewater. To further simplify the reaction system, a ternary self-assembly micelle system was constructed by cationic surfactant, PFOA and 3-IAA/HPAs [112]. Owing to the rapid  $e_{aq}^-$  transfer from 3-IAA/HPAs to PFOA in the micelle, the degradation and defluorination were greatly enhanced even under ambient conditions (Fig. 2). PFOA concentration decreased from 10 mg/L to ~60 ng/L after 2.5 h UV irradiation from a 500 W high-pressure mercury lamp, below the drinking water health advisory level of the US EPA for the combined concentration of PFOA and PFOS (70 ng/L). Due to the quick settlement and automatic separation of the micelle, the dissolved organic carbon content of the reaction solution would be also reduced to ~3 mg/L after the reaction. Attributing to the barrier created by the cationic surfactant, this newly developed composite was also adaptable to a wide pH range from 4 to 10 [113]. In addition, the PFASs decomposition with different indole derivatives was also investigated [47]. By using neutral indole and positively charged donaxine as  $e_{aq}^-$  source materials, hydrogen bonding and electrostatic attraction could be responsible for the interaction between indole/donaxine and anionic PFASs (Fig. 2). In this simple binary system, the molecular attraction enhances the utilization efficiency of  $e_{aq}^-$  generated in the system, thus inducing the highly efficient PFASs degradation and defluorination under ambient conditions. Compared to the UV/KI and UV/sulfite systems, several advantages were demonstrated in the UV/indole systems. Firstly, due to the higher  $e_{aq}^-$  yield of indole derivatives compared to both KI and sulfite, the UV/indole systems consume less  $e_{aq}^-$  substances. Secondly, anaerobic and alkaline conditions may not be necessary, which would simplify the reaction process. However, the toxicity of the systems induced by surfactants should be carefully assessed in subsequent studies for practical applications.

### 3.4. Other hydrated electron basing systems

In addition to the three widely studied  $e_{aq}^-$  based systems, other systems including UV/ $\text{Fe}(\text{CN})_6^{4-}$  [114], UV/diamond [115], and UV/metal-organic framework (MOF, MIL-125-NH<sub>2</sub>) [116] were also investigated to decompose PFASs (Eqs. 32–34).



By using laser flash photolysis, the generated  $e_{aq}^-$  was identified in the UV/ $\text{Fe}(\text{CN})_6^{4-}$  system, and the reaction between  $e_{aq}^-$  and PFOA was demonstrated by the decreased  $e_{aq}^-$  lifetime after increasing PFOA concentration [114]. Similar with the above UV/KI and UV/sulfite systems, the UV/ $\text{Fe}(\text{CN})_6^{4-}$  system also needs alkaline and anaerobic conditions. In addition, some photocatalysts with strong photo reduction capability were also developed, such as diamond and MIL-125-NH<sub>2</sub> [115,116]. Under UV irradiation, the photo-generated electrons on the conductive band of the photocatalyst would be captured by several water molecules to form  $e_{aq}^-$ , which further involve into the PFOA degradation.

Recently, the researchers noticed that a fraction of  $e_{aq}^-$  generated from the source materials could be scavenged by some oxidizing species, resulting in inefficient utilization. Therefore, another strategy was proposed to enhance the utilization efficiency of  $e_{aq}^-$  by quenching the coexisting oxidizing species [117–119]. One such example is nitrotriacetic acid (NTA) [117], which could play two important roles. On the one hand, the additional NTA could act as a photosensitizer to facilitate the  $e_{aq}^-$  generation from water photodissociation (Eq. (35)).

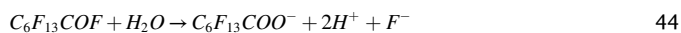
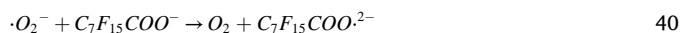


On the other hand, NTA could also react with  $\cdot\text{OH}$ , and the rate constant is  $4.2 \times 10^9/\text{M}\cdot\text{s}$  at pH 10, which protect the generated  $e_{aq}^-$  from quenching by  $\cdot\text{OH}$ . Moreover, after adding a small amount of  $\text{Fe}^{2+}$ , the decomposition of PFOS could be significantly improved [120]. Based on the theory calculations, the enhancement could be attributed to the formation of metal-ligand complex, which occur through a concerted photoinduced intramolecular charge transfer instead of direct attack by  $e_{aq}^-$ . In addition to NTA, ethylenediaminetetraacetic acid (EDTA) could also play the similar role, and highly efficient PFOS decomposition was obtained under anaerobic condition at pH 10 [118]. Some organic solvents, such as alcohols, are also recognized to quench  $\cdot\text{OH}$  with high efficiency, and the promoted PFOA degradation in UV/alcohol systems was also achieved [119]. Besides, alcohols are often used as eluents to extract PFASs from functionalized adsorbents. Therefore, this method is beneficial for the treatment of alcohol-containing wastewater. More meaningfully, since alcohol radicals could be generated from alcohols under UV irradiation, which would rapidly consume dissolved oxygen and proton, the high efficiency could be maintained under ambient conditions.

### 3.5. Other reductive systems

In addition to  $e_{aq}^-$  based systems, other reductive systems using active hydrogen atom, carbon dioxide anion radical and  $\text{O}_2^{\cdot-}$  were also investigated for PFASs degradation. Huang et al. [50] studied the decomposition of PFOA by using SiC/graphene catalyst under UV irradiation. In the system, the generated Si–H bond on the surface of SiC/graphene substituted for silylium ( $\text{R}_3\text{Si}^+$ ) to activate the C–F bond, and a photo-induced hydrodefluorination was inferred. Furthermore, Wang et al. [49] developed a  $\text{TiO}_2$  based photocatalytic system for remediating PFOA-containing wastewater in the presence of oxalic acid. Under UV irradiation, both photo-generated electron and hole would be generated on the surface of  $\text{TiO}_2$ , and the later would react with oxalic acid to

generate carbon dioxide anion radical to degrade PFOA. Moreover,  $O_2^{\bullet -}$  basing systems were also extensively studied for the treatment of PFOA. In the  $H_2O_2$ -carbon/ $MnO_2$  system,  $O_2^{\bullet -}$  and  $\bullet OH$  could be synchronously generated. By quenching experiments, the researchers demonstrated that the  $O_2^{\bullet -}$  plays a dominant role in PFOA degradation [121]. Besides, Mitchell et al. [94] found that  $O_2^{\bullet -}$  could be generated in large quantities in  $H_2O_2/Fe^{3+}$  system (Eqs. 36–39), which would lead to the quick PFOA decomposition. More  $O_2^{\bullet -}$  based systems including plasma activation,  $KO_2$  in dimethyl sulfoxide, xanthine oxidase with hypoxanthine and  $WOX/ZrO_2$  catalyst with  $H_2O_2$  were also developed to degrade PFOA [122], and the overall defluorination of PFOA by  $O_2^{\bullet -}$  could be described as following equations (Eqs. 40–44):



As a green-chemical reductant, ZVI was widely used in the environmental remediation. Arvaniti et al. [123] synthesized a Mg-aminoclay coated with nanoscale ZVI, which could remove more than 38–80% of individual PFASs within 1 h. Yang et al. [124] further utilized ZVI to modify carbon materials, simultaneous enrichment and catalytic defluorination of PFASs were achieved. In the ZVI system, the ZVI can act as the reductant (Eq. (45)), providing two electrons to participate in the pollutant degradation.



In this review, the efficiencies of different reductive systems are further compared from several aspects, e.g., decomposition reaction rate, reaction time and energy consumption as listed in Table 2. Obviously, most of these systems are strongly dependent on energy consumption, which playing critical role in their economic feasibility. By now, some studies also evaluate the scavenging and inhibiting effects from real wastewater matrices on these systems. However, most studies showed the decreased PFASs degradation efficiencies under natural conditions. Although ARPs have a higher defluorination efficiency for PFASs than AOPs, the limitations for their reaction conditions also impede their practical applications. Conclusively, there is still a long way before the ARPs can be successfully applied in practical PFASs pollution remediation.

#### 4. Mechanisms of PFASs destruction

The degradation pathways regarding to PFASs in AOPs and ARPs were proposed based on different research approaches, including the identification of intermediates [125], F mass balance analysis [126] and theoretical calculation with density functional theory (DFT) [127]. Herein, we summarize the conversion pathways of two representative PFASs including PFOA and PFOS in different AOPs and ARPs, respectively.

**AOPs.** For PFOA decomposition, the generated intermediates were

identified by HPLC-MS analysis, and several short-chain PFCAs ( $C_2$ – $C_6$ ) including PFHpA ( $C_6F_{13}COOH$ ), PFHeA ( $C_5F_{11}COOH$ ), PFPeA ( $C_4F_9COOH$ ), PFBA ( $C_3F_7COOH$ ) and PFPrA ( $C_2F_5COOH$ ) are the dominant byproducts [31,42,85]. It is evident that the oxidation potential of  $SO_4^{\bullet -}$  is 2.5–3.1 eV lower than that of the C–F bond (3.6 eV). Therefore, the first reaction site attacked by  $SO_4^{\bullet -}$  could be deduced to occur at the head group of carboxyl [128]. There are a series of reaction revealing the PFOA defluorination mechanism, with one  $CF_2$  unit conversion in each step accompanied by defluorination as shown in Fig. 3. During this pathway, the decarboxylation process induced by  $SO_4^{\bullet -}$  is the predominant step, in which the unstable perfluoroalkyl radical is generated, and the unstable perfluoroalkyl alcohol can be formed after combining with a  $\bullet OH$ . The perfluoroalkyl alcohol would then undergo a continuous hydrolysis process to lose a  $CF_2$  unit. Similar pathway occurs continuously with sufficient  $SO_4^{\bullet -}$  for other shorter chain PFCAs. For PFOS, the first reaction site is the C–S bonds, and there is a consensus that PFOS could be converted to PFOA with a series of reactions as presented in Fig. 3. Under the attack of  $SO_4^{\bullet -}$ , PFOS could be converted to an unstable radical of  $C_8F_{17}SO_3\bullet$ . In the subsequent reactions,  $\bullet OH$  would play a critical role, leading to the formation of  $C_8F_{17}OH$ . Then,  $C_8F_{17}OH$  would be transformed to PFOA by hydrolysis reaction. Although  $SO_4^{\bullet -}$  can degrade a variety of PFASs including PFOA and PFOS, it cannot degrade perfluoroalkyl ether carboxylic acids.

**ARPs.** Different from AOPs, the PFOA decomposition in ARPs could be divided into three pathways as shown in Fig. 4 [104,108]. Firstly, the reaction occurs via the initial two H/F exchanges at the  $\alpha$ -position by hydrogen to form  $C_6F_{13}CH_2COO^-$ , which can undergo homolytic reaction to form  $\bullet C_6F_{13}$  and  $\bullet COO^-$  accompanied with the elimination of  $CH_2$  carbene under UV irradiation. Subsequently, the produced  $\bullet C_6F_{13}$  and  $\bullet COO^-$  would be recombined to form a shorter chain PFCA, then entering the next cycle. Secondly, a decarboxylation–hydroxylation–elimination–hydrolysis pathway is proposed, in which the unstable perfluorinated alcohol would be generated after the decarboxylation reaction induced by  $e_{aq}^-$ , and the defluorination process mainly occurs through the hydrolysis of perfluorinated alcohol. Thirdly, it is also possible that the first step reaction takes place in the middle of the long-chain structure. After the middle  $-CF_2-$  is reduced to  $-CH_2-$ , the PFOA molecule is thus divided into two short fluorocarbon chains, further forming two short chain PFCAs. For PFOS, two types of intermediates were detected, including (1) short-chain fully and partially fluorinated PFCAs and (2) short-chain fully and partially fluorinated PFASs. In prior studies, two main reaction mechanisms were proposed to explain the reductive degradation of PFOS as presented in Fig. 5. During H/F exchange process, the  $F^-$  can be eliminated directly, and this process mainly happens at the C–F bonds with lowest dissociation energy. Among all the C–F bonds, two middle  $CF_2-$  bonds show the relatively lower dissociation energy  $\sim 446.31$  kJ/mol. Desulfonation is another possible PFOS degradation pathway, in which the attachment of  $e_{aq}^-$  breaks down the C–S bond between the headgroup and perfluoroalkyl chain due to the lower bond energy of C–S than C–C. The generated perfluoroalkyl radical can be converted to perfluoroalkyl alcohol, which would be subsequently transformed to PFOA. For the perfluoroalkyl ether carboxylic acids, the main attack sites for  $e_{aq}^-$  are the ether-oxygen bonds due to the lower bond energy, leading to the generation of perfluoroalkyl ether alcohol, which would further eliminate  $F^-$  through hydrolysis, similar to PFCA.

In general, both AOPs and ARPs can degrade PFASs, but the reaction conditions, reaction efficiency and the generated products are different. Compared with AOPs, the ARPs based on hydrated electron can degrade and defluorinate PFASs more completely, and higher defluorination rate could be obtained. In the AOPs, PFASs are converted to short-chain PFCAs. Compared with fluorine ions, short-chain PFCAs have higher toxicity. Therefore, ARPs show superior detoxification effect on PFASs-polluted wastewater. However, compared with ARPs, most AOPs do not need to control the anaerobic and alkaline reaction conditions, exhibiting higher application value.

## 5. Conclusions and perspectives

In the numerous literatures cited in this review, we discussed the current research status of AOPs and ARPs developed for PFASs pollution remediation. Meanwhile, the PFASs decomposition efficiency, reaction time and energy consumption in different AOPs and ARPs were compared. The degradation mechanisms and pathways of some common PFASs, including PFOA and PFOS in different systems were also summarized and analyzed. Indeed, both AOPs and ARPs provide technical feasibility to treat PFASs polluted groundwater and wastewater, while the uniqueness of AOPs and ARPs have profound implications for their practical application.

Based on the systematic review, the main conclusions could be drawn as following:

1. Both AOPs and ARPs could be performed for the decomposition of PFASs with different molecular mechanisms. Compared with AOPs, ARPs based hydrated electron can degrade and defluorinate PFASs more completely, and higher defluorination rate could be obtained.
2. In AOPs, the generated  $\bullet\text{OH}$  cannot destruct PFASs, while  $\text{SO}_4^{\bullet-}$  can efficiently degrade PFASs. However, completed defluorination cannot be achieved, and some F-containing intermediates would be accumulated.
3. In some  $e_{\text{aq}}^-$  based ARPs, PFASs can be completely defluorinated through different routes including defluorinated hydrogenation and dicarboxylic hydrolysis processes due to the strong reductive potential of  $e_{\text{aq}}^-$ .
4. In both AOPs and ARPs, the main degradation pathways of long-chain PFASs are via rapid conversion to short-chain intermediates accompanied by defluorination.

Moreover, the main challenges and perspectives in terms of PFASs remediation could be concluded as following:

1. More attentions should be devoted to the development of novel AOP/ARP techniques, which do not require high amount of additional chemicals, and the methods must be cost-effective for practical applications.
2. The degradation degree of PFASs in AOPs and ARPs is different, leading to the different toxicity after reaction in different systems, thus more attention should be paid to the toxicity changes during the treatment processes in different systems.
3. The actual PFASs-contaminated wastewater often has complex components which may affect the actual reaction efficiency of different AOPs and ARPs. Therefore, actual PFASs-contaminated wastewater should be tested, not just limited to laboratory simulations.
4. Can the reported AOPs/ARPs be combined with other physical/chemical processes to build more efficient multiple barriers for PFAS? For example, the PFAS reduction products generated from the ARP treatment may be efficiently degraded by certain chemical oxidation processes, or further removed by biological degradation when ARPs improve the biodegradability of these contaminants.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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