



# PFAS and their substitutes in groundwater: Occurrence, transformation and remediation

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## ABSTRACT

Poly- and perfluoroalkyl substances (PFAS) are increasingly investigated due to their global occurrence and potential human health risk. The ban on PFOA and PFOS has led to the use of novel substitutes such as GenX, F-53B and OBS. This paper reviews the studies on the occurrence, transformation and remediation of major PFAS i. e. PFOA, PFNA, PFBA, PFOS, PFHxS, PFBS and the three substitutes in groundwater. The data indicated that PFOA, PFBA, PFOS and PFBS were present at high concentrations up to 21,200 ng L<sup>-1</sup> while GenX and F-53B were found up to 30,000 ng L<sup>-1</sup> and 0.18–0.59 ng L<sup>-1</sup>, respectively. PFAS in groundwater are from direct sources e.g. surface water and soil. PFAS remediation methods based on membrane, redox, sorption, electrochemical and photocatalysis are analyzed. Overall, photocatalysis is considered to be an ideal technology with low cost and high degradation efficacy for PFAS removal. Photocatalysis could be combined with electrochemical or membrane filtration to become more advantageous. GenX, F-53B and OBS in groundwater treatment by UV/sulfite system and electrochemical oxidation proved effective. The review identified gaps such as the immobilization and recycling of materials in groundwater treatment, and recommended visible light photocatalysis for future studies.

## 1. Introduction

Poly- and perfluoroalkyl substances (PFAS) are listed as emerging contaminants by the US Environmental Protection Agency (USEPA) in 2014, which have been widely used in surfactants, lubricants, polymer additive and especially in aqueous film-forming foams (AFFF) (Høisæter et al., 2019; Mumtaz et al., 2019), due to their aqueous surface tension-lowering property since the 1950s (Buck et al., 2011). However, when released to the environment, these PFAS can lead to soil, river and groundwater contamination (Ahmed et al., 2020a). Due to their seriously persistent and bio-accumulative nature, PFAS draw widespread public health concerns (Ho et al., 2020; Liu et al., 2020). For example, as a common PFAS, perfluorooctanoic acid (PFOA) is estimated to be

especially harmful to aquatic lives with a half-life in serum of 2.7 years in individuals exposed to PFOA contaminated water (Rodea-Palomares et al., 2015; D. Li et al., 2019; Y. Li et al., 2019). Adverse effects such as genotoxicity, immunotoxicity, neurotoxicity and hepatotoxicity in animals could be caused by PFOA accumulation in vivo (D. Li et al., 2019; Y. Li et al., 2019; Wen et al., 2020). Among those, hepatotoxicity was widely observed in the vertebrate animals, manifested through unusual fat deposits, liver enlargement and hepatocarcinogenesis (Wu et al., 2017). In addition to PFOA, perfluorononanoic acid (PFNA), perfluorobutanoic acid (PFBA), perfluorooctane sulfonic acid (PFOS), perfluorohexane sulfonic acid (PFHxS) and perfluorobutane sulfonic acid (PFBS) belonging to PFAS are also frequently detected in environment as emerging PFAS with potential risk for human beings. Their chemical

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structures are shown in Fig. 1a.

Because of these adverse effects, beginning in 2006, the major manufacturers of PFOA voluntarily phased out their production by USEPA in 2015. However, shorter-chain analogues have been adopted as alternatives, which show similar or even higher persistence and toxicity relative to PFOA (Gomis et al., 2018). One of such compounds is GenX, the commercial name for the ammonium salt of hexafluoropropylene oxide dimer acid (HFPO-DA) (Conley et al., 2019), which has been used as an alternative to PFOA in fluoropolymer or resin manufacture since 2009 (Chen et al., 2020). GenX was firstly detected in Elbe and Rhine Rivers in Germany, the Rhine-Meuse delta in Netherlands, and the Xiaoqing River in China (Heydebreck et al., 2015). Furthermore, recent studies claim that GenX has an even higher toxicity to modeled serum and liver than PFOA (Gomis et al., 2018). Similarly, after a steep decline of PFOS in production as “restricted use” compounds under the Stockholm Convention, two main alternatives are expected to expand a large market share (Suthersan et al., 2016). One of them is potassium 9-chlorohexadecafluoro-3-oxanonane-1-sulfonate (F-53B), which has been initially developed since 1970s, and quickly dominated the Chinese market for its low cost (Wang et al., 2013). Another one is sodium *p*-perfluorooxanonene sulfonate (OBS), which have been produced by a Japanese company (Neos) since 1980s (Funasaki and Hada, 1979), and largely used in China at a volume of 3500 tons per year (Bao et al., 2017). However, these two PFOS substitutes were also found to be not as safe as expected just like GenX. Based on a preliminary study, F-53B was suggested to be moderately toxic (the LC50–96 h of 15.5 mg L<sup>-1</sup> in zebrafish) and OBS was proved to have similar acute toxicity with PFOS (the LC50–96 h of 25.5 mg L<sup>-1</sup> in zebrafish) (Wang et al., 2013; B. Xu et al., 2017b). More data on their toxicity were limit so they are still need to be further investigated. Their chemical structures are presented in Fig. 1b.

Groundwater is easily threatened by chemical and biological contamination (Maskaoui and Zhou, 2010; Talabi and Kayode, 2019). As for PFAS, some studies reported that groundwater was contaminated by PFAS from the release of aqueous fire-fighting foams (AFFFs), discharge from fluorochemical facilities or the migration from environmental soil and water system (Moody et al., 2003; Hoffman et al., 2011). Thus, this becomes a significant issue as at least half of the global population relies

on groundwater (Liu et al., 2019). Relevant local residents would suffer the most via groundwater ingestion from private wells (J. Bao et al., 2019a). For example, in September 2015, the New South Wales Government of Australia announced that PFAS contamination was detected in Williamtown (<https://www.epa.nsw.gov.au>). In August 2016, the Department of Defence (Australia) reported that drinking contaminated groundwater was identified as the major exposure pathway with potential health risks (<https://www.epa.nsw.gov.au>). Therefore, the occurrence of PFAS in groundwater and their potential risk for human beings should be carefully reviewed.

PFAS such as PFOA and PFOS are stable chemicals due to the strong C-F bonding energy (Ahmed et al., 2020b), hence they are persistent in the environment and are difficult to be degraded. Until now, much work has been done to pursue the green treatment for PFAS remediation with high efficiency (Kucharzyk et al., 2017; Lu et al., 2020). Nevertheless, many conventional approaches such as thermal treatment, direct photolysis and general hydroxyl-based chemical oxidation, are ineffective for aqueous PFAS removal (Vecitis et al., 2010; Nzeribe et al., 2019). Therefore, evaluating and selecting the most appropriate remediation technologies for PFAS removal from particular media are crucially important. Meanwhile, the mechanism of PFAS remediation should be explored which is helpful to select the novel and effective methods. In this study, the occurrence, sources and fates of six PFAS (i.e. PFOA, PFNA, PFBA, PFOS, PFHxS and PFBS) and three new substitutes (i.e. GenX, F-53B and OBS) in groundwater are reviewed. In addition, the risk assessment of PFAS is conducted to evaluate their influence on human beings. Novel remediation technologies targeting on PFAS removal in groundwater reported recently are summarized with their mechanistic insights. The challenges and recommendations on PFAS removal in groundwater are elaborated.

## 2. Occurrence of PFAS in groundwater

The concentration levels (mean value) of PFAS in groundwater from different areas in the world are presented in Fig. 2 (Chen et al., 2016; Cao et al., 2019). Six kinds of PFAS, i.e. PFOA, PFNA, PFBA, PFOS, PFHxS and PFBS, were frequently detected in groundwater. Table 1 provides the data in detail including the range, mean value and crucial

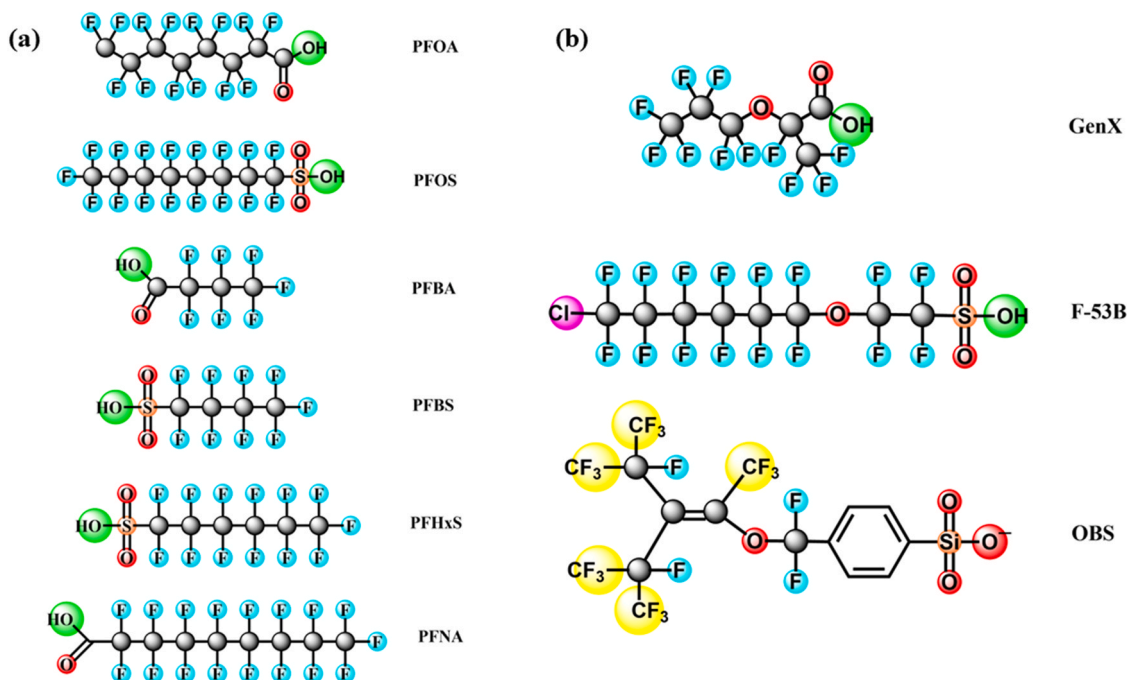


Fig. 1. Chemical structure of PFOA, PFOS, PFBA, PFBS, PFHxS, PFNA (a) and GenX, F-53B and OBS (b).

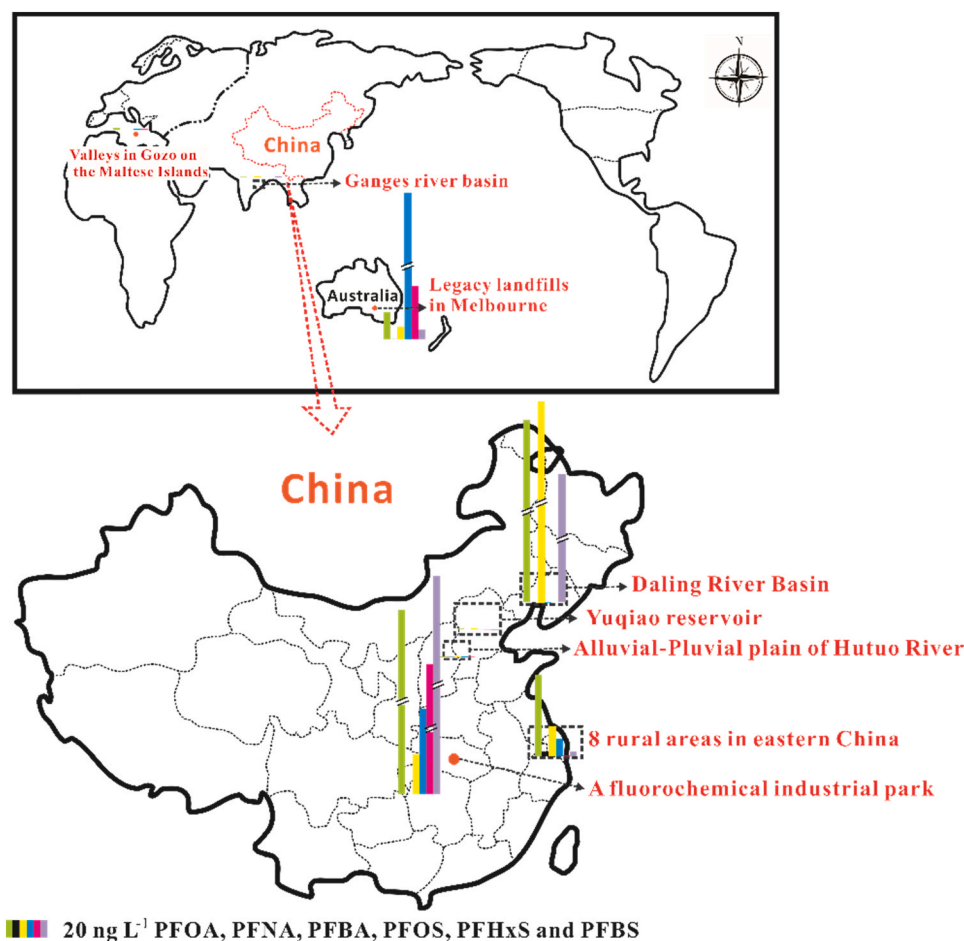


Fig. 2. The average concentrations of PFOA, PFOS, PFBA, PFBS, PFHxS and PFNA in groundwater from different areas in the world. The data in detail were provided in Table 1.

ratios of PFOA/ $\Sigma_6$ PFAS and PFOA/PFOS. Notably, PFOA was at higher concentration levels than other compounds in three of eight locations. For example, in the rural areas of eastern China, PFOA ranged from 7 to 175.2 ng L<sup>-1</sup> with the mean value of 90.8 ng L<sup>-1</sup>, while other compounds were all below 60 ng L<sup>-1</sup> (Chen et al., 2016). In the Alluvial-Pluvial Plain of Hutuo River, China, PFOA ranged from 0 to 1.76 ng L<sup>-1</sup> (mean value = 0.63 ng L<sup>-1</sup>) in the groundwater (Liu et al., 2019), higher than the other compounds. Similarly, PFOA occurred with the range of 0–8.03 ng L<sup>-1</sup> (mean value = 1.46 ng L<sup>-1</sup>) in the groundwater from valleys in Gozo on the Maltese Islands (Sammut et al., 2019), which was higher than PFNA, PFOS and PFHxS, while no PFBA and PFBS were found in this area. In addition, higher concentration levels of PFBA were shown in groundwater from a drinking water source near Yuqiao reservoir, China and 4 villages in Daling River Basin, China with the mean value of 1.13 and 1544 ng L<sup>-1</sup>, respectively, compared to the other compounds (Wang et al., 2016b; Cao et al., 2019). Meanwhile, PFBS was at higher concentration levels in groundwater from the Ganges river basin, India and around a fluorochemical industrial park in China with the mean value of 1.53 and 11,016.2 ng L<sup>-1</sup>, respectively (Sharma et al., 2016; J. Bao et al., 2019a). While PFOS showed higher concentration than others only in 13 shallow monitoring bores surrounding legacy landfills in Melbourne, Australia with the range of 1.3–4800 ng L<sup>-1</sup> and mean value of 413.3 ng L<sup>-1</sup> (Hepburn et al., 2019). Therefore, more attention should be drawn to the PFAS with generally high concentration levels, such as PFOA, PFBA, PFOS and PFBS in groundwater.

Only a limited number of studies were identified where both GenX and PFOA monitoring data in groundwater were presented. Gebbink and

van Leeuwen (2020) concluded five studies reporting the concentrations of PFOA and GenX in groundwater at different locations in the Netherlands. PFOA ranged from 1 to 47,000 ng L<sup>-1</sup> and the mean value was 5754.18 ng L<sup>-1</sup>, while GenX ranged from n.d. to 30,000 ng L<sup>-1</sup> and the mean value was 1895.70 ng L<sup>-1</sup>. They suggested that although lower than PFOA, GenX was existing at a certain level ( $\mu\text{g L}^{-1}$ ) and needed to be examined on its potential contamination in groundwater as a substitute of PFOA. Besides, median PFOA and GenX concentrations of 1.8–12.2 ng L<sup>-1</sup> and 0.21–2.02 ng L<sup>-1</sup>, respectively in various rivers of China, the Thames (UK), the Rhine (the Netherlands) and Delaware river (USA) were explored by Pan et al. (2018). Moreover, the median value of PFOA and GenX were found to be < 10–34 ng L<sup>-1</sup> and < 10–304 ng L<sup>-1</sup>, respectively in drinking water in North Carolina by Mei et al. (2016). However, fewer studies reported the occurrence of F-53B in groundwater. Wei et al. (2018) collected 102 groundwater samples from 13 cities in Jiangsu Province, China in 2016. They found that the concentrations of F-53B in these groundwater samples were ranged from 0.18 to 0.59 ng L<sup>-1</sup>. No more investigation about F-53B in groundwater has been conducted till now, while some previous studies reported its occurrence in different media as shown in Table 2 (Wang et al., 2016a). F-53B was found to occur from n.d. to 78.5 ng L<sup>-1</sup> in river water, < 0.21–7.9 ng L<sup>-1</sup> in seawater, and 0.69–52 in lake water, respectively (H. Chen et al. 2017; Pan et al., 2018). Meanwhile, it was also detected in the riverine sediment, fish muscle and human serum with the concentration of 0.32–7.2 ng g<sup>-1</sup>, 0.6–4.8 ng g<sup>-1</sup> and 1.54 ng mL<sup>-1</sup> (Median value) (F. Chen et al., 2017; Lin et al., 2017; Shi et al., 2015). As for OBS, no investigation has been done in groundwater until recently. Only Xu et al. (2017b) collect the water samples around Daqing Oilfield,

**Table 1**

Summary of reported values of PFAS concentrations and ratios in groundwater by source and region.

Location	Concentration range (mean value) ng L <sup>-1</sup>						Key ratio		Reference
	PFOA	PFNA	PFBA	PFOS	PFHxS	PFBS	PFOA/ Σ <sub>6</sub> PFAS	PFOA/ PFOS	
<i>Rural areas in eastern China</i>									
Surface water	0–223.8 (77.17)	0–4.6 (1.66)	0–99 (29.46)	0–21.5 (8.79)	0–41.7(14.44)	0–15 (7.22)	0.56	8.78	Chen et al., 2016
Groundwater	7–175.2 (90.8)	<0.1–22 (4.7)	<0.1–58.5 (33.1)	<0.5–37 (19.2)	<0.5–1.5 (0.9)	<0.5–7.4 (4.8)	0.59	4.73	
<i>Drinking water source area near Yuqiao reservoir, China</i>									
Surface water	0.48–5.33 (1.88)	0.06–1.0 (0.44)	2.77–67.0 (10.28)	0–5.54 (0.49)	0–0.18 (0.04)	0.09–4.17 (0.74)	0.14	3.84	Cao et al., 2019
Groundwater	0–5.11 (0.8)	0–0.20 (0.08)	0–1.97 (1.13)	0–0.5 (0.17)	0–0.23 (0.09)	0.08–1.21 (0.37)	0.30	4.71	
<i>Ganges River Basin, India</i>									
Surface water	0.08–1.18 (0.40)	0–0.19 (0.06)	<MQL	0–1.73 (0.43)	0–0.3 (0.03)	0–10.19 (2.78)	0.11	0.93	Sharma et al., 2016
Groundwater	0–0.76 (0.46)	0–0.22 (0.05)	0–9.15 (1.30)	0–1.13 (0.16)	0–0.08 (0.02)	0–4.87 (1.53)	0.30	2.88	
<i>Daling River Basin, China</i>									
Groundwater	64.5–4150 (1421.6)	–	352–3610 (1544)	0.15–1.05 (0.4)	–	22.4–865 (374.5)	0.43	3554	Wang et al., 2016a
<i>Bores surrounding legacy landfills in Melbourne, Australia</i>									
Groundwater	1.7–74 (31.2)	<0.2–2.2 (<0.2)	<0.2–49 (14.6)	1.3–4800 (413.3)	2.6–280 (59)	2.0–31 (11.5)	0.06	0.08	Hepburn et al., 2019
<i>Alluvial-Pluvial Plain of Hutuo River, China</i>									
Groundwater	0–1.76 (0.63)	0–1.38 (0.24)	0–0.3 (0.23)	0–0.04 (0.02)	0–0.25 (0.04)	–	0.54	31.5	Liu et al., 2019
<i>Fluorochemical industrial park in China</i>									
Groundwater	105–2510 (1411.6)	<0.1	18–76 (44.4)	<0.1–403 (96.2)	<0.1–1140 (355.2)	64–21,200 (11,016.2)	0.11	14.67	J. Bao et al., 2019a
<i>Valleys in Gozo on the Maltese Islands</i>									
Groundwater	0–8.03 (1.46)	0–0.9 (0.08)	–	0–2.63 (0.48)	0–6.05 (1.1)	–	0.47	3.04	Sammut et al., 2019
<i>Facility with no known AFFF impacts</i>									
Groundwater	15	–	<0.074	300	76	33	–	–	Schaefer et al., 2018
<i>US Department of Defense facility in the vicinity of a fire training area where AFFF was used</i>									
Groundwater	58	–	25	22	160	45	–	–	Schaefer et al., 2018

**Table 2**

Concentration levels of F-53B in different media. Related data were referred with permission from Munoz et al. (2019).

Sample type	Location	Concentration	Reference
Groundwater	13 cities in Jiangsu province, China	0.18–0.59 ng L <sup>-1</sup>	Wei et al. 2018
River water	Xiaoqing River Basin of Chit55556\$%ona	0–78.5 ng L <sup>-1</sup>	Wang et al. 2016a
Seawater	Bohai Sea, China	<0.21–7.9 ng L <sup>-1</sup>	H. Chen et al. 2017
Lake water	Chao Lake, China	0.69–52 ng L <sup>-1</sup>	Pan et al. 2018
Riverine sediment	Fenghua, China	0.32–7.2 ng g <sup>-1</sup>	Lin et al. 2017
Fish muscle	Xiaoqing River and Tangxun Lake, China	0.6–4.8 ng g <sup>-1</sup>	Shi et al. 2015
Human serum	Wuhan, China	1.54 ng mL <sup>-1</sup>	F. Chen et al. 2017

China and OBS was consistently found at the highest concentrations ranging from <MLQ to  $3.2 \times 10^3$  ng L<sup>-1</sup>. Therefore, these new substitutes are widely detected in the environment, and its continuing monitoring should be conducted to prevent its increasing concentration level.

### 3. Source analysis of PFAS in groundwater

Understanding the sources of PFAS in groundwater is essential for the evaluation of PFAS contamination in the environment. The composition of PFAS in related environmental media may provide information on the pollution sources in groundwater. Some indicators, such as the ratios of PFOA to Σ<sub>6</sub>PFAS and PFOA to PFOS, were employed to identify

the potential sources of PFOA in groundwater. In places such as rural areas in eastern China, a drinking source near Yuqiao reservoir of China and Ganges River Basin of India, the difference in the ratios of PFOA/Σ<sub>6</sub>PFAS or PFOA/PFOS between groundwater and surface water was less than three (as shown in Table 1). Thus, the surface water should be considered as a main source contributing to the PFAS occurrence in groundwater. A similar conclusion was also drawn from the literature that PFAS in groundwater may come from seepage of contaminated water and then travel through diffusion, dispersion and advection (Xiao et al., 2015; Liu et al., 2016). These authors estimated that the proportion of surface water seepage in the Northern Plain of China was about 12% (MWR, 2011, 2013, 2014). In addition, Z. Liu et al. (2017) proposed Eq. (1) to estimate the release of PFOS/PFOA through surface water seepage to groundwater ( $G_{\text{seepage}}$ ):

$$G_{\text{seepage}} = E_{\text{surface water}} \times (1 - P_{\text{sediment absorption}}) \times SR_{\text{surface water}} \quad (1)$$

where  $E_{\text{surface water}}$  is the release of PFOS or PFOA via surface water emission,  $P_{\text{sediment absorption}}$  is the proportion of PFOS or PFOA adsorbed by sediment, and  $SR_{\text{surface water}}$  is the seepage rate of PFOS or PFOA from surface water (Liu et al., 2015).

Soil is another important source for PFAS contamination in groundwater via precipitation or irrigation due to their relatively high solubility in water and low log  $K_{\text{oc}}$  values (Xiao et al., 2015). The leaching percentage of PFOS or PFOA was reported to be 90% from soil to groundwater (Gellrich et al., 2012). Cao et al. (2019) investigated PFAS occurrence and source in soil and groundwater from a drinking water source near Yuqiao reservoir. They reported that significant correlations existed among PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFDA, PFBS and TOC in both soil and groundwater, indicating that such compounds shared the similar origins. Notably, groundwater impacted with PFAS originating from the AFFF for the fighting activities has

become a major environmental concern and challenge. Schaefer et al. (2018) investigated the groundwater samples from two areas, of which one was from a facility with no known AFFF impacts, while the other was from a US Department of Defense facility in the vicinity of a fire training area where AFFF was used. No other obvious PFAS input was observed in the two areas. The results in Table 1 suggest that PFOA, PFBA, PFHxS and PFBS were significantly increased from 1.3 to 3.8 times or even from no detection to  $25 \mu\text{g L}^{-1}$  (PFBA) when AFFF was impacted. These findings indicated that the use of AFFF was responsible for the PFAS contamination in groundwater nearby. However, PFOS concentration was  $22 \mu\text{g L}^{-1}$  with AFFF impacted while it was as high as  $300 \mu\text{g L}^{-1}$  with no AFFF impacts, suggesting the potential transformation of PFOS during AFFF irrigation. (Fig. 2).

Fig. 3 presents the sources and fates of PFAS in the environment. In addition to the direct sources from surface water and soil, the indirect sources for PFAS in groundwater include the atmospheric deposition and the precipitation of snow, ice and rainfalls. As Zhao et al. (2020) found that the total PFAS concentrations ranged from 199 to  $678 \text{ pg m}^{-3}$  ( $462 \pm 166 \text{ pg m}^{-3}$ ) in the air of Bohai Sea, China. Moreover, Wang et al. (2018) reported the concentration of  $3.974 \text{ ng L}^{-1}$  for a total of 16 PFAS in surface snow at Yulong, South Asia (X.P. Wang et al., 2019). Other PFAS sources could be the release from related materials such as photograph, non-stick cookware, pesticides, shampoo, paints and fast-food packing which all have been reported previously (Rodrigo et al., 2018; Curtzweiler et al., 2020). And the discharge from PFAS production facilities is also a significant point source pollution for PFAS environmental accumulation (Lambropoulou and Nollet, 2014). Eventually, PFAS in groundwater would be transported to tap water through extraction for drinking water supply. For example, in Malta, tap water consists of approximately 43% groundwater and 57% of desalinated water produced by reverse osmosis plants from seawater (Sammut et al., 2019). Park et al. (2018) evaluated the current contamination status of PFAS in South Korean tap water and detected their total concentration of  $1.44\text{--}224 \text{ ng L}^{-1}$  (median =  $11.9 \text{ ng L}^{-1}$ ). Besides, according to the results, the predominant compounds in tap water were PFOA and PFHxS, which were in accordance with the main components constituted in groundwater (Table 1), further proving the pathway of PFAS from groundwater to tap water. From the risk point of view, total PFAS exposure for an adult via tap water consumption has been estimated at  $46.8 \text{ ng person}^{-1} \text{ day}^{-1}$  (Park et al., 2018). These findings suggest that

PFAS contamination in groundwater could eventually cause the PFAS exposure for human beings and induce potential risks for human health.

As substitutes for PFOA and PFOS, the whole pathways of GenX, F-53B and OBS in the environment are still unclear. In previous studies, GenX has been found in the environmental media of groundwater (Gebbink and van Leeuwen, 2020), soil (Li et al., 2020), surface water and drinking water (Brandtsma et al., 2019). Furthermore, GenX has been detected in human tissues such as urine and serum (Kato et al., 2018). Similarity, F-53B was found in the samples of groundwater, river water, seawater, sediment, and also in the fish tissues and human serum (Munoz et al., 2019). Therefore, GenX and F-53B may have the similar sources and fates in groundwater as other PFAS as shown in Fig. 3, and may eventually impact human health. Nevertheless, there is a lack of investigation on OBS occurrence, so the sources still remain to be further identified.

#### 4. Potential risks of PFAS in groundwater

Groundwater is usually one source of drinking water supply, especially in rural and remote communities (Zhu et al., 2017). Several studies suggested that PFAS were either not or poorly removed during drinking water treatment with conventional treatment processes. Therefore, a health risk assessment of PFAS levels in groundwater is crucial to ensure the safety of local residents. The relevant risk quotient (RQ) was used to estimate health risks, which was calculated as the ratio of the measured environmental concentrations to corresponding regulatory standards. RQ could be at three levels: minimal risk ( $< 0.1$ ), medium risk ( $0.1\text{--}1$ ), and high risk ( $> 1$ ), which were applied frequently in previous studies. Neither water quality standard (WQS) nor recommended guidance values for PFAS in groundwater have been proposed by any agencies (Qi et al., 2016), so the guidance values of drinking water were provisionally used to assess PFAS concentrations in groundwater. Here, only PFOA and PFOS were chosen to be discussed due to their extensive occurrence in the environment. Accordingly, the USEPA guideline values for PFOA ( $400 \text{ ng L}^{-1}$ ) and PFOS ( $200 \text{ ng L}^{-1}$ ) are referenced in groundwater. As shown in Table 1, in the groundwater samples, PFOA concentrations exceeded the limit of  $400 \text{ ng L}^{-1}$  in the villages in Daling River Basin ( $64.5\text{--}4150 \text{ ng L}^{-1}$ ) and around a fluorochemical industrial park in China ( $105\text{--}2510 \text{ ng L}^{-1}$ ). Meanwhile, PFOS in groundwater exceeded the guideline value of  $200 \text{ ng L}^{-1}$

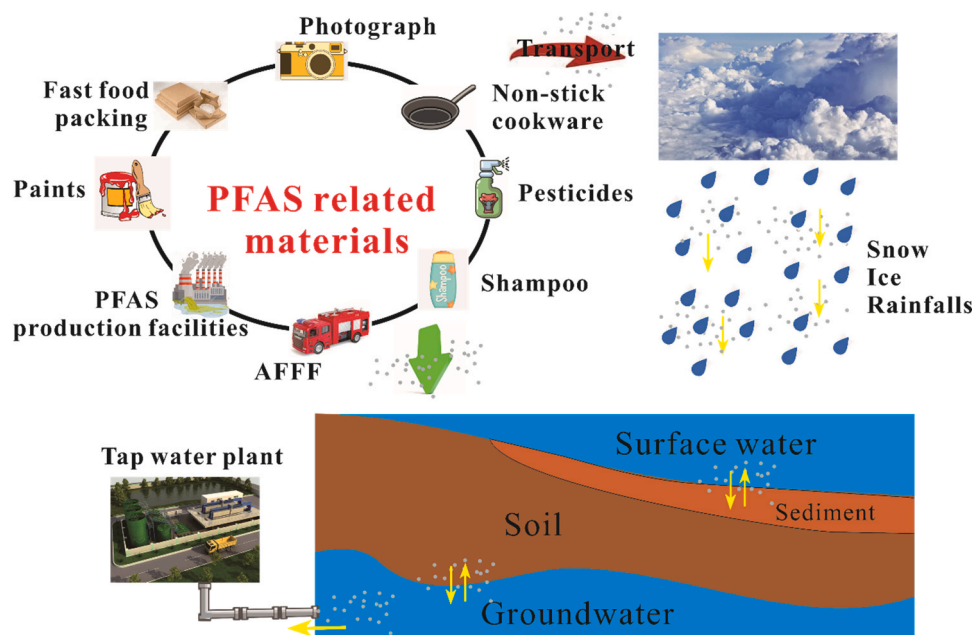


Fig. 3. Schematic diagram of possible sources for PFAS in groundwater.

surrounding legacy landfills in Melbourne, Australia (1.3–4800 ng L<sup>-1</sup>), near a fluorochemical industrial park in China (<0.3–403 ng L<sup>-1</sup>), and from a similar facility in the US (300 ng L<sup>-1</sup>), respectively. Therefore, these places should be paid more attention due to the high risks in order to prevent more contamination which may cause serious illnesses of the local residents.

Recently, WQS for GenX was set at 118 ng L<sup>-1</sup> in groundwater as in surface water (Gebbinck and van Leeuwen, 2020). In the recent work, GenX in the groundwater from the Netherlands (n.d. – 30,000 ng L<sup>-1</sup>), and North Carolina, US (<10–304 ng L<sup>-1</sup>) showed higher concentrations than the WQS value. Such findings suggest that although GenX is the substitute for PFOA in industry, its potential risk still needs to be carefully assessed according to the risk assessment protocols. In addition, Ti et al. (2018) assessed the regional environmental risk of F-53B and demonstrated that the corresponding risk of F-53B on environmental and human health may therefore increase and F-53B has long-range transport potential. Briels et al. (2018) investigated the effects of PFOS and F-53B, separately and as mixtures, on the development of the chicken (*Gallus gallus domesticus*), while PFOS and its alternative F-53B were found to significantly decrease the heart rate of avian embryos immediately before hatching and F-53B significantly increased the liver mass of the hatchlings. However, few document introduced the toxicity of OBS. Recently, Huang et al. (2020) investigated the developmental toxicity of the novel PFOS alternative OBS in developing zebrafish, while found that OBS caused hatching delays, body axis curvature, neurobehavioral inhibition and abnormal cardiovascular development. They also concluded that the developmental effects induced by OBS were generally milder than those of PFOS. In view of these findings, it can be concluded that GenX and F-53B are poor choices as a substitute for PFOA and PFOS, respectively. More in-depth research is also proposed to evaluate the potential risks of OBS compared with PFOS.

## 5. Novel remediation technologies for PFAS in groundwater

Extensive research has been conducted for PFAS remediation in groundwater, and the novel technologies reported recently during 2016–2020 are summarized in Table 3. The removal and degradation mechanisms, as well as the advantages and disadvantages of different methods are discussed below.

**Table 3**  
Comparison among the novel technologies for PFOA removal from groundwater.

Technology	External energy supply	Materials cost	Secondary pollution	Main factor for PFAS removal	PFOA removal rate	Drawback	Reference
NF membrane	–	Membrane	High	Membrane reject	99.49–99.54% rejected	Membrane cost and secondary pollution	Boonya-atichart et al. (2016)
Activated persulfate	Heat (optical)	Sodium persulfate	Low	Sulfate radicals	89% degraded (no heat)	Chemicals cost and low degradation efficacy	Yin et al. (2016)
Starch-stabilized magnetite nanoparticles	–	Ferrous sulfate	Moderate	Fe <sub>3</sub> O <sub>4</sub> nanoparticles sorption	About 70% sorption	Fe <sub>3</sub> O <sub>4</sub> cost and secondary pollution	Gong et al. (2016)
PREC technique	–	Al-Zn electrode	Low	Electron transfer	Almost 100% degraded within 120 min	The device of PREC cost	Liu et al. (2018)
BOHP photocatalysis	UV light	BOHP microparticles	Low	BOHP sorption and photo-induced hole and electron	Almost 100% degraded within 60 min	BOHP cost and UV lamp setup	Sahu et al. (2018)
nZVI photocatalysis	Visible light	nZVI and H <sub>2</sub> O <sub>2</sub> (optical)	Low	photo-induced hole and electron	69.7% and 89.7% removal	nZVI cost and visible lamp setup	J. Liu et al. (2017)
TiO <sub>2</sub> /PMS photocatalysis	Powerful visible light	TiO <sub>2</sub> and PMS	Low	photo-induced hole and electron	Almost 100% degraded within 480 min	TiO <sub>2</sub> /PMS cost and visible lamp setup	Xu et al. (2020a)
PEC technology	UV light and DC power	GOP25 and FTO	Low	photo-induced electron and hydroxyl radical	98.2% degraded within 240 min	GOP/FTO cost and UV light/DC power setup	Yang et al. (2020)
Photocatalysis with membrane filtration	UV light	Membrane and nZVI	Low	Membrane reject and photo-induced hole	99.62% was rejected and 59.64% in the rejected part was degraded.	Membrane and nZVI cost and UV lamp setup	Boonya-atichart et al. (2018)

### 5.1. Membrane technologies

The membrane technologies are well developed and can be customized easily, which increase the versatility and capacity for various applications such as desalination and wastewater treatment (Yadav et al., 2020). Boonya-atichart et al. (2016) used nanofiltration (NF) membrane to remove PFOA in groundwater, and reported the removal efficiency of 99.49–99.54%. Due to the pore size restriction, the membrane has the ability to reject soluble neutral and charged organic compounds with molecular weight > 200 Da. Thus, NF can remove PFOA with a molecular weight of 414 g mol<sup>-1</sup>. Moreover, NF membranes could reject up to 90–99% PFOS according to a study by Tang et al. (2007). The schematic diagram of membrane operation unit is shown in Fig. 4a. However, membrane processes are prone to membrane fouling and poor water flux which could reduce membrane performance over time. High pressure and PFOA concentration increased the removal efficiency, however, the operating cost will be increased. Therefore, the key factors that influence membrane performance for PFOA removal in groundwater should be further studied, by fabricating novel high permeability and antifouling membranes and conducting long-term membrane performance tests using real groundwater.

### 5.2. Chemical redox reactions

Blotevogel et al. (2018) utilized a DFT-based kinetic model to predict the reductive defluorination of perfluorooctanoic acid by nanoscale zero-valent iron (nZVI) and zinc, which revealed that the half-lives for the first reductive PFOA defluorination step were ~8 years for Zn<sup>0</sup> and ~500,000 years for Fe<sup>0</sup> at metal-to-water ratios typically used in permeable reactive barriers (PRB). Thus, they concluded that reductive dehalogenation by zero-valent metals is not a viable remedial approach for PFOA in groundwater unless suitable catalysts with fast defluorination are identified.

Yin et al. (2016) used activated persulfate under acidic conditions (pH 2.0) and achieved 89.9% PFOA degradation. In their discussion, the predominant SO<sub>4</sub><sup>•-</sup> radicals produced by protons were considered to be a significant player in the successful degradation of PFOA. The main degradation mechanism is shown in Eq. (2)–(7). The decarboxylation and HF elimination processes continue until PFOA is converted to CO<sub>2</sub> and fluoride.

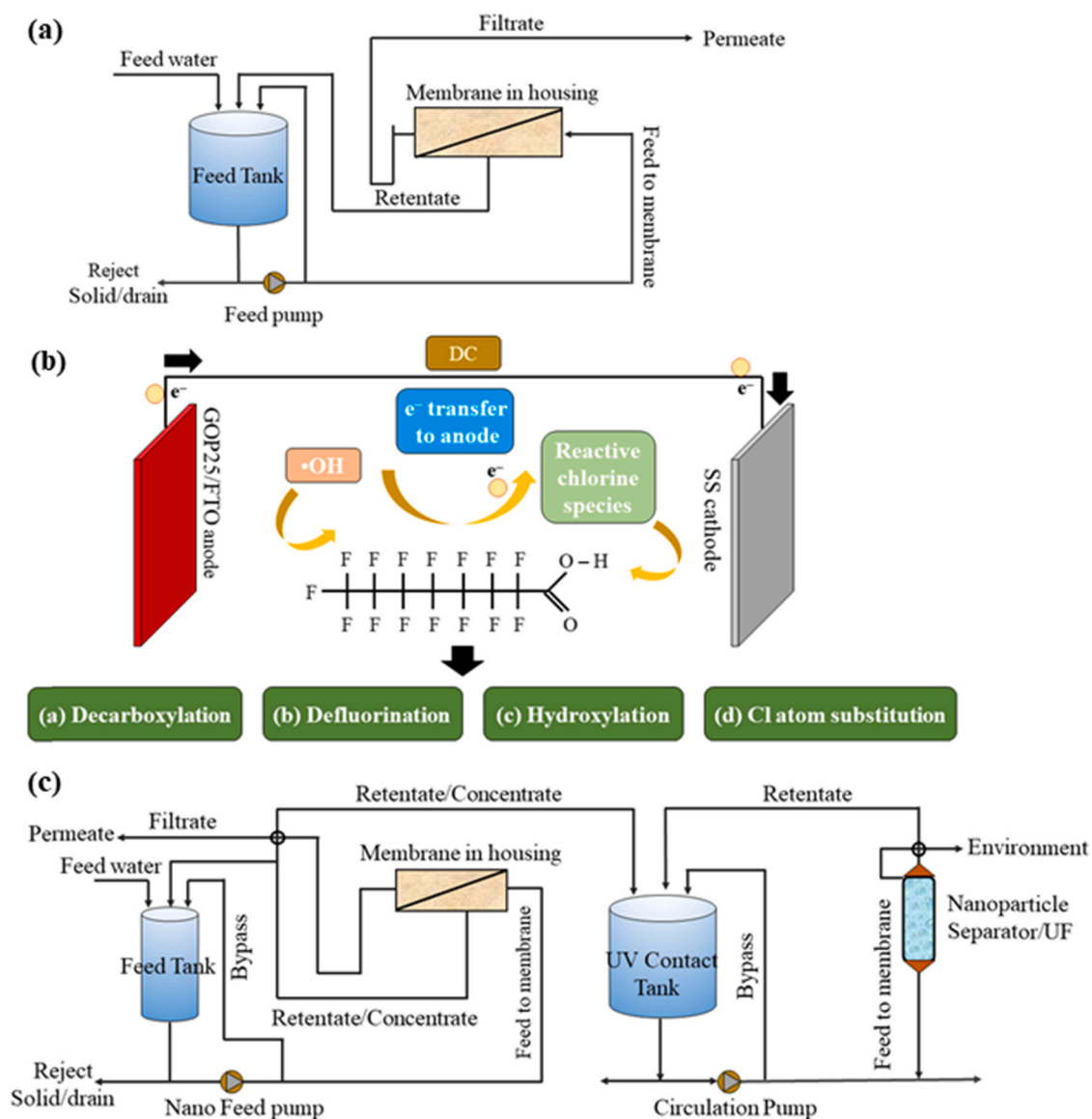
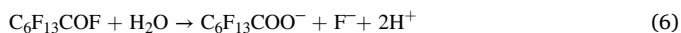
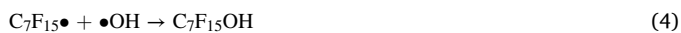


Fig. 4. Schematic diagram of membrane operation unit (a), GOP25/FTO anodes (b) and hybrid membrane filtration and photocatalysis (c). Reproduced with permission from Boonya-atichart et al. (2016), Yang et al. (2020) and Boonya-atichart et al. (2018).



Park et al. (2016) and Bruton and Sedlak (2018) further investigated the heat-activated persulfate oxidation of PFOA for groundwater remediation. For example, at 50 °C, a 5-fold increase in  $\text{S}_2\text{O}_8^{2-}$  led to a 5-fold increase in the kinetics of PFOA degradation. This increase was attributed to the influence of heat activation as shown in Eq. (6), and is consistent with the literature (Hori et al., 2010). Nevertheless, this method was restricted by the comparatively extreme external condition such as low pH or heat. This would be a challenge for the technology application in industry.

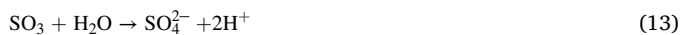
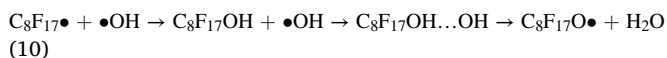
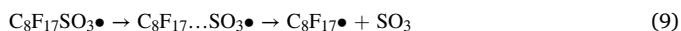
### 5.3. Sorption by nanomaterials

Sorption has been considered to be one of the most useful methods to remove PFOA in water. Various materials have been used as the adsorbents such as activated carbon, carbon nanotubes, polymeric resins and biomaterials. While these adsorbents had some drawbacks including low adsorption capacity, long equilibrium time, high cost and potential secondary pollution. So research has been devoted to new nanomaterials with stronger capacity for PFOA removal. For example, Xiao et al. (2017) used biochar and activated carbon to make the sorption of PFAS relevant to AFFFs impacted groundwater. As a result, their study reveals that granular activated carbon (GAC) systems exhibited poor performance on the removal of PFOA and PFOS in the groundwater impacted by AFFFs. While Gong et al. (2016) removed aqueous PFOA using starch-stabilized magnetite nanoparticles with a maximum adsorption capacity of  $62.5 \text{ mg g}^{-1}$ . They proved that starch was an effective stabilizer to disperse  $\text{Fe}_3\text{O}_4$  nanoparticles and the inner-sphere surface complexation between PFOA and starch-stabilized  $\text{Fe}_3\text{O}_4$  nanoparticles took the main responsible for PFOA sorption. The results demonstrated the promise of starch-stabilized  $\text{Fe}_3\text{O}_4$  nanoparticles as a “green”

adsorbent for effective removal of PFOA in groundwater. However, the nanomaterials usually need carefully prepared and how to deal with these materials with PFAS adsorption was another serious problem which might cause secondary contamination.

#### 5.4. Electrochemical treatment

Electrocoagulation (EC) technique has drawn increasing attentions due to the convenient operation and low energy cost (Islam, 2019). Y. Wang et al. (2016) used stainless steel cathode and zinc anode to treat 200 mg L<sup>-1</sup> PFOA in simulated aqueous solution and achieved 99.7% removal efficiency. Yang et al. (2016) utilized EC with iron electrode to deal with aqueous PFOA with a 90% removal. The long-term use of single electrode may have passivation on its surface during the practical application. Thus, Liu et al. (2018) adopted the periodically reverse electrocoagulation (PREC) with Al-Zn electrode to eliminate the PFOA pollution in the groundwater and generated 79.4% PFOA conversion within 60 min. They claimed that the sorption mechanism was mainly related to the hydrophobic interaction of PFOA and Al-Zn hydroxide flocs, as it may lead to the adsorption bringing and enmeshment of flocs. In addition, Lin et al. (2018) used the porous Ti<sub>4</sub>O<sub>7</sub> ceramic material as an anode and it exhibited superior electrochemical properties. Almost all PFOA (0.5 mM) and 93.1% PFOS (0.1 mM) were removed within 120 min and 180 min, respectively. During the reaction process, the intermediates of PFOA was detected with less than 1% of PFOA removal, suggesting the predominant direct mineralization of PFOA molecules over the anode surface, rather than ripping off a CF<sub>2</sub> step by step. They attributed the results to the reason that Ti<sub>4</sub>O<sub>7</sub> electrode allowed for both direct electron transfer of PFOA and production of highly active •OH, which were the degradation pathways of PFOS. PFOS in electrochemical systems could be degraded as show in Eqs. (8)–(13):



Compared with mineralization process of PFOA, the intermediates between PFOS and CO<sub>2</sub> and HF could not be found during the process, probably due to the higher charge density on the sulfate (PFOS) than the carboxyl group (PFOA) and the stronger acidity of PFOS. Overall, this porous Ti<sub>4</sub>O<sub>7</sub> ceramic anode was successfully applied in the remediation of PFAS impacted groundwater. The main weakness with this method is that macroporous magnéli phase Ti<sub>4</sub>O<sub>7</sub> ceramic materials were prepared by a high-temperature sintering method, which required additional energy cost and comparatively complex preparation.

#### 5.5. Photocatalysis

Photocatalysis is a cost-effective option for PFAS treatment, and various materials have been studied as catalysts for PFAS photodegradation (Xu et al., 2020a). Novel materials synthesized in recent years (2016–2020) irradiated by UV and visible light are discussed here. For example, Sahu et al. (2018) conducted the rapid degradation and mineralization of PFOA by a new petitjeanite Bi<sub>3</sub>O(OH)(PO<sub>4</sub>)<sub>2</sub> (BOHP) microparticle under UV irradiation. BOHP degraded almost 100% PFOA within 60 min, which was explained by the favorable adsorption of deprotonated PFAS to the hydroxylated BOHP surface resulting in stronger attraction. Furthermore, low concentration of PFOA (μg L<sup>-1</sup>) in the presence of natural organic matter was tested and the rapid

degradation suggested the potential of BOHP in the application on PFAS-contaminated groundwater. Nevertheless, UV light as an external energy supply represents an energy cost during groundwater treatment, prompting the investigation on visible light or solar driven photocatalysis treatment. J. Liu et al. (2017) explored a cost-effective, efficient and environmentally-friendly solution to remove PFOA from groundwater, by using nZVI to remediate PFOA contaminated groundwater under visible light. They achieved 69.7% and 89.7% PFOA removal rate without and with H<sub>2</sub>O<sub>2</sub> addition, respectively for a duration of 18 h. Other studies also focused on the visible-light irradiation for PFOA photodegradation and found that TiO<sub>2</sub> with peroxymonosulfate (PMS) assistance could remove all PFOA within 8 h under 300 W visible light (Xu et al., 2020b). In the reaction process, photo-induced electron (e<sup>-</sup>) and hole (h<sup>+</sup>) pairs were produced by powerful visible light (300 W) irradiation. Meanwhile, HSO<sub>5</sub><sup>-</sup> (PMS) could react with e<sup>-</sup> to form sulfate radicals (SO<sub>4</sub><sup>•-</sup>). h<sup>+</sup> and SO<sub>4</sub><sup>•-</sup> were both able to convert C<sub>7</sub>H<sub>15</sub>COO<sup>-</sup> (PFOA) into C<sub>6</sub>F<sub>13</sub>COOH (PFHpA) and finally mineralized to CO<sub>2</sub> and fluoride ions in the stepwise manner. Thus, the recombination of photo-induced electron and hole pairs was inhibited and the degradation efficiency of PFOA degradation was promoted. However, this kind of treatment still needs the powerful light energy, and solar irradiation as a natural resource should be utilized for the PFAS photocatalysis in future.

#### 5.6. Hybrid treatment processes

Photoelectrochemical (PEC) is a combinative method which provides a strong oxidizing environment, fast reaction rate and easy operation. Recently, Yang et al. (2020) reported their work of a PEC system consisting of a graphene oxide-titanium dioxide (GOP25) anode coated on fluorine-doped tin oxide (FTO) glass for removal of aqueous PFOA and PFOS. In the system, FTO was utilized as the anode matrix, graphene oxide (GO) was served as a versatile support and TiO<sub>2</sub> (P25) was used as electrocatalyst. Meanwhile, the potential on the anode can inhibit the recombination of photo-induced electron and hole pairs. The main mechanism was presented in Fig. 4b. As a result, PFOA and PFOS were significantly reduced in 4 h (98.2% removal) and in 3 h (98% removal), respectively. However, high concentration of DOM may become an issue when the PEC system is applied for the real groundwater treatment.

In addition, Boonya-atichart et al. (2018) proposed a combination of membrane filtration and photocatalysis for PFOA removal from groundwater. After filtration, the concentrated contaminants are degraded by photocatalysis with nZVI as the catalyst. Then, UF was used to remove the nanoparticles from the photocatalytic process. The whole system is shown in Fig. 4c. In the application for real groundwater treatment, the removal efficiency of PFOA was 99.62%, and the rejected part was degraded by photocatalysis at an efficiency of 59.64%. Thus, this proves that photocatalysis could become hybridized with membrane filtration for effective removal of the rejected contaminants before being released to the environment. When comparing Fig. 4a and c, it is apparent that hybrid treatment requires more complex setup.

#### 5.7. Comparison among different treatment technologies

Table 3 compared different novel technologies in terms of external energy supply, materials cost, potential secondary pollution, main factor affecting PFAS removal, removal rate of PFAS and likely drawbacks. Overall, light or heat could be considered as a common energy supply used for PFAS treatment or accelerating the efficacy. In the real groundwater treatment, heat supply is not energy efficient and therefore not recommended to be used. Light as a kind of green energy is generally provided in photocatalysis, which could be used in combination with electrochemical or membrane filtration for improving removal efficacy. Thus, compared with single chemical reaction such as activated persulfate, photocatalysis achieved higher degradation efficacy as BOHP



photocatalysis could degrade almost 100% PFOA within 60 min. Materials cost is another expenditure during the application in real groundwater. Membranes need to be fabricated and the novel catalysts such as BOHP need to be synthesized using hydro-thermal methods. Comparatively, only certain chemicals such as activated persulfate and photocatalysis such as  $\text{TiO}_2/\text{PMS}$  are needed in the chemical treatment approaches. Thus, the problems in the application in groundwater treatment mainly concentrate on the related materials and devices setup as shown in Table 3. Taking secondary pollution into consideration, PFAS are still present in the rejected part and need to be further controlled in the treatment of membrane filtration (defined as high level in Table 3). While in the sorption method, the adsorbent such as  $\text{Fe}_3\text{O}_4$  nanoparticles containing PFAS after treatment still needs to be dealt with (defined as moderate level in Table 3). For the treatment including photocatalysis, low risk of secondary pollution is expected as PFAS could have been degraded into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

Furthermore, compared with traditional and widely used technology, the configurations of photocatalysis have their advantages on the cost and effectiveness. For example, biodegradation via microorganisms can be a classic method to treat with many organic pollutants in soil and groundwater (Fahid et al., 2020). However, PFOS and PFOA are considered to be strongly resistant to microbial transformation under aerobic environment as Beskoski et al. (2018) reported that only 46–69% and 16–36% of PFOS and PFOA, respectively were removed by microbial consortia. This is obviously less effectiveness than the performance by photocatalysis as shown in Table 3. In addition, biodegradation need soil or sediment to cultivate microorganism under certain external conditions, which is a more complex and costly procedure compared with configurations setup of photocatalysis (Huang and Jaffe, 2019). Another common technology for PFAS treatment is regular water oxidative/disinfection methods such as chloramination, chlorination, ozonation, chemical oxidation and ultraviolet treatment (Bolan et al., 2021). Nevertheless, this method was found ineffective in most cases as reported by Higgins and Dickenson, 2016. Therefore, photocatalysis should be considered as an ideal technology with comparative low materials cost, good degradation efficiency, little secondary pollution, for potential utilization in the groundwater treatment.

### 5.8. GenX, F-53B and OBS treatment in groundwater

As GenX is a relatively new substitute, the treatment targeting on GenX is seldom investigated. Until recently, only a few publications have focused on GenX treatment by UV/sulfite system and by electrochemical oxidation (Bao et al., 2018). In detail, GenX can be readily degraded and defluorinated within 120 min by hydrated electron ( $e_{\text{aq}}^-$ ) generated in UV/sulfite system reported by Bao et al. (2018). During GenX degradation, TFA and PFA are identified as the main stable intermediates by UV/sulfite and the possible degradation pathways are exhibited in Fig. 5a. Comparatively, PFOA under the same condition by UV/sulfite showed similar degradation efficacy to GenX while the degradation process was quite different, as PFOA was transformed from long carbon chains to shorter chains step by step (B. Xu et al., 2017a). Thus, this study illustrates that the reduction by UV/sulfite might be a promising technology to remove GenX and PFOA in contaminated groundwater. In addition, the investigation by Pica et al. (2019) reported that an NF90 membrane was capable of removing 99.5% GenX from contaminated water and electrochemical treatment could reduce about 60% GenX in the NF rejectate. The electrochemical treatment device included the electrochemical flow cell with a stainless steel cathode and a boron-doped ultrananocrystalline diamond (UNCD) anode. Compared with the reduction by  $e_{\text{aq}}^-$ , the proposed oxidative decomposition pathway for HFPO-DA was different as shown in Fig. 5b. Specifically,  $e_{\text{aq}}^-$  attacked the ether carbon in the perfluorinated side chain with the activation barrier of  $\Delta^\ddagger G = 321 \text{ kJ mol}^{-1}$  (Fig. 5a). In the oxidative process, the attack of hydroxyl radicals at the ether carbon in the carboxylated side chain caused the breaking up of the ether bond ( $\Delta^\ddagger G$

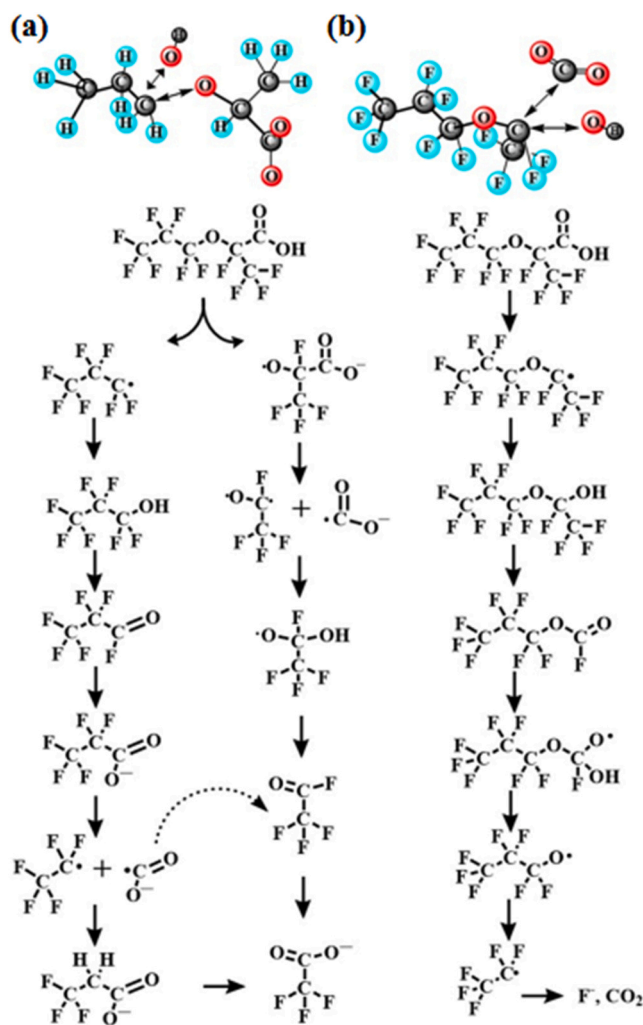


Fig. 5. Possible degradation pathway of GenX in UV/sulfite system (a) and electrochemical oxidation (b).

Reproduced with permission from Bao et al. (2018) and Pica et al. (2019).

$= 143 \text{ kJ mol}^{-1}$ ), and GenX was finally broken into fluoride ion and  $\text{CO}_2$  as shown in Fig. 5b. Overall, UV/sulfite system and electrochemical oxidation proved to be efficient for GenX treatment through different degradation pathways, which could be the basis for further scientific research for GenX control in groundwater.

In addition, Wang et al. (2013) published the first report of F-53B overlooked for 30 years for its toxicity, persistence and presence in the environment. In the report, they claimed that similar to PFOS, F-53B is not readily degradable, considered to be “harmful” to the aquatic environment. Some scientists have explored the F-53B in water by several methods as shown in Table 4. Gao et al. (2017) utilized the

Table 4  
Remediation methods for F-53B and related information.

Methods	Materials cost	Performance of F-53B treatment	Reference
Anion-exchange resin	Resin amberlite IRA67	About 90% absorbed	Gao et al. (2017)
Electrochemical oxidation	modified boron doped diamond (BDD) anodes	About 95% removal within 30 min	Zhuo et al. (2020)
Sodium persulfate	sodium persulfate-NaOH	About 88% removal within 480 min	Yan et al. (2015)
UV/Sulfite reduction	UV lamp and sodium sulfite	100% removal within 60 min	Bao et al. (2019b)

anion-exchange resin to adsorb F-53B and it took about more than 48 h to reach adsorption equilibrium of F-53B by resin IRA67. Zhuo et al. (2020) used electrochemical oxidation of F-53B by modified boron doped diamond (BDD) anodes and achieved 95% removal within 30 min. Yan et al. (2015) destructed F-53B assisted by sodium persulfate and about 88% compound was removal within 480 min. Y. Bao et al. (2019b) removed F-53B in chrome plating wastewater by UV/Sulfite reduction, achieving its entire degradation within 60 min. As for OBS treatment, W. Wang et al. (2019) utilized activated carbon to absorb OBS and its adsorption equilibrium was reached in 24 h. In addition, Bao et al. (2017) firstly used UV/H<sub>2</sub>O<sub>2</sub> or even sole UV (254 nm) system to deal with OBS and more than 96% OBS was degraded in aqueous solution within 20 min by both methods. They also demonstrated OBS better degradability and treatability, compared to other perfluorinated chemicals. Notably, Bao et al. (2018 and 2019b) used UV/Sulfite reduction to treat with GenX and F-53B and both achieved good performance as mentioned above. Thus, it can be concluded that photocatalysis is suitable for not only common PFAS but also new substitutes such as GenX, F-53B and OBS. So it is worthwhile to try the method of UV/Sulfite reduction for more other PFAS and substitutes degradation in future investigation.

## 6. Challenges of PFAS removal from groundwater

As reviewed, substantial progress has been made in the monitoring, identification of sources, and remediation of PFAS in groundwater, using a range of methods and technologies. In addition, there remain knowledge and technology gaps concerning the practical application for PFAS treatment, as summarized below:

- The inability to recycle and reuse photocatalysts is a major limitation when the photocatalysis technology is applied for on-site groundwater treatment. Most of the photocatalysts are nanoparticles dispersed in water. After photocatalysis, the freely suspended photocatalysts would run away with the groundwater being treated.
- The immobilization of photocatalysts during photocatalysis is considered as an essential improvement, so that photocatalysts are maintained intact for continuing operation.
- Visible light is not widely used for PFAS photocatalysis, and the materials which are easily activated by visible light with high potential for radical generation should be further explored for PFAS removal.
- The secondary pollution is considered to be a big challenge due to the extreme solution pH condition, catalysts overflow or incomplete mineralization of PFAS after treatment.
- The devices targeting on PFAS removal should be designed to be suitable for groundwater treatment in the field.
- Low concentration of PFAS with high amount of DOM in real groundwater is difficult to be treated directly and may require additional pre-treatment.
- There may be a need to apply the novel treatment during water supply process to prevent the potential risks of PFAS contamination for local residents.

## 7. Future recommendations of the study

Accordingly, the recommendation of the study could be concluded as follows which might be useful for future research:

- Popular visible light driven materials such as g-C<sub>3</sub>N<sub>4</sub> (Xu et al., 2018), ZnO/Bi<sub>2</sub>S<sub>3</sub> (Medina et al., 2018) and BiOCl (Tian et al., 2019) reported previously should be tested in PFAS photocatalysis in groundwater.
- The mechanism of GenX degradation needs to be further studied to confirm the degradation pathway.

- Optical fiber coating (Hatat-Fraile et al., 2017) could be an ideal method for the catalyst immobilization during the photocatalysis process.
- The concentrations of PFAS in groundwater should be monitored more widely to evaluate their contamination situation worldwide.
- The decomposition and defluorination efficiencies for PFAS removal in groundwater should be further improved to reach the complete mineralization of PFAS into CO<sub>2</sub> and F<sup>-</sup>.
- The PFAS remediation cost in real groundwater site should be carefully estimated to support the application of these novel technologies.

## 8. Conclusions

In summary, six PFAS, i.e. PFOA, PFNA, PFBA, PFOS, PFHxS and PFBS are widely detected in groundwater in the concentration range of 0–21,200 ng L<sup>-1</sup>. In addition, GenX is also widely reported in groundwater with concentrations up to 30,000 ng L<sup>-1</sup>. F-53B existed at the concentration of 0.18–0.59 ng L<sup>-1</sup> in groundwater. The sources of PFAS in groundwater may include surface water, soil, atmospheric deposition and the precipitation of snow, ice and rainfalls. Due to drinking water abstraction from groundwater, PFAS could be transported to tap water, leading to human exposure and subsequent human illness. The novel remediation technologies reported recently such as membrane, chemical redox, sorption, electrochemical, photocatalysis and various hybrid methods are assessed. By comparison, photocatalysis is recommended due to its advantages of low cost and high efficacy. For GenX, F-53B and OBS, UV/sulfite system and electrochemical oxidation are proven to be effective. Further studies should focus on the immobilization of the catalysts in photocatalysis, and the identification of potential secondary pollution after PFAS treatment.

## CRedit authorship contribution statement

**Bentuo Xu:** Conceptualization, Methodology, Software, Writing - original draft preparation. **Shuai Liu:** Methodology, Investigation. **John L. Zhou:** Supervision, Writing - review & editing. **Chunmiao Zheng:** Methodology, Writing - review & editing. **Weifeng, Jin:** Visualization. **Bei Chen:** Software, Validation. **Ting Zhang:** Writing - review & editing. **Wenhui Qiu:** Data curation, Supervision, Writing - review & editing. All authors have read and approved the manuscript for submission to your journal and accept responsibility for the manuscript's contents. The authors declare that there are no conflicts of interest.

## 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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