

Occurrence and removal of poly/perfluoroalkyl substances (PFAS) in municipal and industrial wastewater treatment plants

Sibel Barisci and Rominder Suri*

Civil and Environmental Engineering Department, Water and Environmental Technology (WET) Center, Temple University, 1947 N 12th Street, Philadelphia, PA 19122, USA

*Corresponding author. E-mail: rominder.suri@temple.edu

ABSTRACT

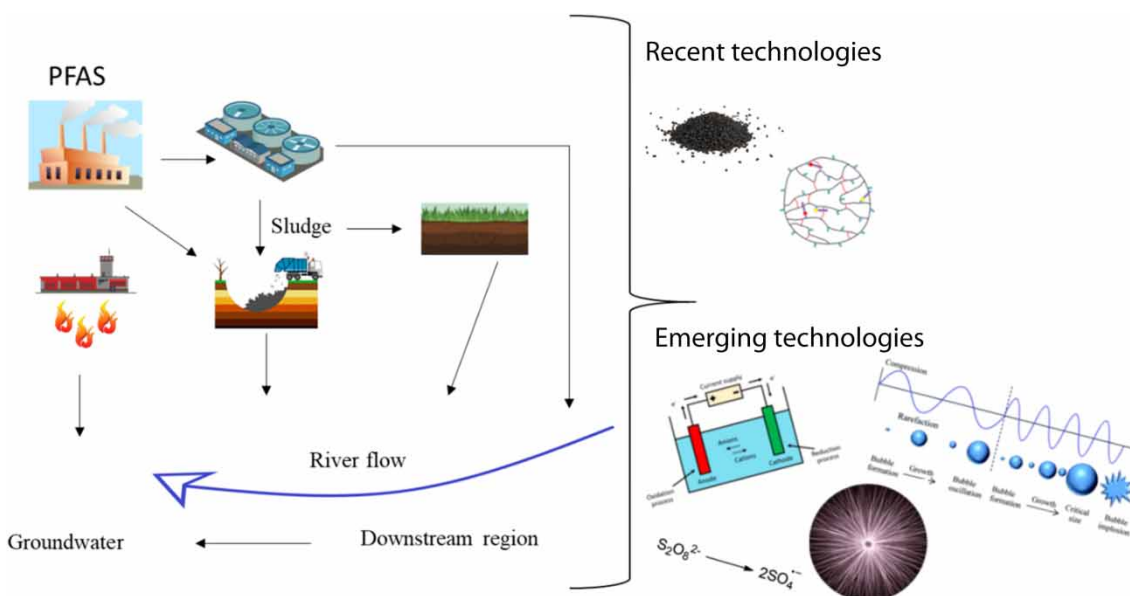
The presence of poly- and perfluoroalkyl substances (PFAS) has caused serious problems for drinking water supplies especially at intake locations close to PFAS manufacturing facilities, wastewater treatment plants (WWTPs), and sites where PFAS-containing firefighting foam was regularly used. Although monitoring is increasing, knowledge on PFAS occurrences particularly in municipal and industrial effluents is still relatively low. Even though the production of C8-based PFAS has been phased out, they are still being detected at many WWTPs. Emerging PFAS such as GenX and F-53B are also beginning to be reported in aquatic environments. This paper presents a broad review and discussion on the occurrence of PFAS in municipal and industrial wastewater which appear to be their main sources. Carbon adsorption and ion exchange are currently used treatment technologies for PFAS removal. However, these methods have been reported to be ineffective for the removal of short-chain PFAS. Several pioneering treatment technologies, such as electrooxidation, ultrasound, and plasma have been reported for PFAS degradation. Nevertheless, in-depth research should be performed for the applicability of emerging technologies for real-world applications. This paper examines different technologies and helps to understand the research needs to improve the development of treatment processes for PFAS in wastewater streams.

Key words: emerging water technologies, industrial wastewater, municipal wastewater, PFAS, poly- and perfluoroalkyl substances, wastewater treatment plants

HIGHLIGHTS

- PFOA and PFOS are frequently detected in both WWTPs, in spite of their limited use.
- Most PFAS in both WWTPs show negative removal rates.
- GAC and ion-exchange resins are ineffective at removing short-chain PFAS.
- Positive results for EOX, ultrasound, plasma, and new generation adsorbents.
- Further studies are required for the practicability of emerging technologies at real scale.

GRAPHICAL ABSTRACT



1. INTRODUCTION

Poly-/perfluoro alkyl substances (PFAS) are a class of man-made chemicals that have been used in numerous products, such as coating materials, surfactants, and fire retardants, for decades. These chemicals get discharged into the environment throughout their production, application, waste disposal, and many other routes (Figure 1). Extensive use and non-biodegradable properties of these compounds have resulted in a widespread presence in the environment. Two 8-carbon PFAS, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), are well known and widely used and have been detected in surface water (Gobelius *et al.* 2018), seawater (Brumovský *et al.* 2016), groundwater (Cousins *et al.* 2016), and tap water (Scher *et al.* 2018) in many locations around the world.

Due to their strong C–F bonds, PFAS are reported to be very persistent when released into the environment and therefore tend to bioaccumulate in the food chain. When exposed to eight or more carbon chain length PFAS, vertebrate animals suffer instabilities in the liver and pancreas (Li *et al.* 2017; Mahapatra *et al.* 2017). In particular, PFOA affects lipid and glucose metabolism, mitochondrial dysfunction, and oxidative phosphorylation in zebrafish, mice, and humans (Nelson *et al.* 2010; Abbott *et al.* 2012; Yan *et al.* 2015). The toxicity of PFAS is closely linked to the length of their carbon chain (Kleszczyński *et al.* 2007; Ulhaq *et al.* 2015), which can directly influence their removal and bioaccumulation rates (Kudo *et al.* 2006). *In vitro* toxicity tests in mammalian cells show this positive relationship between the chain length and the toxicity (Mulkiewicz *et al.* 2007). Shorter chain PFAS can be excreted faster from the body and therefore have been shown to result in minor accumulation in the liver tissues and serum of mice (Kudo *et al.* 2001).

Over the last decade, many manufacturers have phased out the production of C8-based PFAS, and the United States and European Union have regulated or limited the production of PFOA and PFOS. Therefore, industrial releases for PFOA and PFOS have decreased in developed countries since 2006 due to regulations and voluntary phaseout. However, industrial environmental releases of PFAS have increased in many other countries, like China, due to an expansion of the fluorochemical industry. Consequently, since C8 productions have been restricted, the production of short-chain PFAS (C2–C7) has increased (Wang *et al.* 2013b; Houtz *et al.* 2016). The degree of the environmental impact of a PFAS source would depend upon the scale of PFAS release, specific compounds, and their concentrations. The identification of PFAS sources to surface water is important to establish effective strategies for controlling their release. However, there is a lack of literature review on the occurrence, type, and concentration of PFAS in both municipal and industrial wastewater treatment plants (WWTPs) which seem to be the major point sources. Table 1 shows PFAS which have been reported in the literature to be present in municipal and industrial WWTP effluents.

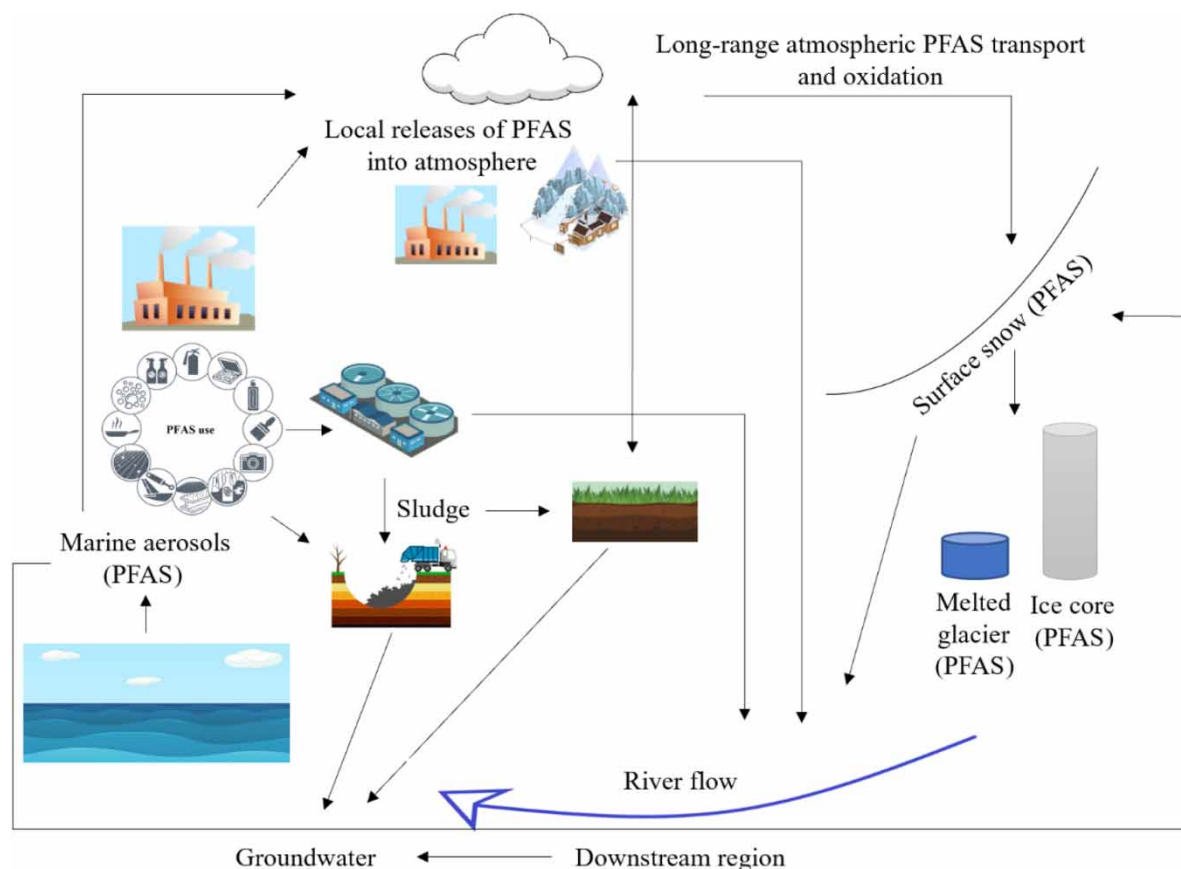


Figure 1 | Environmental PFAS transport and fate.

PFAS review papers published to date have mostly evaluated PFAS occurrence in drinking water, surface, and groundwaters, or only municipal WWTPs and there is a lack of studies on their presence, concentrations, and fate in industrial WWTPs. Hence, the purpose of this review is to deliver comprehensive information on the occurrence of PFAS in both municipal and industrial wastewater, and compare the type and concentration of PFAS detected in both industrial and municipal WWTPs. Providing a detailed assessment of PFAS problems linked to both industrial and municipal wastewater, this literature review emphasizes the occurrence of a broad group of PFAS in these sources. Furthermore, assessment of treatment technologies in the literature typically focused on novel technologies (i.e., plasma) or only a specific class of technology (i.e., chemical oxidation, electrochemical technologies, and advanced oxidation). In addition, those reviews mostly considered PFAS remediation from surface water or groundwater. This paper reviews both recent and emerging technologies in removing PFAS from wastewater streams with a scale of technology ranging from laboratory studies to full-scale treatment systems. Literature gaps and recommendations for future research were compiled using these data.

2. PFAS SOURCES IN MUNICIPAL AND INDUSTRIAL WASTEWATER

PFAS can be found in many customer products, including food packaging materials, stain-resistant carpets, furniture, paints, non-stick cookware, cleaning products, waxes, and fire-fighting foams. When these PFAS-containing products are used in our daily life, they can enter municipal wastewater treatment plants (WWTPs) and landfills. Moreover, many PFAS sorb on biosolids that are produced in WWTP operations. Land application of PFAS-contaminated biosolids was observed to pollute soil, groundwater, and surface waters. In addition, some biosolids are directly sent to landfills and many landfills send their leachates to municipal WWTPs. Similarly, manufacturing facilities or industries such as chrome plating, electronics, and oil recovery that use PFAS significantly contribute to the occurrence of PFAS in industrial wastewater samples. Because conventional wastewater treatment processes are not sufficient to remove and degrade these compounds, PFAS in both municipal and industrial WWTPs have received a great amount of attention. Although some fluorotelomers (FTs) can get oxidized

Table 1 | PFAS and their structures which have been detected in municipal and industrial WWTP influents and effluents

Class	Compound	Abbreviation	Chemical formula	Molecular weight (g/mol)	pK _a	Concentration range	Identified source	Reference
Perfluorocarboxylates (PFCAs)	Perfluorohexanoate	PFHxA	F(CF ₂) ₅ CO ₂ ⁻	314.05	-0.16	165–847 ng/L	Industrial influent	Kim <i>et al.</i> (2021), Kunacheva <i>et al.</i> (2011)
	Perfluoroheptanoate	PFHpA	F(CF ₂) ₆ CO ₂ ⁻	364.06	-2.29	662–1,143 ng/L	Industrial effluent	Kunacheva <i>et al.</i> (2011)
	Perfluorooctanoate	PFOA	F(CF ₂) ₇ CO ₂ ⁻	414.07	-0.5 to 4.2	103–443 ng/L	Municipal effluent	Chen <i>et al.</i> (2016c)
	Perfluorononanoate	PFNA	F(CF ₂) ₈ CO ₂ ⁻	464.08	0	0.05–4.9 ng/L	Municipal influent	Dauchy <i>et al.</i> (2017)
	Perfluorodecanoate	PFDA	F(CF ₂) ₉ CO ₂ ⁻	514.08	-5.2	0.1–8.3 ng/L	Municipal effluent	Dauchy <i>et al.</i> (2017)
	Perfluorotridecanoate	PFTTrDA	F(CF ₂) ₁₂ CO ₂ ⁻	664.11	0.52	15.2 ng/L	Industrial effluent	Kim <i>et al.</i> (2021)
	Perfluoroundecanoate	PFUnDA	F(CF ₂) ₁₀ CO ₂ ⁻	564.09	-5.2	0.031–<2 µg/L	Industrial effluent	Kunacheva <i>et al.</i> (2011)
	Perfluorododecanoate	PFDoA	F(CF ₂) ₁₁ CO ₂ ⁻	614.10	0.52	0.039–<2 µg/L	Industrial effluent	Kunacheva <i>et al.</i> (2011)
	Perfluoropentadecanoate	PFPA	F(CF ₂) ₁₄ CO ₂ ⁻	764.12	n/a	8.8–20 ng/L	Municipal influent	Houtz <i>et al.</i> (2016)
	Perfluorohexadecanoate	PFHxDA	F(CF ₂) ₁₅ CO ₂ ⁻	814.13	0.52	<MLQ –22.8 ng/L	Municipal effluent	Sinclair & Kannan (2006)
	Perfluorobutanoate	PFBA	F(CF ₂) ₃ CO ₂ ⁻	214.04	n/a	15–23 ng/L	Municipal effluent	Houtz <i>et al.</i> (2016)
	Perfluorosulfonates (PFSAs)	Perfluorobutane sulfonate	PFBS	F(CF ₂) ₄ SO ₃ ⁻	300.10	-3.51	1.29–195 ng/L	Municipal influent
Perfluorohexane sulfonate		PFHxS	F(CF ₂) ₆ SO ₃ ⁻	399.11	-3.45	2.6–15 ng/L	Municipal influent	Kunacheva <i>et al.</i> (2011)
Perfluorooctane sulfonate		PFOS	F(CF ₂) ₈ SO ₃ ⁻	500.13	<1	<0.44–461.7	Municipal effluent	Chen <i>et al.</i> (2012), Gallen <i>et al.</i> (2018), Pan <i>et al.</i> (2016)
Fluorotelomer alcohols (FTOHs)	6:2 fluorotelomer alcohol	6:2 FTOH	F(CF ₂) ₆ CH ₂ CH ₂ OH	364.10	>7	0.89–12.29 ng/L	Municipal influent	Dauchy <i>et al.</i> (2017), Zhao <i>et al.</i> (2013)
	8:2 fluorotelomer alcohol	8:2 FTOH	F(CF ₂) ₈ CH ₂ CH ₂ OH	464.12	>7	0.144–10.3 ng/L	Municipal influent	Dauchy <i>et al.</i> (2017), Zhao <i>et al.</i> (2013)
	10:2 fluorotelomer alcohol	10:2 FTOH	F(CF ₂) ₁₀ CH ₂ CH ₂ OH	526.14	>7	0.07–1.1 ng/L	Municipal influent	Dauchy <i>et al.</i> (2017), Zhao <i>et al.</i> (2013)
Fluorotelomer carboxylates (FTCAs)	6:2 fluorotelomer carboxylate	6:2 FTCA	F(CF ₂) ₆ CH ₂ CO ₂ ⁻	358.08	n/a	8.62 µg/L	Municipal effluent	Gremmel <i>et al.</i> (2017)
Fluorotelomer sulfonates (FTSAs)	6:2 fluorotelomer sulfonate	6:2 FTS	F(CF ₂) ₆ CH ₂ CH ₂ SO ₃ ⁻	428.17	n/a	242.5 µg/L	Industrial influent	Gomez-Ruiz <i>et al.</i> (2017a)
	8:2 fluorotelomer sulfonate	8:2 FTS	F(CF ₂) ₈ CH ₂ CH ₂ SO ₃ ⁻	528.18	n/a	874 ng/L	Industrial influent	Gomez-Ruiz <i>et al.</i> (2017a)
Fluorotelomer sulfonamidealkylbetaine (FTABs)	6:2 fluorotelomer sulfonamidealkylbetaine	6:2 FTAB	C ₆ F ₁₃ C ₂ H ₄ SO ₂ – NHC ₃ H ₆ N ⁺ (CH ₃) ₂ CH ₂ COO ⁻	556.14	n/a	45.5 mg/L	Industrial influent	Dauchy <i>et al.</i> (2017)
Fluorotelomer iodides (FTIs)	6:2 fluorotelomer iodide	6:2 FTI	F(CF ₂) ₆ CH ₂ CH ₂ I	473.90	n/a	0.74–3.5 µg/L	Industrial effluent	Bach <i>et al.</i> (2016)
Perfluorooctane sulfonamides (FOSAs)	N-ethyl perfluorooctane sulfonamidoacetic acid	NEtFOSAA	C ₈ F ₁₇ SO ₂ N(C ₂ H ₅)CH ₂ CO ₂ H	585.20	n/a	4.3–5.9 ng/L	Municipal influent	Boulanger <i>et al.</i> (2005)
Chlorinated polyfluorinated ether sulfonates	6:2 chlorinated polyfluorinated ether sulfonate (F53-B)	6:2 Cl-PFAES	C ₈ F ₁₆ ClO(SO ₃ K)	570.6	n/a	10–50 ng/L	Industrial effluent	Ruan <i>et al.</i> (2015), Wang <i>et al.</i> (2013a)
Perfluoroalkyl ether carboxylic acids with one ether group (mono-ether PFECAs)	Hexafluoropropylene oxide dimer acid (GenX)	HFPO-DA (GenX)	C ₆ F ₁₁ O ₃ H	330.2	n/a	Total PFAS concentration of 40,000 ng/L	Industrial influent	Hopkins <i>et al.</i> (2018)
	Perfluoro-2-methoxyacetic acid	PFMOAA	C ₃ HF ₅ O ₅	180.0	n/a			
Perfluoroalkyl ether carboxylic acids with multiple ether group (multi-ether PFECAs)	Acetic acid, 2-[[difluoro(trifluoromethoxy)methoxy]-2,2-difluoro-	PFO2HxA	C ₄ HF ₇ O ₄	246.0	n/a			
	perfluoro-3,5,7-trioxaoctanoic acid	PFO3OA	C ₅ HF ₉ O ₅	312.0	n/a			
	2-[[[difluoro(trifluoromethoxy)methoxy]-difluoromethoxy]-difluoromethoxy]-2,2-difluoroacetic acid	PFO4DA	C ₆ HF ₁₁ O ₆	378.1	n/a			

during treatment processes, they are converted to recalcitrant perfluorocarboxylic acids (PFCAs) (Bach *et al.* 2016; Kim *et al.* 2021). Thus, WWTP effluents may contain a relatively high amount of PFAS, and effluent discharge to surface waters may result in toxic effects on aquatic organisms and bioaccumulation of PFAS. Effluents from WWTPs in different countries have been stated to have PFOA and PFOS concentrations measured as <0.28–1,057 ng/L and <0.44–462 ng/L, respectively (Bossi *et al.* 2008; Guo *et al.* 2010; Kunacheva *et al.* 2011; Chen *et al.* 2012, 2016a, 2016c; Zhang *et al.* 2013; Subedi & Kannan 2015; Hamid & Li 2016; Pan *et al.* 2016; Dauchy *et al.* 2017; Gremmel *et al.* 2017; Gallen *et al.* 2018; Nguyen *et al.* 2019).

2.1. The occurrence of PFAS in industrial wastewater

In the literature, there are limited studies that examine the discharge of PFAS from industrial WWTPs to evaluate the occurrence of PFAS and their total discharge loads, especially for emerging PFAS. However, understanding PFAS pollution from the PFAS manufacturing and utilizing industries are crucial in regulating the sources of such compounds. PFAS are not effectively removed in WWTPs. Kunacheva *et al.* (2011) reported similar findings when conducting a study in two industrial zones (located in Central and Eastern Thailand) that have biological treatment processes. The study shows that ten different known PFAS, namely, PFOA, PFOS, PFPA, PFHxA, PFHpA, PFHxS, PFNA, PFDA, PFUnDA, and PFDoA, were identified in both industrial WWTPs. While total average concentrations of PFAS in industrial wastewater samples ranged between 674 and 847 ng/L in influent, effluent samples ranged between 662 and 1,143 ng/L. The abundant compounds were determined as PFOA, PFOS, PFNA, PFDA, PFUnDA, and PFHpA accounting for more than 87% of total PFAS, while other identified PFAS were less than 10%. Concentrations of most PFAS were higher in effluent samples than in influent samples, demonstrating no removal of most PFAS in the treatment process (Kunacheva *et al.* 2011), or conversion of precursors materials to PFAS. Another study investigated mass flows and the fate of 51 legacy PFAS in the WWTP of a fluorochemical manufacturer in France (Dauchy *et al.* 2017). Accordingly, one PFCA (PFHxA) and nine FTs, namely 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, 12:2 FTOH, 6:2 fluorotelomer sulfonic acid (6:2 FTSA), 8:2 FTSA, 6:2 fluorotelomer iodide (6:2 FTI), 6:2 fluorotelomer sulfonamide alkylbetaine (6:2 FTAB and M4), were identified in influent samples. 6:2 FTAB was found to be the dominant PFAS, reaching a concentration of 45.5 mg/L. It was found that mass flows of PFCA considerably increased after biological treatment leading to the conclusion that the degradation of precursors was forming PFCA. However, PFCA concentrations decreased remarkably after the air flotation process due to sorption onto flotation bubbles and sludge. But, PFCA concentrations were still high in the final effluent (from 21 to 247 g/day). Another example of the increasing tendency of mass flow was observed for PFCAs from four industrial WWTPs in Denmark. Among them, the textile industry contributed to the highest concentration of PFCAs. This was reported as a result of FTOH degradation, which is widely used as saturating agents for textiles (Bossi *et al.* 2008). However, a recent study reported that while 6:2 FTS was detected in 12 different industrial influents at concentrations reaching up to 145 ng/L, it was detected in only one effluent sample. It was concluded that it was sorbing onto the sludge (Kim *et al.* 2021).

In the last decade, emerging PFAS have also been detected together with legacy PFAS. For example, emerging PFAS such as 6:2 chlorinated polyfluorinated ether sulfonate (F-53B), which is a PFOS replacement chemical, has been detected in electroplating industry wastewater at similar levels as PFOS (10–50 ng/L) in China (Wang *et al.* 2013a; Ruan *et al.* 2015). In addition, GenX (PFOA replacement compound) and other emerging PFAS including perfluoro-2-methoxyacetic acid (PFMOAA), acetic acid, 2-[difluoro(trifluoromethoxy)methoxy]-2,2-difluoro- (PFO2HxA), perfluoro-3,5,7-trioxaoctanoic acid (PFO3OA), Nafion byproduct, and 2-[[[difluoro(trifluoromethoxy)methoxy]-difluoromethoxy]-difluoromethoxy]-2,2-difluoroacetic acid (PFO4DA) have been detected in industrial wastewater with a total concentration of about 40,000 ng/L (Hopkins *et al.* 2018). Additionally, a recent study reported the identification of 37 new PFAS (6 classes), mostly chlorine-substituted PFCAs, together with 12 legacy PFAS (2 classes; PFCAs and PFSAs), 41 previously discovered PFAS (7 classes including perfluorinated dicarboxylates and perfluorinated ethers/alcohols) in the nearby Yangtze River (Wang *et al.* 2018). It was mentioned that only one PFAS class (per- or polyfluorinated monocarboxylates) was removed after the treatment. By contrast, the concentration of four classes of PFAS increased after the treatment process. The tendency of rising PFAS concentrations in effluents could be ascribed to existing PFAS precursors in wastewater and their biodegradation during the activated sludge process. There is also a possibility that compounds with a short carbon chain (C4) may be degraded into their PFCA or PFSA homologs (D'eon *et al.* 2009). Some scientists have stated that laboratory-scale experiments support the field studies indicating biodegradation of some precursors in aerobic conditions can contribute significant amounts of PFAS (Rhoads *et al.* 2008; Kibambe *et al.* 2020). However, further research on this process is still required to understand the actual behavior and chemical reactions during biodegradation of PFAS. Also, the identification

of precursors is critical for the information of secondary sources of PFAS, such as PFOA and PFOS. Furthermore, it is still essential that numerous unregulated and emerging PFAS in the aquatic environment should be determined and quantitated. The behavior of PFAS may differ during the treatment process due to different functional groups, physicochemical properties, existing ions, and other compounds in wastewater. In some cases, long-chain PFAS have a greater tendency to sorb to sediment, while sorption of short-chain PFAS is more difficult due to their higher water solubility (Wang *et al.* 2020b). For instance, in contrast to increasing PFAS concentrations in effluents, a study stated that the typical concentrations of PFAAs were lower in the effluent (106 ng/L) than in influent (411 ng/L), associated with the paper and textile industries (Kim *et al.* 2016). Also, some authors reported that while PFOS levels showed a decreasing trend in effluent samples, PFOA concentration increased similar to the other studies mentioned above (Schultz *et al.* 2006; Guo *et al.* 2010). The higher normalized organic carbon partition coefficient of PFOS may be the reason for this tendency as compared to that of carboxylate analog, which points to the favored uptake of some PFAS by the sludge or biosolids (Guo *et al.* 2010). In addition, existing cations in wastewater may provide the required ion bridges for the sorption of negatively charged PFAS. For example, PFAS sorption to the sludge (biosolids) increased with higher cation concentrations and it was greater in the presence of divalent cations compared to monovalent cations (Ebrahimi *et al.* 2021). This could be ascribed to electrostatic interaction between a divalent cation and the anionic PFAS head group, as well as with a negative charge on the sludge. It was also observed that PFOS accumulated in higher amounts (400 ng/g) in sludge in comparison with other PFAS with accumulation ranging between 2.9 and 327.7 ng/g (Kunacheva *et al.* 2011). Dauchy *et al.* 2017 also observed a remarkable decrease in the concentration of some PFAS after the flotation tank as the compounds were adsorbed onto air bubbles. Remarkably high concentrations of PFAAs have been detected in the sludge from electronics (91 ng/g) and chemical (81.5 ng/g) industries (Dauchy *et al.* 2017). These results show that PFAS removal occurs primarily by sorption on sludge during conventional treatment. In summary, four factors affect the fate of PFAS in WWTPs: (1) physicochemical properties of PFAS, (2) existing cations in wastewater, (3) precursors of PFAS in wastewater, and (4) produced sludge or biosolids. It should also be noted that the behavior of a single-compound system is different from the behavior of a multi-component system, and multi-component interactions play a significant role in the removal rates of pollutants. For example, sorption capacities of seven PFAS, namely PFOA, PFOS, PFBA, PFBS, PFHxA, PFHxS, and PFDoA, onto sludge were evaluated, and the authors mentioned that the sorption of PFAS greatly diminished in the multi-component system in comparison with individual PFAS in the single-component system (Zhou *et al.* 2010; Zhao *et al.* 2013). This behavior might be attributed to hydrophobic properties, ionic head groups, and chain length of PFAS. In summary, the examination of the fate of numerous and different PFAS classes at several wastewater treatment steps (i.e., activated sludge and flotation) indicates that biodegradation is responsible for the increasing PFAS concentrations due to the transformation of PFAS precursors to perfluoroalkyl acids (PFAAs) in WWTPs. Besides, sorption onto sludge and/or bubbles may occur resulting in decreased PFAS concentrations in the effluent. Further research studies are needed to increase our knowledge of these fate mechanisms.

2.2. The occurrence of PFAS in municipal wastewater

Municipal WWTPs are a significant source of PFAS which can bioaccumulate in food chains and eventually result in human consumption. Clara *et al.* (2009) indicated that more than half of the total PFAS detected in the Danube River, Eastern Europe can be ascribed to municipal wastewater discharges (Clara *et al.* 2009). In addition, PFOS detected in rivers in Japan is correlated to the discharges from municipal WWTPs (Murakami *et al.* 2008; Zhang *et al.* 2013). Another study showed that municipal WWTP effluents were the main source of the PFAS discharged into Lake Ontario (Boulanger *et al.* 2005).

PFAS and their precursors for domestic use are usually categorized as fluorophosphonate (FP)-based products, perfluorooctane sulfonyl fluoride (POSF)-based products, and FT-based products. FP-based products may contain small amounts of releasable PFAS residuals by means of PFAS-based emulsifiers usage (Larsen *et al.* 2006), such as polytetrafluoroethylene (PTFE)-coated non-stick cookware, polyvinylidene fluoride (PVDF) coatings, and woven fiberglass cloths. Non-polymeric POSF-based materials contain releasable precursors of PFAS and are indirectly released into the environment, while their impurities, such as coated paper and package products and pesticides based on perfluorooctane sulfonamides (FOSAs), are released directly into the environment. Non-polymeric FT-based materials contain 0.04–3.8% of releasable unbound FTs (indirect environmental releases) and <1–100 ppm of PFAS impurities (direct environmental releases) (Dinglasan-Panlilio & Mabury 2006).

A study reported the results of a screening survey of PFAS from six municipal and four industrial WWTPs and landfill sites in Denmark (Bossi *et al.* 2008). PFOA and PFOS were observed as dominant species in all municipal WWTPs, including both

influent and effluent waters. It was stated that PFOA and PFOS levels were higher in effluent samples, except at one municipal WWTP which provided complete removal of both compounds. Increasing concentration levels of PFOA and PFOS in effluent samples was also observed in other studies (Sinclair & Kannan 2006; Clara *et al.* 2009; Zhang *et al.* 2013). According to a study (Zhang *et al.* 2013) conducted in China, 16 PFAS were detected in municipal wastewater samples, and their concentrations ranged between 0.04 and 91 ng/L for influent and 0.01–107 ng/L for effluent. PFOA had the highest concentrations for both influents (2–91 ng/L) and effluents (3–107 ng/L). They postulated that these high PFOA concentrations may be due to the surrounding industries. The second leading compound was PFOS with concentrations of 1–32 ng/L in the influent and 1–67 ng/L in the effluent. It is also reported that many investigated WWTPs showed higher concentrations of PFAS (PFOA, PFOS, PFNA, PFHpA, PFBS, and PFDA) in effluent than in influent samples, with a cumulative increase of 32–290 times. This trend is linked to the PFAS precursors in wastewater and their biodegradation to form PFAS. Accordingly, PFOS may come from biodegradation of *N*-ethyl-perfluorooctane sulfonamido acetate (EtFOSAA) which can transform to *N*-ethylperfluorooctane-1-sulfonamide (EtFOSA), which is converted to FOSA and finally to PFOS. PFOA may be formed due to the biodegradation of 8:2 FTOH and polyfluoroalkyl phosphate esters (Martin *et al.* 2004). Another reason for the increasing trend in effluents may also be the desorption of PFAS from solids (Zhang *et al.* 2013).

Xiao *et al.* (2012) conducted experimental data analysis for the contribution of PFAS from municipal WWTPs (Xiao *et al.* 2012). They identified PFAS in 37 WWTPs in more than 40 cities in Minnesota, USA. Substantially high levels of PFHxA, PFOA, and PFOS in influents have been found in almost half of the WWTPs surveyed. Per capita discharges were measured as 0.30–7.6, 0.17–1.4, 0.67–5.1, 0.35–7.8, and 0.17–1.4 µg/capita/d for PFOA, PFNA, PFHxA, PFOS, and PFHpA, respectively. A considerable increase in influent samples for PFHxA and PFOA was detected in 59% of the WWTPs studied, indicating high-level inputs of precursors. Indeed, the authors modeled the fate of one precursor (8:2 FTOH) using fugacity analysis which showed that 9.0% of 8:2 FTOH is biodegradable to PFOA or other analogs during the activated sludge process. These high PFAS levels in influents were observed especially in WWTPs situated in industrial areas. Furthermore, a noteworthy correlation was observed in PFAS concentrations and population in the influent water for some WWTPs, demonstrating PFAS were primarily from local sources and the use of PFAS-based products by the residents has a large impact (Xiao *et al.* 2012).

Another study investigated PFAS discharge from municipal WWTPs, including river and coastal release straight to the Bohai Sea, China. Accordingly, they sampled effluents from 15 drain channels including 10 river outfalls, 3 WWTPs, and 2 industrial WWTPs. Ten PFCAs (C4–C12) and four PFSAs (C4–C10) were identified in all effluents with levels of 103–443 ng/L. While PFHxA and PFOA were the main PFAS in the effluents from municipal drain channels and rivers, PFOA and PFHxS were leading PFAS in the effluents of industrial drain outlets. Furthermore, the average concentrations of PFOA and PFHxA found in rivers and municipal drain channels were much higher than those in seawater samples, demonstrating wastewater from drain outlets was a major pollution source of PFHxA and PFOA in the Bohai Sea (Chen *et al.* 2016a).

A study conducted in 2014 detected PFAS in eight municipal WWTP which discharge effluents to San Francisco Bay, USA. It was mentioned that the concentrations of short-chain PFCAs, such as PFBA and PFHxA, increased compared to municipal wastewater effluents sampled in 2009. Most of the effluents showed similar trends for total PFAS concentration. While PFHxA had the highest average concentration with 24 ng/L, the concentrations of PFOA, PFOS, and PFBA ranged between 15 and 23 ng/L. However, effluents from two WWTPs contained higher concentration levels for all PFAS (i.e., the median concentration of PFOS was 420 ng/L). Similar to previously mentioned studies, increasing concentrations were observed for effluents due to the precursors of PFAS. They observed that PFAS precursors were the reason for 33–63% of the total concentration of PFAS for all effluents (Houtz *et al.* 2016).

Similar to industrial wastewater, emerging types of PFAS were also detected in municipal wastewater samples. For instance, emerging PFAS including H–PFCAs, H–PFESAs, and PFSMs were detected at WWTPs in China, and their concentrations were equal to or higher than legacy PFAS in WWTPs (Wang *et al.* 2020d). While some classes of PFAS were removed, the class of perfluoroalkyl ether alcohol (PFEA) increased during the treatment due to biodegradation of other ether-PFAS.

With regard to the aforementioned studies, emerging and previously discovered PFAS seem to be a challenging target since PFAS have been found in municipal and industrial WWTPs. Despite the restriction and regulation of the manufacturing of C8-based compounds (i.e., PFOA and PFOS), PFOA and PFOS are still identified as the dominant compounds in most cases. This may be related to the persistency, accumulative behavior, and other physicochemical properties of these compounds

(Pan *et al.* 2016; Li *et al.* 2020). The biodegradation of precursors and abiotic transformations may also contribute to the occurrence of PFOA and PFOS (Eriksson *et al.* 2017; Chen *et al.* 2019). The main gap in the literature is that there is inadequate experimental data on the related physicochemical properties of the compounds, such as their solubilities in water, soil–water partitioning coefficients, and bioaccumulation factors. This information would be valuable to model the fate and transport of PFAS during and after treatment. Aside from PFOA and PFOS, short-chain PFCAs (C4–C7) and PFSAs (C4) are the most detected PFAS in municipal and industrial WWTP influents and effluents as a result of the replacement of C8-based products. Longer chain PCASs (C7–C12) and one PFSAs (C6) are also identified in many WWTPs, and other fluorinated compounds, such as FTOHs and FTSA, also seem to be present in WWTPs. More research is required to identify and examine the fate of emerging PFAS classes.

3. RECENT TREATMENT TECHNOLOGIES FOR PFAS

Conventional treatment processes, such as biological activated sludge, cannot provide efficient removal and/or degradation of PFAS, since they are resistant to biodegradation. Although activated carbon adsorption and ion-exchange processes are being used at full scale and pilot scale for the removal of PFAS mostly for drinking water and groundwater, currently there are some studies focusing on these technologies for PFAS removal from wastewater at various Technology Readiness Level (TRL) stages, as reported in the literature. This paper makes an attempt to summarize the key features of these technologies.

3.1. Activated carbon adsorption

Carbon adsorption process is well known and the most commonly used treatment technology for PFAS removal. In this process, four mechanisms have been reported: (1) dispersion in the liquid phase, (2) mass transfer through the solid phase, (3) pore diffusion inside an adsorbent, and (4) electrostatic interface between pollutant and exchange site (Qiu 2007; Park *et al.* 2020). Most full-scale treatment systems using activated carbon are focused on PFAS removal from impacted drinking water sources. There is a lack of information on the removal of PFAS from industrial and municipal wastewaters. A more complex matrix of wastewater may limit its direct usage for wastewater treatment, but carbon-based adsorption can be utilized after pretreatment systems and/or reclamation of wastewater effluents. For example, Thompson *et al.* (2011) examined the removal of different PFCAs and PFSAs from treated water of WWTP in Australia. Plant A used adsorption via biologically activated carbon (BAC) and other treatment methods (including filtration and ozonation) to purify recycled water. PFOA, PFHxA, PFOS, and PFHxS were the most abundant compounds in effluent water. While PFOS and other long-chain PFAS removal occurred in Plant A during the adsorption/filtration processes, PFOS and shorter chain PFAS were not removed completely (Thompson *et al.* 2011). Similarly, the effectiveness of powdered activated carbon (PAC) was examined at a large scale to remove emerging pollutants, including PFOA and PFOS, from wastewater. While PFOS was poorly removed by PAC adsorption with removal ratios ranging between 6 and 52%, negative removals were reported for PFOA because concentrations were continuously higher in effluents compared to influents, and which was attributed to potential contamination due to the usage of Teflon[®] pipes (Mailler *et al.* 2015). Another study reported pilot-scale research on the removal of PFBA, perfluoropentanoic acid (PFpNA), PFHxA, PFHxS, PFHpA, PFOA, PFOS, PFNA, and PFDA from effluent water by granular activated carbon (GAC) made from peach pit and spruce pine wood biochars. GAC was found to be very effective in the removal of PFpNA, PFHxA, PFOA, and PFOS. PFOS was removed to a higher extent on GAC (61%) than PFOA (35%), while both are of the same chain length. PFOS has a higher molecular weight and has a lower water solubility (0.57 g/L) compared to PFOA (3.4 g/L), thus it characteristically shows a higher sorption affinity to solids because of its hydrophobic sulfonic acid group (Inyang & Dickenson 2017).

By contrast, some bench-scale studies were conducted using activated carbon to remove several PFAS from wastewater effluents. For example, a study investigated the removal of PFOA, PFHxA, and PFHpA at concentrations of 0.29 mmol/L, 0.1 mmol/L, and 0.11 mmol/L, respectively, from actual wastewater using coal-based activated carbon adsorption (Du *et al.* 2015). They observed more than 88% PFOA removal with the adsorbent dose of 0.3 g/L, while a dose of 1.9 g/L was required to provide 90% removal of other PFCAs. This indicates the presence of co-existing ions and other organics in wastewater significantly affected the efficiency of activated carbon adsorption for other PFCAs. Another study evaluated the performance of GAC (bituminous coal) for the removal of 13 PFAS from wastewater (Rostvall *et al.* 2018). GAC showed 95% average removal efficiency for the target PFAS because of its very high specific surface area (950 m² g/L) and average pore size of 2.2 nm. It was also mentioned that there was no specific relationship between removal efficiencies and the functional group using GAC due to

the low number of treated bed volumes. FOSA was an exception, possibly due to its neutral sulfonamide head group (Rostvall *et al.* 2018). GAC (bituminous coal and coconut shell) efficacy was also tested by Appleman *et al.* (2013) for the removal of PFAAs in the presence of natural organic matter (NOM). GAC was less efficient for the shorter chain PFCAs, such as PFBA and PFPeA, as increased concentrations were observed in treated samples. This was attributed to the competitive effects of other adsorbing species, such as longer chain PFAAs and DOM, which caused desorption of adsorbed PFBA and PFPeA. This conclusion was verified with higher removal efficiencies in lower DOC values. The presence of DOM affected GAC performance for PFAA removal because it occupied pores and sorption sites of GAC (Appleman *et al.* 2013).

A relationship between chain length/functional group and treatment efficiency is usually observed during GAC treatment. For example, PFAS with carboxylate groups showed lower removal efficiency than those with sulfonate functional groups. In addition, the time for column breakthrough decreased with decreasing chain length, indicating that agglomeration and/or micelle formation for long-chain PFAS was poorer for the PFCAs than PFSAs. Current concerns about the adsorption of PFAS are that longer chain PFAS potentially tend to be adsorbed by GAC whereas short-chain PFAS do not, and the presence of competing ions reduces the removal efficiencies (McCleaf *et al.* 2017). Therefore, more attention should be given to enhancing GAC efficiency and lowering the operation cost by the addition of pretreatment or using other sorbents.

3.2. Ion exchange

Ion-exchange resins, particularly anion-exchange resins for PFAS, can efficiently remove most of the PFAS from water due to their molecular structure and their simultaneous removal mechanisms of anion exchange and adsorption. PFAS compounds have two functional components, namely fluorinated carbon chain which is hydrophobic with a non-ionic tail and negatively charged anionic head. The anion-exchange resin consists of neutral co-polymers (mostly plastics) and exchange sites with a positive charge. The PFAS' *hydrophobic tail* is adsorbed to the hydrophobic backbone on the resin, and the *anionic head* of the PFAS attracts to the ion-exchange sites of the resin, which is positively charged. The typical structure of anion-exchange resin is given in Figure 2.

The removal efficiency of PFAS by anion-exchange resins strongly depends on the type and concentration of inorganic content in water and the affinity of resin for PFAS (Lampert *et al.* 2007; Deng *et al.* 2010; Maimaiti *et al.* 2018; Zeng *et al.* 2020). Some resins have less sensitivity for inorganic ions and more affinity for PFAS. While most of the PFAS molecules have an *anionic head*, some PFAS molecules have a *cationic head*, and others have both *anionic and cationic heads* (*zwitterionic*). Bench-scale column tests should be conducted to find out the most suitable resin for PFAS removal.

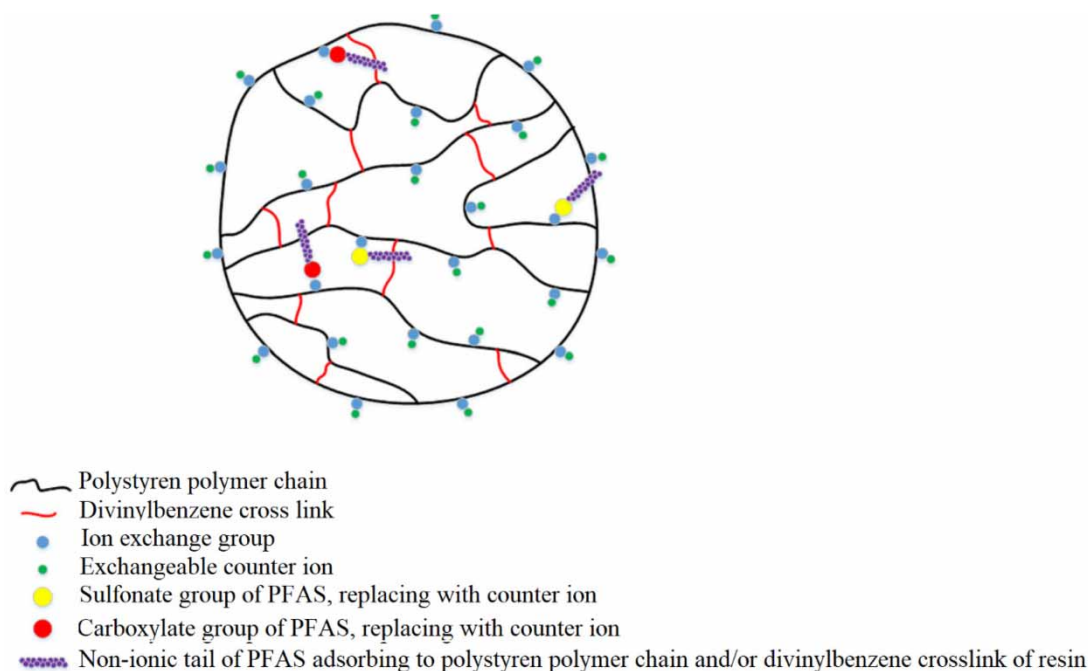


Figure 2 | The structure of a typically used anion-exchange resin.

A study explored the effect of resin functional groups during PFOS removal (Chularueangaksorn *et al.* 2013). The polystyrene divinylbenzene resins were more hydrophobic than polyacrylic resins. The hydrophobicity of the resins increased the hydrophobic interactions between the PFOS molecule and the resin. Hence, polystyrene divinylbenzene structure and the gel type increased the adsorption of PFOS (Chularueangaksorn *et al.* 2013). Conversely, Deng *et al.* (2010) observed that the resin matrix exhibited a substantial effect on the PFOS sorption capacity from wastewater in bench-scale experiments. Resins made of polyacrylic showed higher and faster removal of PFOS than the polystyrene resins as a result of a more hydrophilic structure. The sorption capacity of PFOS on polyacrylic resins was determined to be 4–5 mmol/g. The authors also observed that the amount of adsorbed PFOS on the resins was more than the release of chloride from resins, demonstrating the contribution of other interactions, such as adsorption, apart from anion exchange in the removal mechanism. It was also stated that the presence of co-existing ions such as sulfate and chromium in wastewater inhibited the sorption of PFOS due to a competing effect on the exchange sites (Deng *et al.* 2010).

Functional group of PFAS removal could affect their removal via ion-exchange resins. Strong base anion (Cl and OH ionic form) resins were used in a study to remove PFOS and PFOA from processed wastewater in batch and continuous flow column experiments (Lampert *et al.* 2007). PFOS concentration was reduced to below detection limits after treatment, while PFOA was reduced to low levels. The PFOA and PFOS loadings onto the resin were measured as 686 mg/g and 151 mg/g, respectively. According to the isotherm tests, PFOA/chloride isotherm showed an incurvated shape, indicating the exchange of PFOA with chloride was more satisfactory than the exchange of PFOS. PFOA/PFOS isotherm also showed that PFOS was favored over PFOA (Lampert *et al.* 2007). Poly(*N*-[3-(dimethylamino)propyl]acrylamide, methyl chloride quaternary, and (DMAPAA-Q) hydrogel matrix was reported to remove long- and short-chain PFAS, including PFBA, PFBS, and GenX, from treated wastewater samples in bench-scale studies (Ateia *et al.* 2019b). Equilibrium time ranged between 60 and 120 min for complete removal of PFAS and was mentioned that higher removal was observed for sulfonated PFAS as compared to carboxylic PFAS, regardless of chain length (Ateia *et al.* 2019b).

Ion-exchange resins usually offer more efficient adsorption for short-chain PFAS as compared to activated carbon. Du *et al.* (2015) reported higher adsorption capacities for PFOA, PFHpA, and PFHxA by ion-exchange resin (IRA67) compared to a bamboo-derived AC at acidic pH in perfluorooctanesulfonyl fluoride (PFOSF) washing wastewater. Ion-exchange resins have provided efficient removal of PFOA and PFOS. More research is needed to reduce the operating cost and enhance the removal effectiveness of different types of PFAS in the presence of competing organics, ions, and co-contaminants in wastewater.

4. EMERGING TREATMENT TECHNOLOGIES FOR PFAS

The physical and chemical properties of PFAS, such as high energy carbon–fluorine bonds, hydrophobicity, and thermal stability, pose challenges to many treatment technologies. In addition, many of those technologies have been developed and designed for other classes of pollutants, not for PFAS. Thus, the existing treatment options for PFAS are inadequate in number as compared to other pollutants. Although recent technologies, such as carbon adsorption and ion exchange, show high removal efficiencies, secondary pollutants and/or high cost of regeneration procedures make it difficult to apply these technologies. Thus, innovative technologies are being developed, focusing on PFAS degradation rather than transferring from one phase to another. For this reason, advanced oxidation processes (AOPs), such as electrooxidation (EOX), photocatalysis, plasma, and ultrasound, are receiving increasing attention.

Many innovative technologies are being investigated in laboratories, but the scale-up also must be considered to deal with challenges when translating from laboratory-scale to pilot- and full-scale applications. Considering the extremely high persistence and mobility of PFAS, emerging treatment technologies should be designed to achieve efficient degradation for even very low concentration levels.

4.1. Electro-oxidation

Electro-oxidation (EOX) processes have attracted considerable attention in the last few years due to their simplicity and efficiency of the degradation of various harmful contaminants. This technology may also be called ‘green technology’ since little or no chemicals are added during water and wastewater treatment. The electrode material is one of the most significant factors in the EOX process; thus, the development of novel electrode materials is a key factor to increase treatment efficiency. EOX can be used for treating different kinds of wastewaters, disinfecting drinking water, and degrading harmful target pollutants (Sirés & Brillas 2012; Brillas & Martínez-Huitle 2015; Gomez-Ruiz *et al.* 2017a; Barişçi *et al.* 2018a, 2018b; Turkay *et al.* 2018; Barisci & Suri 2020; Barisci & Suri 2021). EOX involves two mechanisms that occur simultaneously during the

oxidation of pollutants: (1) direct electron transfer to the anode surface, and (2) indirect oxidation with powerful reactive oxygen species (ROS) generated from water oxidation, such as hydroxyl radical or active oxygen (Sirés *et al.* 2014; Brillas & Martínez-Huitle 2015; Schaefer *et al.* 2015). Ozone and hydrogen peroxide can also be produced during the EOX process. Depending on the existing components in water or the chemicals added to the water, indirect oxidation may occur via other oxidants, such as chlorine and hypochlorite (also called mediated oxidation).

Different behaviors were observed when using various electrode materials (Comninellis 1994). Accordingly, 'active' electrodes, such as Pt, IrO₂, and RuO₂, strongly react with sorbed hydroxyl radical on the anode surface (M(OH*)) to form superoxide (MO) surface Equations (1) and (2). Conversely, 'non-active' anodes, such as boron-doped diamond (BDD), PbO₂, and SnO₂, show no or little interaction with formed M(OH*), providing the direct reaction of hydroxyl radical and target pollutants until complete mineralization is achieved; in other words, reaction of Equation (2) does not occur:



Gomez-Ruiz *et al.* (2017a, 2017b) investigated the treatment of eight PFAS from industrial wastewater by EOX using the BDD anode in bench-scale experiments (Gomez-Ruiz *et al.* 2017b). The industrial WWTP received wastewater from four manufacturing plants, with one of them producing PFAS, and contributed 3–17% to the overall flow treated in the industrial WWTP. The total concentration of PFAS in the industrial effluent was 1,652 µg/L, in which 6:2 FTAB and 6:2 FTSA were the most significant contributors with 92% (w/w). In their experiments, a BDD anode with an active surface area of 0.007 m² was used to treat 2 L of industrial effluent with an applied current density of 50 mA/cm². After 10 h of process time, 99.7% total PFAS removal occurred while more than 90% TOC removal was achieved. All analyzed PFAS, except 6:2FTSA, were found to be below detection limits after treatment, while 6:2 FTSA was the only compound identified in the treated water. The energy consumption was estimated as 256 kWh/m³ to achieve 99.7% removal. Barisci & Suri (2020) studied short- and long-chain PFCA degradation in different water matrices, i.e., ultrapure water, surface water, and domestic wastewater effluent using BDD anodes at bench-scale. More than 95% degradation was reported for all long-chain PFCAs (except C7), regardless of chain length in ultrapure water. Here, 37% defluorination and 74% TOC removal were reported in the same study during the treatment of 10 mg/L PFOA in ultrapure water. In contrast to long-chain PFCAs, strong chain-length dependence was observed for short-chain PFCAs. It was also mentioned that water matrix did not have an effect for short-chain PFCAs; however, degradation efficiencies were in the order of ultrapure water > WWTP effluent > river water for long-chain PFCAs. The reason for this behavior was explained by higher concentrations of nitrite and bromide, which are known ·OH scavengers, in river water as compared to WWTP effluent. However, when a Ti/RuO₂ electrode was used, to study the electrochemical degradation of PFCAs and PFASs in a laboratory-scale study (Barisci & Suri 2021), the effect of PFAS chain length on the degradation rate was reported to be significant. For example, the degradation of short-chain PFAS ranged between 16 and 67% while it was 64–91% for long-chain PFAS. The TOC removals were 64 and 39% for PFOA and PFOS, respectively. Recently, the Magnéli phase titanium sub-oxide (Ti₄O₇) electrode has been reported as a promising candidate for the EOX process due to its chemical inertness, high conductivity, and relatively low production cost (Walsh & Wills 2010). This material, also known as Ebonex[®] (Atraverda Ltd, UK), has the generic formula of Ti_nO_{2n-1} (3 ≤ n ≤ 10) with >2.0 V and ~-1.4 V anodic and cathodic polarization, respectively. Unlike BDD anode, which is not effective at high pH, the Magnéli phase anode is extremely stable over a wide range of pH, including very high and low values. However, recent applications of a Magnéli phase electrode have been limited to deionized water at bench-scale for degradation of PFOA and PFOS. Only one study examined Magnéli phase electrodes for degradation of PFAAs from still bottoms recovered from regenerated saturated ion-exchange resin media. Still bottom samples had a TOC value ranging between 13,280 and 201,529 mg/L with a chloride content of 62.7 mg/L. The degradation ratios of monitored PFAS including PFOA, PFOS, PFHxS, PFHpA, and perfluoro-1-heptanesulfonate (PFHpS) were 98.9%, 94.8%, 95.0%, 56.9%, and, 96.8%, respectively, while a 79.5% TOC reduction was achieved after 40 h of process time. However, the increase in short-chain PFAS (PFBA, PFBS, PFPeA, and PFHxA) concentration was observed which was concluded to possible incomplete degradation of precursors and long-chain PFAAs. The authors also mentioned that no considerable adsorption of PFAS on the magnéli phase anode was detected and the removal of PFAS was mostly attributed to electrochemical reactions (Wang *et al.* 2020a).

In the literature, there are numerous scale-up studies for the EOX process of wastewater containing many organic contaminants. However, limited scale-up studies for PFAS-containing wastewater have been reported. In one study, a pilot-scale EOX process was used to treat industrial wastewater containing PFAS (Fath *et al.* 2016). The process was automated and the pilot-scale reactor consisted of 36 lead (Pb93Sn7) electrodes having an active surface area of 700 mm × 400 mm connected parallelly. The process successfully degraded C6–C8 PFAS with up to 99% efficiency. However, the process was reported to be less efficient for short-chain PFAS (PFBS). It was reported that PFAS degradation produced hydrogen fluoride under the acidic operating conditions (Fath *et al.* 2016). Operational cost was calculated as US\$4500/year (140 L/h, 10 ppm PFAS with 95% degradation) in this study. Both laboratory- and pilot-scale studies show that this technology could be used for efficient degradation of PFAS-containing wastewater in full scale, but more research should be conducted to determine optimum operating conditions and to provide a cost-effective process. Furthermore, the presence of chloride in wastewater may lead to the formation of toxic byproducts, i.e., chlorate and perchlorate, during EOX treatment of PFAS (Yang *et al.* 2019), and which should also be considered before using this technology.

4.2. Sonochemical degradation (ultrasound)

The sonochemical process uses an acoustic field to produce chemical reactions in an aqueous media. Cavitation occurs through the collapse of bubbles formed in the solution by sound waves. This results in high temperatures at cavity collapse points and at the bubble–water interface (Fu *et al.* 2007; Suri *et al.* 2007; Cheng *et al.* 2008; Suri *et al.* 2008; Andaluri *et al.* 2012; Hao *et al.* 2014; Shende *et al.* 2019; Shende *et al.* 2021a, 2021b). Characteristic ultrasound frequencies range between 20 and 1,000 kHz during the sonochemical degradation of PFAS.

Vecitis *et al.* (2010) reported the ultrasound treatment of AFFF-contaminated wastewater (FC-600), containing PFOS ($3,650 \pm 710$ mg/L), PFHS (820 ± 140 mg/L), PFBS (254 ± 13 mg/L), PFOA (161 ± 13 mg/L), and PFHA (53 ± 13 mg/L). The primary constituent in FC-600, PFOS, was removed by more than 90% in 2 h with a frequency of 505 kHz. Additionally, the TOC decreased by almost 50% from 270 to 140 ppm after 120 min of process time (Vecitis *et al.* 2010). Moreover, ultrasound treatment of AFFF stockpiles has been also examined using a dual-transducer system that consists of supersonic and megasonic frequencies (Kucharzyk *et al.* 2017). The system would be scaled up for the treatment of a large volume of PFAS solutions. This novel approach will be useful for managing the inventory of AFFF products kept at defense sites to develop a system which could generate high temperatures for PFAS thermal degradation in presence of select reactive oxidizing chemicals. The authors contend that this approach could lead to lower energy requirements (Kucharzyk *et al.* 2017).

Based on these studies and data in the literature, more research is required for the application of ultrasound technology at pilot- and field-scale to treat wastewater influents/effluents with a high concentration of PFAS. Due to its high energy needs, the technology is more favorable for treating small wastewater volumes but at high PFAS concentrations. This technology could be used in combination with other processes such as physical separation and/or other AOPs to avoid the negative effects of competing ions and organics and provide higher PFAS degradation efficiencies at a lower cost.

4.3. Plasma-based technologies

Plasma-based treatment technology uses only electricity, converting water in an air or oxygen environment into a mixture of extremely oxidative species, such as OH[•], H₂O₂, HO₂[•], H[•], O₂^{-•}, O₃, H₂ and hydrated electrons (e_{aq}⁻) (Thagard *et al.* 2009; Joshi & Thagard 2013). These species have a very short lifetime. However, the electrical discharges take place close to the water surface in the reactor (i.e., just above the water level), and some of these radical species may get into the water and destroy the pollutants (Burlica *et al.* 2006). It must be mentioned that there are approaches to generate plasma inside the aqueous solution but is not very efficient. Plasma-based water/wastewater treatment technologies can have diverse discharge types, namely pulsed corona, direct current (DC) pulseless corona, gliding arc, dielectric barrier, DC arc, and DC glow discharges. Different oxidative species with different degradation efficiencies can be formed during plasma water treatment based on the type of applied discharge. For example, in some cases, reactive nitrogen species (RNS), including peroxy-nitrite and peroxy-nitrate, can also be generated (Lewis *et al.* 2020). For pollutant degradation, plasma is usually generated through a high voltage between two electrodes: one grounded electrode within or contacting the polluted water and one high voltage electrode. Up until now, several attempts have been made for the utilization of plasma to degrade PFAS from synthetic and groundwater samples (Yasuoka *et al.* 2011; Takeuchi *et al.* 2013; Stratton *et al.* 2017; Singh *et al.* 2019; Lewis *et al.* 2020) using different types of electrical discharge plasma reactors with different electrode configurations. Studies investigating reactive species generated during plasma treatment show that hydroxyl and other superoxide radicals, which are characteristically

the main plasma-based oxidizing agents, do not play an important role in PFOA degradation. Instead, it is reported that hydrated electrons comprise a substantial fraction of the PFOA transformation. Some linear chain PFCAs with carbon chain-length C4–C7 have been identified as byproducts during degradation of PFOA and PFOS in plasma-based treatment in the literature (Singh *et al.* 2019). PFOA, PFBS, and PFHxS were also identified as byproducts of the degradation of PFOS. In addition, numerous PFOA- and PFOS-related intermediates at trace amounts and gaseous byproducts in small amounts have also been identified where defluorination ratios ranged between 58 and 77%. Those identified byproducts, including short-chain PFCAs, suggest a stepwise degradation of the PFAS molecule, following degradation of perfluoroalkyl radicals, intermediates, and perfluoro alcohols/ketones (Singh *et al.* 2019; Lewis *et al.* 2020).

A recent study investigated a bench-scale plasma reactor for degradation of PFAS from landfill leachate samples containing six short-chain, five long-chain perfluoroalkyl acids (PFAAs), and eight PFAA precursors at concentrations ranging 102–105 ng/L. The concentrations of PFOS and PFOA were 2,000 and 3,000 ng/L, respectively. Here, 500 mL of samples were treated by plasma, resulting in higher degradation efficiencies of longer chain PFAAs compared with shorter chain PFAAs. Both PFOS and PFOA were degraded by 90% in 10–75 min. Other long- and short-chain PFAAs were degraded by >99% (Singh *et al.* 2020a). Another bench-scale batch plasma reactor was used to degrade PFAS from ion-exchange regenerant still bottom solutions containing a high concentration (~100 mg/L) and a low concentration (<1 µg/L) of PFAS. In the plasma reactor for the high concentrations, the precursors of PFAS and long-chain PFAAs were degraded by >99.9% in 2 h, where short-chain PFAAs were degraded by >99% in 6 h of treatment. To degrade additional PFAAs, another plasma reactor was used for low concentrations. In this reactor, the authors added a cationic surfactant (cetrimonium bromide) which promoted the removal of short-chain PFAAs (below detection limits) in 1.5 h. Overall, >99% of PFAS from wastewater was removed during the treatment with corresponding fluorine recoveries of 47–117% (Singh *et al.* 2020b).

Plasma-based processes achieved efficient degradation of PFAS in synthetic water, contaminated groundwater, and wastewater samples. This technology seems to be less affected by competing ions and other organic contaminants present in real wastewater samples, as chemical reactivity mostly occurs in the plasma–liquid interface in comparison with other AOPs, including ultrasound and persulfate. According to these, plasma-based processes are promising for PFAS degradation from wastewater. However, further studies should be done to confirm its efficiency for wastewater treatment, degradation of intermediates, and scale-up. In addition, safety aspects need to be considered due to the high voltage discharges needed to generate the plasmas.

4.4. Heterogenous photocatalysis using nanomaterials

Direct photolysis has been recognized as a promising option for the removal of a variety of organic pollutants, however, direct photolysis for the degradation of PFAS in wastewater is of low efficiency due to the strong energy of C–F bonds of PFAS (Panchangam *et al.* 2009). In comparison, heterogeneous photocatalysis has been developed to degrade PFAS by applying certain catalysts with photon ($h\nu$) absorption capacity. During heterogeneous photocatalysis, the pollutant and catalyst occur in various stages and the process can be defined as absorbing $h\nu$ and then producing electrons (e^-) and positively charged electron–hole pairs (h^+), which can migrate to the photocatalysts' surface and react directly or indirectly with pollutants (Suri *et al.* 1993; Crittenden *et al.* 1997; Suri *et al.* 1999). It has been demonstrated that heterogeneous photocatalysts such as gallium oxide (Ga_2O_3) and indium trioxide (In_2O_3) are much more effective for the degradation of PFAS compared to direct photolysis (Chen *et al.* 2011; Li *et al.* 2012, 2013, 2014; Tan *et al.* 2020; Xu *et al.* 2020). However, light penetration and separation or immobilization of catalysts on support materials is limiting the application of this technology (Thiruvengkatachari *et al.* 2008).

4.4.1. Ga_2O_3 -based nanomaterials

β - Ga_2O_3 is an extensive bandgap semiconducting material ($E_g = 4.8$ eV) (Zhao & Zhang 2009) that finds multipurpose use in electronic devices with high temperature and gas sensors (Lin *et al.* 2007). Various nanostructures of Ga_2O_3 have been synthesized, such as nanoplates, nanosheets, nanowires, and nanobelts (Huang & Yeh 2010; Yan *et al.* 2010; Muruganandham *et al.* 2012). For example, Shao *et al.* (2013a, 2013b) synthesized sheaf-like Ga_2O_3 consisting of nanoplates with high crystallinity for PFOA removal from secondary effluent (Shao *et al.* 2013a). The sheaf-like Ga_2O_3 had a high specific surface area (36.1 m²/g) and a large number of nanopores (2–4 and 8 nm). The feasibility of sheaf-like Ga_2O_3 photocatalysis to degrade PFOA in a municipal wastewater plant in Beijing, China has been tested. 81% of PFOA was degraded within 3 h by photocatalysis processes in the presence of sheaf-like Ga_2O_3 . However, the PFOA degradation reduced in the secondary effluent

compared to ultrapure water due to the impeding effect of bicarbonate and organic constituents since bicarbonate concentration was approximately 3,000 times higher than the concentration of PFOA in the secondary effluent. Due to the competition between bicarbonate and PFOA for the surface of Ga_2O_3 , PFOA adsorption was inhibited (Li *et al.* 2012). The authors also mentioned that after adjusting the pH of the secondary effluent as 4.3 to transform bicarbonate into carbonic acid, the degradation of PFOA increased to 100% from 81% after 3 h. However, PFOA degradation was still significantly slow as compared to results for pure water, and this was attributed to adsorption and attenuation of UV penetration by organic matters in the secondary effluent. The same research group also investigated the needle-like Ga_2O_3 for PFOA degradation from wastewater; 100% PFOA degradation was achieved with an initial concentration of 500 $\mu\text{g}/\text{L}$ in wastewater. The required treatment time was 180 min which was much longer compared to ultrapure water (Shao *et al.* 2013b).

4.4.2. In_2O_3 -based nanomaterials

Electron-hole pair separation and band gap are important properties to improve photocatalyst performance. Nanocrystals such as In_2O_3 have lower band gaps (2.9–3.0 eV) and larger available surface areas (Li *et al.* 2013). Compared to TiO_2 nanoparticles, In_2O_3 nanocrystals have a higher activity to degrade PFAS because the transformation of photogenerated holes to OH^\cdot is extremely lower for In_2O_3 nanocrystals (Vecitis *et al.* 2009). Accordingly, OH^\cdot generated in In_2O_3 solution is less than the amount produced in TiO_2 solution with the same UV dosage (Li *et al.* 2013). This implies that the reaction between photogenerated holes in the valence band of In_2O_3 and the interface of water or hydroxyl group would be slower. Therefore, most of the photogenerated holes on the surface of In_2O_3 would not be converted to OH^\cdot but conserved under UV radiation. This was confirmed by other authors demonstrating that direct oxidation due to the generated hole provided dramatically higher PFOA decay than oxidation with OH^\cdot (Kutsuna *et al.* 2006; Vecitis *et al.* 2009).

Li *et al.* (2012) investigated photocatalysis of PFOA in the presence of an In_2O_3 catalyst. They mentioned that while 69% PFOA (initial concentration of 100 $\mu\text{mol}/\text{L}$) was degraded in pure water by In_2O_3 within 180 min, the efficiency was reduced to only 10% in wastewater (Li *et al.* 2012). However, once the pH value was adjusted to 4 for the secondary effluent and ozone gas was concurrently added ($\sim 8 \text{ mg}/\text{L}\cdot\text{h}$), almost similar PFOA degradation (69%) was achieved. The ozone addition can promote the efficiency of PFOA degradation in wastewater because it can promote the reaction of photo-produced h^+ with PFOA instead of recombination with photo-produced e^- (Zsilák *et al.* 2014). In other words, ozone acts as an electron acceptor and reduces the recombination of electron and hole. PFOA degradation using In_2O_3 catalyst in simulated wastewater showed that wastewater constituents such as sulfate, chloride, and NOM significantly affected PFOA degradation. However, it was reported that when pH was adjusted to 2, PFOA degradation was 97.6% with complete defluorination (Jiang *et al.* 2016). The results show that PFAS degradation in wastewater could be significantly diminished by bicarbonate and NOM, however their adverse effects can be reduced by pH adjustment and the addition of ozone. It must be stated that changing the pH of large volumes of water may not be practically (economically) feasible.

4.5. New generation adsorbents

New nanoscale generation of adsorbents (nano-adsorbent) generally has advantages as compared to conventional adsorbents due to their larger and more reactive specific surface areas. The PFAS adsorption mechanism on nanoscale adsorbents includes the electrostatic interface, hydrogen bonds, hydrophobic effect, and ion exchange, which can be different from conventional adsorbents. Amongst them, both hydrophobic and electrostatic interactions are believed to be the key reasons for the adsorption of PFAS (Du *et al.* 2014; Muruganandham *et al.* 2015). Electrostatic interaction can occur between the negatively charged PFAS molecule and positively charged nano-adsorbents. Each fluorine atom in the PFAS molecule has a high electronegativity, giving it the tendency to attract electrons (Xiao *et al.* 2011). Therefore, along with the negative charge due to the ionization of the PFAS molecule, the strong electronegativity of its fluorine atoms also produces negatively charged shells covering the PFAS molecule, which can enhance the electrostatic force. PFAS usually consists of a hydrophilic head and a hydrophobic tail, as mentioned previously. Because of the hydrophobic interaction, the hydrophobic fluorinated tail which is negatively charged can be adsorbed onto the hydrophobic nano-adsorbents' surface, in spite of electrostatic repulsion since some nano-adsorbents have a negative charge such as carbon nanotubes, (Fuji *et al.* 2007). Aside from the electrostatic and hydrophobic interactions, self-aggregation, such as the generation of hemi-micelles and/or micelles, may also increase the adsorption of PFAS. Considering these factors, many innovative nano-adsorbents have been synthesized and evaluated to improve PFAS adsorption. Most of the studies conducted at laboratory scales provide information that is helpful in developing field-scale treatment processes for PFAS removal from wastewaters.

4.5.1. Covalent organic frameworks

Covalent organic frameworks (COFs) are crystalline, covalent porous polymers containing various light elements (C, H, O, N, and B) (Peng *et al.* 2016). COFs display several attractive properties including large surface area, configurable porosity, outstanding stability, low mass densities, adaptable function, and faster charge carrier mobility (Zhang *et al.* 2020). Different synthesis methods of COFs have been utilized by compression reactions using covalent bonds such as imine (Chandra *et al.* 2013), hydrazine (Uribe-Romo *et al.* 2011), keto-enol (Kandambeth *et al.* 2012), and boroxine (Wan *et al.* 2009) linkages. Recent studies specify that mainly hydrophobic interactions are the key forces that provide the adsorption of hydrophobic PFOA on COFs (Yu *et al.* 2008; Kawano *et al.* 2013; Ateia *et al.* 2018; Ateia *et al.* 2019a), because the major skeleton of COFs is typically hydrophobic, which favors for PFOA adsorption. The sorption capacity usually increases with increasing perfluorocarbon chain length because of the higher hydrophobic properties of PFAS (Zhang *et al.* 2011; Ji *et al.* 2018; Xiao *et al.* 2019). However, evidence indicates that electrostatic reactions of the PFOA carboxylate headgroup and the cationic amine groups of the sorbent also take place during the adsorption process (Niu & Cai 2009; Mitra *et al.* 2016; Ateia *et al.* 2019b). For other PFAS having more hydrophilic character, electrostatic interactions play a predominant role depending on pH for the adsorption of PFAS on COFs (Du *et al.* 2014; Gao *et al.* 2017). In general, the long-chain PFAS have high hydrophobicity which provides higher adsorption affinity when compared to hydrophilic short-chain PFAS. Hence, while long-chain PFAS can be adsorbed via electrostatic and hydrophobic interactions, short-chain PFAS can be adsorbed mostly by electrostatic interactions (Senevirathna *et al.* 2010; Wang *et al.* 2019).

Recently, several applications of COFs for PFAS removal have been conducted at a bench-scale. Ji *et al.* (2018) investigated 2D amine-functionalized COF for the adsorption of PFOA, PFOS, and ammonium perfluoro-2-propoxypropionate (GenX) (Ji *et al.* 2018). It was reported that COF with partial amine incorporation exhibited more than 90% removal of PFAS, signifying the role of synergetic interaction between hydrophobic surfaces and polar groups for PFAS removal. A very recent study reported that the cationic COF with quaternary ammonium displayed 2.06 mmol/g of adsorption capacity for GenX which was more effective than traditional activated carbons and resins (Wang *et al.* 2020c). Another study reported the application of hybrid hydrogel matrix COF (DMPAA-Q) for the removal of 16 PFAS including PFBA, PFBS, and GenX from industrial wastewater effluents (Ateia *et al.* 2019b). The results displayed fast removal kinetics at equilibrium times of 60–120 min. A higher removal was obtained for sulfonated PFAS compared to carboxylic PFAS, and no chain-length effect was observed. It was also mentioned that hydrogel COF showed an additional advantage over conventional adsorbents since no desorption was observed when the process time was extended to 24 h. Furthermore, the removal efficacy was similar at different pH range of 4–10 (Ateia *et al.* 2019b).

COFs were assessed in batch and column application modes for PFAS removal. Batch tests are useful and essential for the fast evaluation of adsorption kinetics and capacity of the COFs. However, batch application modes could be limited in real-scale applications for PFAS adsorption from industrial and municipal wastewater because the recovery of COFs is difficult in large-scale applications. Hence, more column tests, where solid to water volume is much higher compared to batch tests, should be performed since column tests can specify the performance of COFs in real-scale applications.

4.5.2. Metal-organic frameworks

Metal-organic frameworks (MOFs) are an innovative class of porous and crystalline materials composed of organic bridging linkers and metal/metal oxide-containing nodes (Barpaga *et al.* 2019). MOFs have recently gained attention due to their high surface area, tunable porosity, very high stability, easily adaptable functionalities, and reusability with relatively simple washing procedures compared to AC (Xue *et al.* 2016; Moreton *et al.* 2020).

PFAS sorption mechanism onto MOFs mostly relies on both electrostatic and hydrophobic interactions (Merino *et al.* 2016). The solution pH and other constituents of water affect electrostatic interactions between MOFs and PFAS molecules (Barpaga *et al.* 2019). In addition, as known, the hydrophobicity of PFAS molecule increases with the presence of more C–F bonds (Chen *et al.* 2016b). For example, Barpaga *et al.* (2019) synthesized chromium and iron analogs of the MOF for PFOS sorption at a laboratory scale. It has been reported that the sorption capacity of chromium analog MOF was higher as compared to iron analog MOF due to stronger interaction between the metal node and sulfur moieties of PFOS molecule (Barpaga *et al.* 2019). Another study developed an aluminum-based MOF for PFOA uptake from water at a laboratory scale and sorbent performance was compared with AC (Hakim Mohd Azmi *et al.* 2021). The much stronger adsorption capacity of PFOA (340 mg/g) compared to AC (120 mg/g) was observed, and which was attributed to the electrostatic bonds formed between the anionic functional group of PFOA and the aluminum-based MOF. A fluorinated zirconium-based

MOF also presented high adsorption capacities for both PFOA (1.13 mmol/g) and PFOS (0.51 mmol/g) owing to the high interaction of fluoride moieties of the MOF and the PFAS molecule. Sini *et al.* (2018) employed zirconium-based MOF to display an improved affinity for PFOA and PFOS with fluorinated functionalities in the pores of MOF that can provide fluorine–fluorine interactions.

Although MOFs represented promising performances, these materials are still at a very early stage of development and testing. In addition, there is a lack of studies on MOF applications for domestic and industrial wastewater, thus, more research is required before they become a feasible technology for field-scale applications for wastewater treatment.

4.5.3. Carbon nanotubes

Carbon nanotubes (CNTs) are a promising nanoscale adsorbent that can provide effective PFAS removal due to their physicochemical properties, adsorption affinity, and exceptional structure. Although no field tests have been reported for wastewater treatment, Deng *et al.* (2012) studied bench-scale adsorption of PFOA, PFOS, PFHxS, PFHxA, PFBA, and PFBS on unchanged CNTs, namely, single-/multiwalled (MWCNT) CNTs and functionalized CNTs (MWCNT-OH and MWCNT-COOH). The authors observed that the PFAS adsorption on CNTs diminished for shorter chain PFAS. The main adsorption mechanism was the hydrophobic interaction between PFAS and the walls of CNTs. Hence, CNTs with hydrophilic -OH and -COOH groups significantly lowered the adsorption capacity as compared to the unchanged CNTs. Nevertheless, electrostatic repulsion could hinder the adsorption capacity, as both CNTs and PFAS had negative charges. Furthermore, the authors did not observe the formed hemi-micelles and micelles on the CNT surface. Consequently, the authors stated that the adsorption of PFAS on CNTs was less effective than other well known adsorbents, such as active carbon and resins (Deng *et al.* 2012). The oxygen content could be increased in MWCNTs to 18% to increase the sorption efficiency (Li *et al.* 2011b). A different study also showed that MWCNTs with electrochemical assistance were able to enhance the adsorption of PFAS from water containing CaCl₂ and NaN₃ (Li *et al.* 2011a). This enhancement was attributed to the improved electrostatic interaction between PFAS and MWCNTs. Comparing MWCNTs without electrochemical assistance, the kinetic model presented that the adsorption rates of PFOS and PFOA initially increased 41- and 60-fold, respectively. This study showed a promising process for the removal of PFAS (Li *et al.* 2011a). The data from existing studies might help to apply CNTs for field-scale wastewater treatment systems.

4.5.4. Organically modified silica

One of the next-generation adsorbents involves organically modified silica adsorbents which can provide effective removal of PFAS. Silica-based adsorbents have available pores with mesoscale which allow modifiers to be suitably mounted on their surfaces, giving the adsorbents high adsorption capacity and selectivity. Several compounds, such as 3-aminopropyltriethoxysilane, 1,8-bis(dimethylamino)naphthalene, hexadecyl trimethyl ammonium bromide, and cross-linked alkoxysilanes have been considered as a coating for the silicas to allow for higher adsorption of PFAS (Edmiston 2013).

β -Cyclodextrin (β -CD)-coated silica adsorbents were synthesized and investigated for PFOA removal (Bhattarai *et al.* 2014). The adsorbent prepared by using a crosslinking agent of hexamethylene diisocyanate was reported to remove more than 90% of PFOA. The authors also mentioned that increasing β -CD loading enhanced PFOA removal (Bhattarai *et al.* 2014). Another study investigated the removal of PFOA and PFOS by β -cyclodextrin–ionic liquid with the magnetic Fe₃O₄ nanoparticle adsorbent (Badruddoza *et al.* 2017). The sorption capacities were reported as 13,200 and 2,500 μ g/g for PFOS and PFOA, respectively, and the higher PFOS removal was ascribed to hydrophobicity and functional groups of PFOS (Abu *et al.* 2017).

A novel modified organo-clay adsorbent (matCARE™) has been developed and evaluated for the PFOS removal from AFFF-polluted wastewater (Das *et al.* 2013) in laboratory batch experiments. It took only 1 h to reach equilibrium with significantly higher adsorption capacity (0.09 mmol/g) compared to activated carbon (0.07 mmol/L). This material was then used at field-scale in AFFF wastewater treatment plants in Australia (Arias Espana *et al.* 2015). For example, almost 1 million liters of wastewater were effectively treated at one of the WWTPs with an average influent concentration of 0.02 mmol/L and 0.004 mmol/L for PFOS and PFOA, respectively, to below detection limits, using matCARE™ cartridges (1.2 kg each).

Tables 2 and 3 summarize recent and emerging technologies on PFAS removal and advantages/disadvantages for each technology, respectively.

Table 2 | Summary of recent and emerging treatment technologies for PFAS degradation/removal

Treatment technology		Target PFAS	Water matrix	Initial concentration	Degradation/sorption	Scale	Reference
Recent technologies	AC	PFOA, PFOS, PFHxS, PFHxA,	Municipal WWTP effluent	3.7–16 ng/L	PFOS and short-chain PFAS not removed	Full scale	Thompson <i>et al.</i> (2011)
	PAC	PFOA, PFOS	Municipal WWTP effluent	25–44 ng/L	6–52% for PFOS, PFOA not removed	Full scale	Mailler <i>et al.</i> (2015)
	GAC	PFOA, PFOS, PFNA, PFDA, PFHpA, PFHxA, PFHxS, PFPnA, PFBA	Municipal WWTP effluent	1 µg/L	Complete removal except PFOS (40%)	Pilot scale	Inyang & Dickenson (2017)
	AC	PFOA, PFHxA, PFHpA	Industrial WWTP effluent	0.1–0.29 mmol/L	88–90%	Laboratory scale	Du <i>et al.</i> (2015)
	GAC	13 PFAS	Municipal WWTP effluent	2 µg/L	95% on average	Laboratory scale	Rostvall <i>et al.</i> (2018)
	GAC (Calgon Filtrasorb® 500)	PFAAs	DI water + NOM	1 µg/L	>20% breakthrough for all PFAAs and negative removal for PFBA and PFPeA	Laboratory scale	Appleman <i>et al.</i> (2013)
	Ion exchange (PFA 300)	PFOS	DI water	0.01–1 mg/L	99%, 455 mg/g adsorption capacity	Laboratory scale	Chularueangksorn <i>et al.</i> (2013)
	Ion exchange (IRA67)	PFOS	Simulated industrial WW	400 mg/L	4–5 mmol/g adsorption capacity	Laboratory scale	Deng <i>et al.</i> (2010)
	Ion exchange (A714)	PFOA, PFOS	Simulated industrial WW	1,000–3,000 mg/L	PFOS below detection limit, 99.6% PFOA removal	Laboratory scale	Lampert <i>et al.</i> (2007)
	Ion exchange	11 short-chain, 5 long-chain including PFBA, PFBS, GenX	Surface water	1 µg/L	80–100%	Laboratory scale	Ateia <i>et al.</i> (2018)
Ion exchange (IRA67)	PFOA, PFOS, PFBA, PFBS, PFHxA, PFHxS	Simulated AFFF-impacted groundwater	0.1–0.5 mmol/L	90% of PFOS, 10% of PFBA (PFOS > PFHxS > PFOA > PFBS > PFHxA > PFBA)	Laboratory scale	Maimaiti <i>et al.</i> (2018)	
Emerging technologies	EOX (BDD)	PFBA, PFPeA, PFHxA, PFHpA, PFOA, FTSA, 6:2 FTCA, 6:2 FTAB	Industrial WWTP effluent	ΣPFAS = 1,642 µg/L	Σ99.7%	Laboratory scale	Gomez-Ruiz <i>et al.</i> (2017b)
	EOX (Ti/RuO ₂)	PFOA, PFOS and PFAAs	AFFF-impacted groundwater	0.7–65 µg/L	98% for PFOS and 58% for PFOS	Laboratory scale	Schaefer <i>et al.</i> (2015)
	EOX (BDD)	Short- and long-chain PFCAs	DI water, river water and municipal WWTP effluent	200 µg/L each	>92 and 75% defluorination for long-chain PFCAs in DI water and effluent	Laboratory scale	Barisci & Suri (2020)
	EOX (TiRuO ₂)	PFCAs and PFSAs	DI water	100 µg/L each	16–67% for short-chain PFAS, 64–91% for long-chain PFAS.	Laboratory scale	Barisci & Suri (2021)
	EOX (magnéli phase)	PFOA, PFOS, PFHxS, PFHpA, PFHpS	Still bottom wastewater	Not mentioned	56.9%–98.9%	Laboratory scale	Wang <i>et al.</i> (2020a)
	EOX (Lead)	C6–C8 PFAS	Industrial WWTP effluent	1,000–20,000 µg/L	99%, less effective for short-chain	Pilot scale	Fath <i>et al.</i> (2016)
	Ultrasound (505 kHz)	PFOA, PFOS, PFHS, PFBS, PFHA	AFFF-contaminated wastewater	53 ± 13–3,650 ± 710 mg/L	90% removal in 2 h with 50% TOC removal	Laboratory scale	Vecitis <i>et al.</i> (2010)
	Ultrasound (354–612 kHz)	PFOA, PFOS	DI water and groundwater below a landfill	~100 µg/L	Rate constant reduced by 56–61% in groundwater	Laboratory scale	Cheng <i>et al.</i> (2008)
	Plasma-based treatment	PFOA, PFOS	DI water	8.3 mg/L	Complete removal in 120 min	Laboratory scale	Singh <i>et al.</i> (2019)
	Plasma-based treatment	Five long-chain, six short-chain PFAAs and eight PFAA precursors	Landfill leachate	102–3,000 ng/L	Both PFOS and PFOA were removed by 90% in 10–75 min. Other long- and short-chain PFAAs were removed by >99%	Laboratory scale	Singh <i>et al.</i> (2020a)
Plasma-based treatment	Short- and long-chain PFAAs	Still bottom wastewater	~0.01–100 mg/L	>99% of short- and long-chain PFAAs were degraded in 2–6 h	Laboratory scale	Singh <i>et al.</i> (2020b)	
Emerging technologies	Photocatalysis with needle-like Ga ₂ O ₃	PFOA	Municipal wastewater influent	500 µg/L	100% PFOA degradation was achieved in 180 min which was	Laboratory scale	Shao <i>et al.</i> (2013b)

(Continued)

Table 2 | Continued

Treatment technology	Target PFAS	Water matrix	Initial concentration	Degradation/sorption	Scale	Reference
Photocatalysis in the presence of In ₂ O ₃ catalyst	PFOA	Municipal wastewater effluent	100 µmol/L	much longer compared to ultrapure water While 69% PFOA was degraded in pure water within 180 min, the efficiency was reduced to only 10% in wastewater, however, with pH adjustment and ozone addition similar PFOA degradation (69%) was achieved	Laboratory scale	Li <i>et al.</i> (2012)
Photocatalysis in the presence of In ₂ O ₃ catalyst	PFOA	Simulated municipal wastewater	100 mg/L	PFOA degradation was 97.6% with a complete defluorination at pH 2	Laboratory scale	Jiang <i>et al.</i> (2016)
Electro assisted MWNTs	PFOA, PFOS	DI water with ionic strength	100 µg/L	92%	Laboratory scale	Li <i>et al.</i> (2011a)
Organo-clay (matCARE™)	PFOS	AFFF-contaminated wastewater	0.6 mmol/L	0.09 mmol/L adsorption capacity	Laboratory scale	Das <i>et al.</i> (2013)
Organo-clay (matCARE™)	PFOA, PFOS	Municipal wastewater influent	0.04–0.02 mmol/L	Complete removal	Full scale	Arias Espana <i>et al.</i> (2015)
Photocatalysis with sheaf-like Ga ₂ O ₃	PFOA	Municipal wastewater effluent	500 µg/L	81% removal within 3 h with 66% defluorination, 100% after adjusting pH to 4.5	Laboratory scale	Shao <i>et al.</i> (2013a)
COF	PFOA, PFOS, GenX and other PFAS	DI water	100 µg/L	> 90%	Laboratory scale	Ji <i>et al.</i> (2018)
COF	GenX and HFPO-TA	DI water	0.0756 mmol/L	100% for HFPO-TA and 80% for GenX	Laboratory scale	Wang <i>et al.</i> (2020c)
COF	16 PFAS including PFBA, PFBS, and GenX	Industrial wastewater effluent	1,000 ng/L	Fast removal kinetics in 60–120 min with no desorption in 24 h	Laboratory scale	Ateia <i>et al.</i> (2019b)
MOF	PFOS	DI water	1–100 mM	100%	Laboratory scale	Barpaga <i>et al.</i> (2019)
MOF	PFOA and PFOS	DI water	100–1,000 mg/L	> 90%	Laboratory scale	Sini <i>et al.</i> (2018)

CONCLUSIONS

PFAS consist of fluorinated hydrophobic fluorocarbon chains attached to a hydrophilic functional group and are very stable chemicals. The exclusive features of PFAS have led to their widespread industrial and domestic applications, predominantly in surfactants, fire-fighting foams, textile, and food-packing papers. These compounds do not undergo hydrolysis or photolysis, and their biodegradation under typical environments is very weak, which makes them difficult to remediate. Thus, the development of replacement chemicals for these compounds is vital. Several producers have begun to substitute long-chain PFAS with short-chain PFAS. However, short-chain PFAS have been linked to serious health and environmental effects, similar to their homologs. Regarding legislation of PFAS, while the United States Environmental Protection Agency (US EPA) has issued health advisory as 70 ng/L for the combination of PFOA and PFOS in drinking water, similar to the Australian guidelines, the Germany Ministry of Health projected guidance of 300 ng/L for both PFOA and PFOS. Furthermore, several US states have PFAS guidelines that range from 13 to 1,000 ng/L for PFOA and PFOS. PFAS regulations seem to be challenging due to considerable differences in characteristics among PFAS compounds, and lack of monitoring and toxicity studies. The occurrence of PFAS in industrial and domestic WWTPs has been extensively reviewed in this paper. Investigating the role of WWTPs will lead to a better understanding of the universal cycling of recalcitrant PFAS and in possible environmental regulations. This review suggests that industrial WWTP effluents are a major source of PFAS as compared to domestic wastewater effluents. Despite the phaseout of C8-based PFAS, PFOA and PFOS are still the dominant compounds in most WWTPs. Thus, well known and emerging precursor compounds that breakdown to

Table 3 | Advantages and disadvantages of the recent and emerging technologies used for the treatment of PFAS from wastewater

Treatment technology	Advantages	Disadvantages
Activated carbon adsorption	<p>Technically simple process and adaptable to many existing treatment plants</p> <p>Can be applied for large-scale operations</p> <p>Inexpensive process</p> <p>Extensive range of available commercial products</p> <p>Highly effective process with fast adsorption kinetics</p> <p>High quality of the treated effluent</p>	<p>Nondestructive method</p> <p>Not effective for short-chain PFAS</p> <p>Efficiency reduces in the presence of other constituents</p> <p>Costly reactivation process</p> <p>Requirement of further disposal of the adsorbent if not reactivated</p>
Ion-exchange resins	<p>Technically simple operation</p> <p>Wide range of commercially available products</p> <p>Easy operation and maintenance</p> <p>Easy integration to other wastewater treatment processes</p> <p>Possibility of regeneration and reuse</p> <p>High quality of the treated effluent</p>	<p>Nondestructive method</p> <p>Economic limitations (high capital and maintenance cost of the selective resin and time-consuming regeneration process)</p> <p>Clogging of columns in the presence of particulates and organic matter, and may require a physicochemical pre-treatment</p> <p>Performance sensitive to pH</p> <p>Not very effective for short-chain PFAS</p> <p>Requirement of further disposal of the resin if not regenerated</p>
Electrooxidation	<p>Destructive technology</p> <p>High mineralization efficiency</p> <p>No need for addition of external chemicals in most cases</p> <p>Effective for many different types of PFAS including short-chain</p> <p>Relatively inexpensive operation cost</p> <p>Simple operation</p> <p>Rapid degradation</p>	<p>High initial cost of the electrodes</p> <p>Cost of the maintenance (depends on electrode inertness and stability)</p> <p>Anode passivation and sludge deposition on the electrodes which can reduce the process efficiency in continuous mode of operation</p> <p>Foam formation during wastewater treatment</p> <p>Possible toxic byproducts formation (chlorate and perchlorate) in the presence of chloride</p> <p>Mostly suitable for small- or medium-sized communities</p>
Ultrasound	<p>Destructive technology</p> <p>No need for addition of external chemicals</p> <p>No secondary pollution</p> <p>Simple operation</p> <p>No sludge production</p>	<p>High operational cost</p> <p>Management of generated heat energy</p> <p>Scale-up challenges</p> <p>Mostly suitable for small waste streams</p>
Plasma-based technologies	<p>Destructive technology</p> <p>Inexpensive operation cost</p> <p>High mineralization efficiency</p> <p>Effective for short-chain PFAS</p> <p>No need for addition of external chemicals</p>	<p>Scale-up is challenging</p> <p>Toxic byproduct formation</p> <p>Safety issues due to high voltage discharge for plasma generation</p>
Photocatalysis using nanomaterials (Ga ₂ O ₃ and In ₂ O ₃ -based)	<p><i>In situ</i> production of reactive radicals</p> <p>Little or no consumption of chemicals</p> <p>Mineralization of the pollutants</p> <p>No sludge production</p> <p>Rapid degradation</p>	<p>Separation of catalyst material from treated water</p> <p>Limited light penetration in solution for reaction to occur</p> <p>Mass transfer limitations</p> <p>Susceptible to inactivation from presence of NOM and ions</p>

(Continued)

Table 3 | Continued

Treatment technology	Advantages	Disadvantages
New generation adsorbents (COFs, MOFs, CNTs, and organically modified silica)	High chemical stability (COFs and MOFs) Pre-designable porous structure (COFs and MOFs) Effective for low concentrations Ease of operation High surface areas Tunable functionalities	Currently limited to laboratory scale Narrow pH range (MOFs) Relatively high synthesis cost (COFs and MOFs) Poor dispersibility in water (CNTs) Not effective for short-chain PFAS

PFCAs should also be identified and their physicochemical properties should be explored for improving the knowledge for the fate and transport of PFAS.

To mitigate associated negative impacts on humans and aquatic organisms, several treatment technologies have been reported. Commonly used PFAS treatment technologies include carbon adsorption and ion-exchange resins. Both, GAC and ion-exchange processes are efficient for the removal of PFAS from water; however, the presence of competing organics and ions can negatively affect these processes. These technologies have limited capacity to remove short-chain PFAS, and which can render them expensive. Research continues to improve the effectiveness of these processes and decrease operational cost. Emerging technologies, such as electrooxidation, plasma, sonochemical degradation, and new generation adsorbents, are being developed as viable options with promising results. Positive preliminary results at the laboratory scale and some pilot-scale studies were reported. Additional studies are desirable to conduct an assessment of the feasibility of emerging technologies at a larger scale and for complex wastewater streams. Due to the difficulty of in degradation and co-occurrence of many types of PFAS (molecular structure, size, charge, and functional groups), combined or hybrid treatment approaches may be required for effective removal/degradation of PFAS. Combined, hybrid or sequentially arranged treatment technologies may provide higher degradation efficiencies for PFAS, their precursors, and additional co-contaminants, and reduce the overall operational cost.

ACKNOWLEDGEMENT

This article is based upon research supported by the National Science Foundation (NSF), Water and Environmental Technology (WET) Center, and Temple University. The opinions expressed in this article are of the authors and do not necessarily reflect the views of WET Center or Temple University.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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First received 29 July 2021; accepted in revised form 29 October 2021. Available online 9 November 2021