

Occurrence of perfluoroalkyl and polyfluoroalkyl substances in the water environment and their removal in a water treatment process

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ABSTRACT

Perfluoroalkyl and polyfluoroalkyl substances (PFASs) such as perfluorooctanoic acid (PFOA), and perfluorooctane sulfonate (PFOS) are found in aquatic environments worldwide. The presence of these compounds in the water environment is still unclear, even though direct or indirect discharges of these compounds from industries to the aquatic environment are the potential routes. In this paper, PFOA and PFOS contamination of aquatic ecosystems, and their removal efficiency by different water treatment processes are reviewed. Typically, PFOS and PFOA contamination levels are higher in industrialized countries than in non-industrial countries. Coagulation, sand filtration, sedimentation, oxidation and disinfection are mostly ineffective in removing PFASs from drinking and wastewater. Granular activated carbon demonstrated the removal of PFASs and the extent of removal depends on operational conditions, such as temperature, operational life period and empty bed contact time. High-pressure membrane systems are the most suitable processes for removing the PFOS and PFOA in water sources. In the high-pressure membrane, removal of those chemicals occurs through rejection via electrostatic interaction. The extent of the reduction efficiency depends on the solution chemistry of the sample; lower pH and higher calcium ion addition in the water sample enhance the reduction efficiency in the high-pressure membrane application.

Key words | contamination, conventional water treatment, granular activated carbon, high-pressure membrane, perfluoroalkyl and polyfluoroalkyl substances, water environment

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INTRODUCTION

Perfluoroalkyl and polyfluoroalkyl substances (PFASs) such as perfluorooctanoic acid (PFOA), and perfluorooctane sulfonate (PFOS) have been recognized as emerging environmental pollutants (Giesy & Kannan 2001) because of their ubiquitous occurrence in aquatic systems such as municipal wastewater, surface water and tap water. PFASs can also be found in snow and rain water (Liu *et al.* 2009; Dreyer *et al.* 2010). In PFASs, the hydrogen atoms attached to the alkyl chain carbons have been replaced by fluorine (Schuetze *et al.* 2010). The carbon–fluorine bonds are very strong and have thermal and chemical stability. This stability makes the fluorinated compounds desirable for commercial use and also makes them persistent environmental

contaminants due to their resistance to natural breakdown processes (Key *et al.* 1997); in this context, PFOS was listed as a persistent organic pollutant (POP) under the Stockholm Convention on POPs (Wang *et al.* 2009).

PFAS compounds have been used for many industrial purposes and consumer-related products such as firefighting forms, mining, photolithography, electronics chemicals, hydraulic fluid additives, floor polishes, photographic film, denture cleaners, soap, shampoos, cosmetics, coating of cooking pans, oil repellents for leather, paper, and textiles. Paul *et al.* (2009) suggest that 45,000 tons of PFOS was released into the global environment between 1970 and 2012. During that time, the 3M Company was the primary

global producer of PFOS and PFOS-related substances, and although 3M phased out production of these chemicals in 2002, contamination from PFOS is expected to continue because of its own persistence and that of its transformation products.

The relative importance of the various pathways is not well understood; however, contamination of aquatic systems by industrial products like PFASs can only be through a limited number of mechanisms, e.g. through atmospheric transport and deposition, run-off from industrial sites, breakdown and run-off from domestic uses, and disposal of PFASs to sewer. Moreover, these chemicals are introduced into the aquatic environment as a result of degradation in the environment of precursor compounds or reaction impurities (Boulanger *et al.* 2005). PFASs have already been found to cause a variety of toxicological effects in humans (Suja *et al.* 2009). The concentration of PFOS and PFOA in cord blood and maternal pregnancy serum were negatively associated with human birth weight, ponderal index, and head circumference of new born babies (Apelberg *et al.* 2007). There have been several reviews on the toxicity and bioaccumulation of PFASs (Lau *et al.* 2004, 2007; Suja *et al.* 2009), so this review focuses on the contamination of the aquatic environment by PFASs and their removal by water treatment processes.

OCCURRENCE OF PFAS IN THE AQUATIC ENVIRONMENT

Several studies have reported on PFASs found in the water environment, which is a crucial environmental concern. PFOA and PFOS were detected in tap water in Georgia, where several secondary manufacturers are located, which produce non-woven, household additives, apparel, carpet, and household textiles (3M 2001). Lai *et al.* (2009) reported higher PFOS concentrations in tap water in the Kansai region than in the other 47 regions of Japan. Mak *et al.* (2009) studied tap water from different cities of China and they found that PFAS contamination decreased in the following order Shanghai > Wuhan > Nanjing > Shenzhen > Xiamen > Shenyang > Beijing. Atkinson *et al.* (2008) monitored the presence of PFOA and PFOS in tap water from different sites in England. They found that the highest

levels of PFOS (162 ng/L) were observed south of Cambridge near an airstrip, indicating that airstrips are a potential source of perfluorinated chemicals (PFCs) to the environment. The PFOS and PFOA concentrations in the water environment throughout the world are shown in Table 1.

A comprehensive study on the occurrences of PFOS (0.89–5.773 ng/L) and PFOA (0.97–21.5 ng/L) at 79 sampling sites in Japanese rivers revealed widespread occurrences of these compounds (Saito *et al.* 2004). Hansen *et al.* (2002) found that the PFOS and PFOA concentration was 50 times higher in Tennessee River than in the Elbe River. This was because of fluorochemical manufacturing facility discharge into the Tennessee River bodies. Jin *et al.* (2009) found that the level of PFAS contamination was greater in urban rivers than in rural areas in China. Seasonal changes have a significant effect on the loading of PFASs in surface water. So *et al.* (2004) found that higher concentrations were detected in winter than in summer. A similar observation was reported by Tsuda *et al.* (2010) in Japan, and is attributed to both the effects of different sampling seasons and the presence of algal blooms in summer, which may affect the distribution of different PFAS forms.

PFOA have been found in the coastal water of Japan in different places such as Hiroshima Bay, Kin Bay, and Lake Shikatsu (Taniyasu *et al.* 2003). Hart *et al.* (2008) found that Tokyo Bay had 2–3 times greater PFOS concentration in coastal water than in offshore locations of Japan. So *et al.* (2004) found that the concentration of PFOS in coastal waters of Hong Kong was up to 3.1 ng/L, which is greater than those observed in Gyeonggi Bay (South Korea) but approximately 10 times less than those observed in Lake Shihwa (China). Finally, Kim & Kannan (2007) found that the PFOA concentrations in lake water were significantly greater than the concentrations found in rainwater, suggesting that snowfall meltwater is the source of PFOA contaminations in lake water in the spring.

PFASs have been observed in the effluent from municipal wastewater treatment plants (WWTPs). For instance, Loganathan *et al.* (2007) found that the concentration of PFOA and PFOS in secondary effluent was 227 ng/L and 22 ng/L, respectively. Another study in Singapore by Yu *et al.* (2009a) found that the concentration of PFOA and PFOS in WWTP secondary effluent was 1,057 ng/L and

Table 1 | Contamination by PFOS and PFOA in the water environment

Water source	Country, Region	No. of samples	PFOA (ng/L)		PFOS (ng/L)		Reference
			Range	Mean	Range	Mean	
Tap water	China, Shenzhen	nr	nr	nr	nr-11	nr	Mak <i>et al.</i> (2009)
	China, Shanghai	nr	78	nr	nr-7.6	nr	Mak <i>et al.</i> (2009)
	China, Shenyang	nr	2.6	nr	nr-0.39	nr	Mak <i>et al.</i> (2009)
	Japan, Morioka	nr	nr	nr	0.1-0.5	nr	Harada <i>et al.</i> (2003)
	Japan, Miyako	nr	nr	nr	nr	0.1	Harada <i>et al.</i> (2003)
	Japan, Kyoto	nr	nr	nr	3.0-4.0	nr	Harada <i>et al.</i> (2003)
	Japan, Setagaya	nr	nr	nr	2.4-43.7	nr	Harada <i>et al.</i> (2003)
	Japan, Kansai	15	4.9-42.2	15.3	0.3-12.7	3.8	Saito <i>et al.</i> (2004)
	Japan, Kanto	19	<5-25	<5	<5-37	6.4	Mitsuya <i>et al.</i> (2007)
	Japan, Tohoku	15	0.01-1.0	0.3	0.1-0.5	0.2	Saito <i>et al.</i> (2004)
	Italy, Northern	6	1.0-2.9	2.4	6.2-9.7	8.1	Loos <i>et al.</i> (2007)
Spain, Catalonia	nr	0.32-6.28	nr	0.39-0.87	nr	Ericson <i>et al.</i> (2008)	

(continued)

Table 1 | continued

Water source	Country, Region	No. of samples	PFOA (ng/L)		PFOS (ng/L)		Reference
			Range	Mean	Range	Mean	
Surface water	Austria, river water	nr	<1.1–19	nr	<4.0–35	nr	Clara <i>et al.</i> (2009)
	Australia, Sydney Harbour and surroundings	20	4.2–6.4	5.7	7.5–21	14	Thompson <i>et al.</i> (2011b)
	Brazil, South eastern	nr	0.35–2.82	nr	0.58–6.70	nr	Quinete <i>et al.</i> (2009)
	Brazil, Guanaba Bay	nr	0.77–3.25	nr	0.40–1.32	nr	Quinete <i>et al.</i> (2009)
	Canada, Lake Ontario	2	nr	8.7	nr	13	Myers <i>et al.</i> (2012)
	China, Wuhan	69	<LOD–256	81	<LOD–88.9	51.8	Wang <i>et al.</i> (2013)
	China, Wuhan	nr	2.8–5.6	nr	2.3–5.3	nr	Jin <i>et al.</i> (2006)
	China, Dongguan	nr	0.85–4.4	nr	0.90–99	nr	So <i>et al.</i> (2007)
	China, Chongqing	nr	nd–35	nr	nd–0.35	nr	So <i>et al.</i> (2007)
	China, Yichang	nr	4.1–4.9	nr	0.29–0.61	nr	So <i>et al.</i> (2007)
	China, Nanjing	nr	2.1–2.4	nr	0.33–0.38	nr	So <i>et al.</i> (2007)
	China, Shanghai	nr	22–260	nr	0.62–14	nr	So <i>et al.</i> (2007)
	China, Guangzhou	nr	0.85–13	nr	0.9–99	nr	So <i>et al.</i> (2007)
	China, Pearl and Yangtze rivers	nr	0.85–260	nr	<0.01–99	nr	So <i>et al.</i> (2007)
	China, Hun river	nr	<0.1–1.6	nr	0.2–44.6	nr	Jin <i>et al.</i> (2009)
	China, Yangtze river	nr	0.2–297.5	nr	0.2–25.5	nr	Jin <i>et al.</i> (2009)
	China, Liao river	7	nd–27.9	10.9	nd–6.6	0.33	Yang <i>et al.</i> (2011)
	China, Taihu lake	22	10.6–36.7	19.5	3.6–394	26.5	Yang <i>et al.</i> (2011)
	China, Pearl river	13	0.71–8.7	3.7	0.52–11	3.3	Zhang <i>et al.</i> (2013)
	China, Haihe river	9	4.4–42	15	2.0–7.6	3.7	Li <i>et al.</i> (2011)
	China, Jiangsu, Huai river basin	nr	nr	18	nr	4.7	Yu <i>et al.</i> (2013)
	China, Jiangsu, Taihu lake	nr	nr	56	nr	15	Yu <i>et al.</i> (2013)
	China, Bohai coastal region	17	0.96–4,534.41	nr	nr	nr	Wang <i>et al.</i> (2014)
	China, Lake Taihu	nr	nr	136	nr	29.2	Pan <i>et al.</i> (2014)
	China, Liaoning	nr	nr–82	27	nr–31	4.7	Wang <i>et al.</i> (2012)
	China, Tainjin	nr	nr–12	6.8	nr–11	2.6	Wang <i>et al.</i> (2012)
	China, Shanxi	nr	nr–15	2.7	nr–5.7	0.93	Wang <i>et al.</i> (2012)
	China, Hohhot	nr	nr–1.8	1.2	nr–1.1	0.32	Wang <i>et al.</i> (2012)
	China, Guanting	nr	nr–2.3	1.2	nr–0.52	0.16	Wang <i>et al.</i> (2012)
	England, Cambridge	nr	nt	nr	nr–162	nr	Atkinson <i>et al.</i> (2008)
	France, nr (surface water)	99	nr–7	1	nr–62	4	Boiteux <i>et al.</i> (2012)
	France, nr (ground water)	163	nr–12	1	nr–50	1	Boiteux <i>et al.</i> (2012)

(continued)

Table 1 | continued

Water source	Country, Region	No. of samples	PFOA (ng/L)		PFOS (ng/L)		Reference
			Range	Mean	Range	Mean	
	France, Orge River	nr	9.4	nr	17.4	nr	Labadie & Chevreuril (2011)
	Germany, Rhine River	38	2–48	4.9	2–26	6.5	Skutlarek <i>et al.</i> (2006)
	Germany, Ruhr River	22	9–3,640	102	4–193	11.7	Skutlarek <i>et al.</i> (2006)
	Germany, Roter main river	nr	3.2–3.4	nr	2.2–2.6	nr	Weremiuk <i>et al.</i> (2006)
	Germany, Rhine river (upstream)	8	0.61–3.4	2.1	1.4–6.4	3.7	Möller <i>et al.</i> (2010)
	Germany, Rhine river (downstream)	8	2.3–4.1	3.1	3.0–7.3	4.1	Möller <i>et al.</i> (2010)
	Germany, River Ruhr	8	8.9–18	14.3	–0.89–10	4.2	Möller <i>et al.</i> (2010)
	Germany, River Elbe	nr	2.8–9.6	nr	0.5–2.9	nr	Ahrens <i>et al.</i> (2009)
	Germany, nr (surface water)	24	0.16–6.5	2.1	0.04–4.6	2.1	Llorca <i>et al.</i> (2012)
	Germany, nr (tap water)	5	0.16–1.9	1.3	0.04–0.4	0.4	Llorca <i>et al.</i> (2012)
	Hong Kong	nr	0.73–5.5	nr	0.09–3.1	nr	So <i>et al.</i> (2004)
	India, Ganges River	nr	<0.04–0.2	nr	<0.04–1.81	nr	Yeung <i>et al.</i> (2009)
	Italy, Po river	nr	1–1,270	nr	nd–25	nr	Loos <i>et al.</i> (2007)
	Italy (Northern)	8	1.8–2.9	2.4	7.2–8.6	7.8	Loos <i>et al.</i> (2007)
	Japan, Arakawa River	nr	nr	nr	2.8–51	nr	Takazawa <i>et al.</i> (2009)
	Japan, Chubu	17	0.3–16.3	2.5	0.3–6.0	1.1	Saito <i>et al.</i> (2004)
	Japan, Chugoku	9	0.5–8.1	1.5	0.4–25.1	1.0	Saito <i>et al.</i> (2004)
	Japan, Kansai	8	2.1–456.4	21.2	0.8–37.3	5.7	Saito <i>et al.</i> (2004)
	Japan, Kyushu	8	0.2–33	1.3	0.3–1.7	0.7	Saito <i>et al.</i> (2004)
	Japan, Kanto	14	0.3–15.1	2.8	0.3–31.4	3.7	Saito <i>et al.</i> (2004)
	Japan, Shikoku	7	1.4–13.8	3	0.2–14.9	1.1	Saito <i>et al.</i> (2004)
	Japan, River basins	nr	7.9–110	nr	0.8–11	nr	Senthikumar <i>et al.</i> (2007)
	Japan, nr	nr	5.2–80	nr	0.26–3.2	nr	Takagi <i>et al.</i> (2008)
	Japan, nr	nr	20–92	nr	1.0–4.6	nr	Takagi <i>et al.</i> (2008)
	Japan, nr	nr	nr	nr	0.3–1.57	1.68	Saito <i>et al.</i> (2003)
	Japan, nr	nr	nr	nr	<2.5–21	nr	Taniyasu <i>et al.</i> (2003)
	Japan, Tohoku	15	0.1–4.2	1.1	0.3–4.6	1.2	Saito <i>et al.</i> (2004)
	Japan, Tsurumi River Basin	nr	13.4–15.9	nr	179.6–179.9	nr	Zushi <i>et al.</i> (2008)
	Japan, Tama river	nr	nr	nr	0.5–58	nr	Takazawa <i>et al.</i> (2009)
	Japan, Tone River	nr	nr	nr	0.9–20	nr	Takazawa <i>et al.</i> (2009)
	Japan, Yodo river	nr	3.8–311	nr	1.6–104	nr	Takagi <i>et al.</i> (2007)
	Japan, Yodo river	18	4.2–901	23.8	0–49	2.4	Lien <i>et al.</i> (2008)
	Japan, Yodo river	30	7.4–1,044	29.4	0.4–56	3.8	Lien <i>et al.</i> (2008)
	Japan, Yodo river	33	6 = 2,568	36.6	0.8–123	5.6	Lien <i>et al.</i> (2008)
	Japan, Tokyo (groundwater)	53	<0.25–1,800	8.5	<0.25–990	5.7	Kuroda <i>et al.</i> (2014)
	Japan, Tokyo (tap water)	5	4.7–12	6.1	1.7–11	4.5	Kuroda <i>et al.</i> (2014)
	Japan, nr	18	0.76–192	35	<0.1–143	0.97	Murakami <i>et al.</i> (2008)

(continued)

Table 1 | continued

Water source	Country, Region	No. of samples	PFOA (ng/L)		PFOS (ng/L)		Reference
			Range	Mean	Range	Mean	
	Japan, Northern basin of Lake Biwa	nr	7.0–10	nr	0.8–16	nr	Tsuda <i>et al.</i> (2010)
	Japan, Southern basin of Lake Biwa	nr	8.3–13	nr	0.9–1.7	nr	Tsuda <i>et al.</i> (2010)
	Japan, Akanoi Bay	nr	9.1–17	nr	1.4–2.8	nr	Tsuda <i>et al.</i> (2010)
	Singapore	nr	5.7–9.15	nr	2.2–87.3	nr	Hu <i>et al.</i> (2011)
	Switzerland, Glatt river	nr	7.0–7.6	nr	43–60	nr	Huset <i>et al.</i> (2008)
	Spain, Ebro River, Catalonia	nr	1.45–1.90	nr	1.59–2.47	nr	Ericson <i>et al.</i> (2008)
	Spain, Coastal water, Catalonia	nr	<0.08–9.13	nr	<0.03–9.56	nr	Sanchez-Avila <i>et al.</i> (2010)
	Spain, nr (surface water)	24	0.16–68	13	0.04–2,709	264	Llorca <i>et al.</i> (2012)
	Spain, nr (tap water)	84	0.16–35	6.7	0.04–258	46	Llorca <i>et al.</i> (2012)
	South Korea, Western coast	nr	2.95–68.6	nr	4.11–450	nr	Naile <i>et al.</i> (2010)
	South Korea, Youngsan river (artificial lake)	3	4.1–7.1	5.2	1.7–7.1	4.4	Hong <i>et al.</i> (2013)
	South Korea, Youngsan river (Inland creek)	7	2.6–10	6.2	0.38–68	20	Hong <i>et al.</i> (2013)
	South Korea, Youngsan river (Estuarine area)	8	1.3–3.6	2.4	0.57–5.8	2.2	Hong <i>et al.</i> (2013)
	South Korea, Nakdong river (artificial lake)	2	11–12	11.4	6.5–12	9.2	Hong <i>et al.</i> (2013)
	South Korea, Nakdong river (Inland creek)	7	8.9–28	16	5.3–66	26	Hong <i>et al.</i> (2013)
	South Korea, Nakdong river (Estuarine area)	7	11–23	15	2.5–26	8	Hong <i>et al.</i> (2013)
	USA	nr	27–50	nr	21–70	nr	Boulanger <i>et al.</i> (2004)
	USA, New York	51	15–49	nr	1.6–756	nr	Sinclair <i>et al.</i> (2006)
	USA, New York (lake water)	11	nr–9.3	nr	3.27–15.8	nr	Kim & Kannan (2007)
	USA, New York (rain water)	11	nr–1.51	nr	nr–7.27	nr	Kim & Kannan (2007)
	USA, Tennessee	40	140–498	366	16.8–144	55.1	Hansen <i>et al.</i> (2002)
	USA, Lake Ontario	nr	18–34	nr	2.9–30	nr	Sinclair <i>et al.</i> (2006)

(continued)

Table 1 | continued

Water source	Country, Region	No. of samples	PFOA (ng/L)		PFOS (ng/L)		Reference
			Range	Mean	Range	Mean	
WWTP	Austria	nr	2–73	15.1	1–66	13.3	Clara <i>et al.</i> (2009)
	Canada, Lake Ontario	nr	6.5–54.7	nr	8.6–208–5	nr	Völkel <i>et al.</i> (2008)
	China, Shanghai	16	2–91	nr	1–32	nr	Zhang <i>et al.</i> 2013a)
	China, Shenyang	nr	18.4–41.1	nr	1.69–3.85	nr	Sun <i>et al.</i> (2011)
	Europe, different countries	90	1–15,900	255	0.5–2,101	62.5	Loos <i>et al.</i> (2013)
	Germany	nr	12.3–77.6	nr	0.4–82.2	nr	Ahrens <i>et al.</i> (2009)
	Germany, nr	2	0.04–1.8	1.8	nr	nr	Llorca <i>et al.</i> (2012)
	Japan, nr	6	10–68	61	42–635	87	Murakami <i>et al.</i> (2008)
	Japan, nr	5	14–41	23	14–336	28	Murakami <i>et al.</i> (2009)
	Singapore	nr	11.2–1,057	nr	5.3–560.9	nr	Yu <i>et al.</i> (2009a)
	Singapore	nr	7.9–1,060	nr	5.8–35.3	nr	Hu <i>et al.</i> (2011)
	Spain, Catalonia	nr	3.47–61.9	nr	<0.03–72.1	nr	Sanchez-Avila <i>et al.</i> (2010)
	Spain, nr	3	0.04–17	17	0.22–501	214	Llorca <i>et al.</i> (2012)
	Switzerland	nr	nr	12	nr	57	Huset <i>et al.</i> (2008)
	USA	nr	nr	11	nr	42	Sinclair & Kannan (2006)
USA, Kentucky and Georgia,	nr	1–334	nr	1.8–149	nr	Loganathan <i>et al.</i> (2007)	

nd, not done; nr, not reported.

461 ng/L, respectively. Pan *et al.* (2014) found that PFOA concentrations in Lake Taihu (China) were higher than PFOS concentrations (136 ng/L and 29.2 ng/L, respectively), perhaps due to the higher water solubility of PFOA.

REMOVAL OF PFASS IN WATER TREATMENT PROCESSES

The ability of wastewater treatment technologies to remove or degrade PFASs depends on the water treatment process. For instance, Ochoa-Herrera & Sierra-Alvarez (2008) reported that granular activated carbon (GAC) could effectively remove PFOS from aqueous solutions (Table 2). Flores *et al.* (2013) found that GAC removed PFOS and PFOA concentration with removal efficiency of $64 \pm 11\%$ and $45 \pm 19\%$, respectively. The explanation for this was that the molecular size of PFOS is slightly larger than the PFOA which is slightly more hydrophilic. Takagi *et al.* (2011) reported that GAC could effectively remove the PFOS and PFOA when it was used for less than 1 year. In contrast, the effluent concentration of those compounds was higher than the influent concentration when it used for a longer time (>1 year), possibly due to growth of the biofilm into the pores and surface of the carbon, exhausting the adsorption capacity and possibly interaction between those compounds and between those compounds and the biofilm, producing lowered concentrations initially and higher concentrations after significant use.

The adsorption capacity of the GAC is also related to the temperature of the water sample. Takagi *et al.* (2008) found that the removal of PFOA was 36–56% in summer and 31–58% in winter. Knepper & Lange (2012) made a statement that the adsorption capacity of PFASs was low for GAC treatment because of the presence of organic matter in the water sample, considering the organic fractions of the dissolved organic matter adsorb more strongly than PFOS and PFOA compounds. The removal efficiency of PFOA and PFOS by GAC also depends on the volumes of activated carbon. Lampert *et al.* (2007) found in their batch test that more than 90% of both PFOA and PFOS were removed when the activated carbon was 0.1047 g or greater at 7 days of contact time. However, at a similar contact time, the reduction efficiency was decreased to about

50% for PFOA and 82% for PFOS when 0.0587 g GAC was used. Therefore, use of GAC with greater volume and suitable regeneration regimes appear to be the important parameters in the efficient removal of PFASs.

Deng *et al.* (2011) found that coagulation (polyaluminium chloride) could remove the PFOA from water. This was because some PFOA transferred from aqueous phase to solid phase. They also found that the addition of powdered activated carbon (PAC) before the coagulation process significantly enhanced the PFOA removal efficiency. This was explained as the negative PFOS adsorbing onto the PAC via electrostatic interaction, resulting in removal with the precipitate form in the coagulation process. A similar observation was made by Yu *et al.* (2009b) that PAC could effectively remove the PFOA concentration through the electrostatic interaction and hydrophobic interaction between them. A greater coagulation dosage (>60 mg/L) and lower pH (4.5–6.5) can enhance the PFAS removal (Xiao *et al.* 2013). Knepper & Lange (2012) mentioned that the combination of PAC with microfiltration/ultrafiltration is a promising advance for conventional PAC treatment for the removal of PFASs, because of improving sorption kinetics.

There are many studies demonstrating that the high pressure membranes such as those in nanofiltration (NF) and reverse osmosis (RO) can effectively remove the PFAS compounds (Tang *et al.* 2006; Zhao *et al.* 2013). Tang *et al.* (2006) investigated the use of RO membrane in removing PFOS from wastewater with the concentration range of 0.5 to 1,500 mg/L and they found that $>90\%$ reduction was achieved by RO. Tang *et al.* (2007) further studied the use of RO and NF to removal PFOS from wastewater and they got $>99\%$ and 90–99% removal for RO and NF membranes, respectively. Knepper & Lange (2012) mentioned that 99% rejection of PFOS was achieved by RO over a wide range of feed concentrations of 1–1,000 mg/L. They explained that the passage of up to 1% PFOS through RO membranes was by diffusion through the polyamide separation layer. Zhao *et al.* (2013) studied the NF membrane for removing PFOS from simulated surface water and found that the membrane can effectively reduce the concentration. They also investigated the effects of PFOS concentration, pH and calcium concentration on PFOS rejection. They found pH leads to an increase in the PFOS rejection when the

Table 2 | PFCs removal during water treatment processes

Treatment processes	Water source	PFOS reduction (%)	PFOA reduction (%)	References
GAC	Synthetic wastewater	nr	nr	Knepper & Lange (2012)
GAC	Wastewater	82–90	50–90	Lampert <i>et al.</i> (2007)
GAC	Simulated water	<20	<20	Appleman <i>et al.</i> (2013)
GAC	Secondary effluent	97	95	Schröder <i>et al.</i> (2010)
GAC	Tap water	99.99	nr	Senevirathna <i>et al.</i> (2010)
GAC	Aqueous solution	nr	nr	Ochoa-Herrera & Sierra-Alvarez (2008)
PAC	Secondary effluent	22	16	Yu <i>et al.</i> (2012)
PAC	Synthetic industrial wastewater	>97	>97	Rattanaoudom <i>et al.</i> (2012)
PAC + microfiltration/ultrafiltration	Synthetic wastewater	nr	nr	Knepper & Lange (2012)
PAC + coagulation	Synthetic wastewater	>90	>90	Bao <i>et al.</i> (2014)
Carbon nanotubes	Simulated water	nr	nr	Chen <i>et al.</i> (2011)
Carbon nanotubes	Simulated water	95	95	Deng <i>et al.</i> (2012)
Carbon nanotubes	Aqueous solution	nr	nr	Dai <i>et al.</i> (2013)
Coagulation	Drinking water	<20	<20	Xiao <i>et al.</i> (2013)
Coagulation	Synthetic wastewater	32	12	Bao <i>et al.</i> (2014)
Coagulation (polyaluminium chloride)	Surface water	nr	nr	Deng <i>et al.</i> (2011)
Coagulation + DAF	Secondary effluent	49	nr	Appleman (2012)
Membrane, Cl ₂	River water	>22	44	Takagi <i>et al.</i> (2008)
NF	Simulated water	>99	>97	Appleman <i>et al.</i> (2013)
NF	Wastewater	90–99	nr	Tang <i>et al.</i> (2007)
NF	Wastewater	90–99	nr	Tang <i>et al.</i> (2007)
NF	Simulated surface water	95	nr	Zhao <i>et al.</i> (2013)
RO	Wastewater	>99	nr	Tang <i>et al.</i> (2007)
RO	Wastewater	>90	nr	Tang <i>et al.</i> (2006)
RO	Wastewater	>99	nr	Tang <i>et al.</i> (2007)
RO	Secondary effluent	86	90	Schröder <i>et al.</i> (2010)
RO	Synthetic wastewater	99	nr	Knepper & Lange (2012)
Ozonation under alkaline condition	Secondary effluent	42	56	Lin <i>et al.</i> (2012)
Ozonation	Secondary effluent	32	18	Schröder <i>et al.</i> (2010)
Ozonation + UV	Secondary effluent	46	48	Schröder <i>et al.</i> (2010)
Fenton	Secondary effluent	68	70	Schröder <i>et al.</i> (2010)
Fenton + UV	Secondary effluent	68	75	Schröder <i>et al.</i> (2010)
UV	nr	nr	61.7	Chen <i>et al.</i> (2007)
UV	nr	nr	nr	Hori <i>et al.</i> (2004)
Photo-degradation	nr	8–68	nr	Yamamoto <i>et al.</i> (2007)
RBF	River water	nr	nr	Eschauzier <i>et al.</i> (2010)
RBF	Surface water	nr	nr	Skutlarek <i>et al.</i> (2006)

(continued)

Table 2 | continued

Treatment processes	Water source	PFOS reduction (%)	PFOA reduction (%)	References
AIX	Wastewater	>99	>99	Lampert <i>et al.</i> (2007)
Ultrafiltration, Cl ₂	Groundwater	0	-164	Atkinson <i>et al.</i> (2008)
Rapid sand filtration (RSF), O ₃ , GAC, Cl ₂	River water	7	-28	Takagi <i>et al.</i> (2008)
RSF, GAC, Cl ₂	Lake water	97	90	Takagi <i>et al.</i> (2008)
Cl ₂ , coagulation/flocculation, RSF, O ₃ , GAC	Surface water	69	52	Flores <i>et al.</i> (2013)
Cl ₂ , coagulation/flocculation, RSF, O ₃ , GAC, UF, RO	Surface water	86	89	Flores <i>et al.</i> (2013)
Coagulation/flocculation/sedimentation, SF, O ₃ , GAC Cl ₂	River water	-185 (summer), 60 (winter)	-220 (summer), 0 (winter)	Takagi <i>et al.</i> (2011)
Coagulation/flocculation/sedimentation, SF, O ₃ , GAC (reactivated), Cl ₂	Lake water	>89 (summer), >88 (winter)	85 (summer), 78 (winter)	Takagi <i>et al.</i> (2011)
Zeolite	Aqueous solution	nr	nr	Ochoa-Herrera & Sierra-Alvarez (2008)
Sludge	Aqueous solution	nr	nr	Ochoa-Herrera & Sierra-Alvarez (2008)
Deep bed filtration (DBF), medium pressure UV, Cl ₂	Groundwater	6	0	Quinones & Snyder (2009)
O ₃ , coagulation/flocculation, DBF, Cl ₂	Surface water	0	0	Quinones & Snyder (2009)
PAC, chloramination, DBF	Surface water	-12	0	Quinones & Snyder (2009)
Cl ₂ , coagulation/flocculation, DBF, UV	Surface water	0	3	Quinones & Snyder (2009)

pH increases from 3 to 9 which leads to an increase in the PFOS rejection from 86 to 95% and 93 to 97% in the presence of 0.1 mM Ca²⁺ and 1 mM Ca²⁺ at 0.4 MPa, respectively, because the increasing pH generally increases electrostatic interactions which play a role in PFOS rejection. Similarly, increasing calcium concentration decreased the permeate PFOS concentration because calcium ions bridge PFOS and the negatively charged membrane surface, which enhances the adsorption of PFOS on the membrane. Another study shows that average rejections of the PFASs were 99.3% for virgin RO membranes, but 95.3% for fouled RO membranes (Appleman *et al.* 2013). The transmembrane pressure was not increased to maintain a constant flux across the membrane's surface for the fouled membranes. Although Tang *et al.* (2006) recommended that high flux RO membranes should be avoided when treating water with high concentrations of PFOS (>30 mg/l PFOS), these membranes normally have a low rejection effect and the advantage of a high flux cannot be maintained for a long time.

UV photolysis has been demonstrated to be effective at degrading PFOS and PFOA (Hori *et al.* 2004; Chen *et al.* 2007). Fujii *et al.* (2007) demonstrated that photocatalysis (reaction time up to 3 days) and advanced oxidation (with high temperature and pressure) could effectively degrade the PFOS and PFOA to CO₂ and 'hydrogen fluoride'. Lampert *et al.* (2007) demonstrated more than 99% removal of PFOS and PFOA using anion exchange (AIX) resins (Table 2).

Conventional water treatment processes are not effective in removing PFASs. For instance, Zhang *et al.* (2011) found that PFASs are partly reduced by a drinking water treatment system in China where surface water was the source sample. Another study by Eschauzier *et al.* (2010) shows that river bank filtration did not remove the PFASs. Skutlarek *et al.* (2006) also clearly demonstrated that PFASs were not removed by water treatment steps and the concentrations in the surface waters corresponded to PFAS levels in drinking water. Recently Quinones & Snyder (2009) confirmed that the PFAS concentration of

influent and effluent was similar in drinking water treatment plants in the USA, suggesting that treatment systems were ineffective in removing these compounds. Sand filtration and ozonation processes were also ineffective in removing PFOS and PFOA during drinking water treatment (Takagi *et al.* 2011). A similar result was found by Thompson *et al.* (2011a) in a water reclamation plant in South East Queensland, Australia. Appleman (2012) investigated the efficiency of PFAS removal using coagulation followed by sedimentation or dissolved air flotation (DAF) and/or filtration. They found that coagulation (aluminium sulfate) followed by sedimentation did not lead to PFAS removal, but where sedimentation was replaced by DAF, a 49% removal of PFOS was observed.

CONCLUSIONS

PFASs are globally distributed in the aquatic environment, including drinking water and wastewater. The clear pathways are still poorly understood for this group although the manufacture of PFASs and use of products containing PFASs are direct sources for the release of these compounds to the aquatic environment. Developed countries are more highly affected by PFAS contamination than developing countries due to their increased use of PFAS-containing goods. Several treatment processes are used in the removal of PFAS compounds. Conventional water treatments are ineffective in removing these compounds. Activated carbon may be a good choice to reduce the concentration if the activated carbon is used for a year. High pressure membrane systems are the most suitable processes for reducing these chemicals from water and wastewater and the extent of their reduction efficiency depends on the solution chemistry of the water sample.

PFASs are listed as chemicals of concern, so regular monitoring of the contamination level of these chemicals in the water environment is required for regulatory purposes. Although biological processes are mostly ineffective in removing these chemicals, there is a possible biological conversion of these compounds during water treatment processes. Therefore further investigation regarding the mechanisms of the biological degradation of these chemicals is required. Moreover, other treatment processes such

as GAC and/or high pressure membranes are essential to equip the water treatment processes to remove these chemicals for drinking purposes and for safe water disposal to the environment.

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