

Per- and polyfluoroalkyl substances: problematic emerging pollutants of aquatic environment

Mariusz Grabda^{1*}, Sylwia Oleszek², Michiaki Matsumoto³

¹General Tadeusz Kosciuszko Military University of Land Forces, Wrocław, Poland

²Department of Environmental Engineering, Kyoto University, Kyoto, Japan

³Department of Chemical Engineering and Materials Science, Doshisha University, Kyoto, Japan

*Corresponding author's e-mail: mariusz_grabda@icloud.com

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Highlights

- up-to-date summary of the most critical information on PFASs
- review of environmental regulations
- complete review of PFASs removal methods with an emphasis on the most recent findings

Abstract: Per- and polyfluoroalkyl substances (PFASs) are human-invented chemicals that were created in the middle of the 20th century. They were synthesized for the first time in 1949, and because of their exceptional surfactant properties, they have been widely used in many industrial applications and daily life products. The common use of PFASs resulted in their worldwide dissemination in natural environment. PFASs are reported to be ubiquitous in surface and drinking waters, but also may be present in soils, animals, milk and milk-products, plants, food. Contaminated drinking water and food are the most significant exposure sources to these chemicals. Ingested PFASs are bio-accumulative and have adverse effect on health of humans as well as animal organisms. This paper reviews the most significant information on the origin, properties, distribution, environmental fate, human exposure, health effects, and the environmental regulations on PFASs and summarizes the latest advances in the development of novel methods for the effective removal of these chemicals from the aqueous environment. Recognized (reverse osmosis, adsorption on activated carbon) and most promising developing removal methods such as adsorption on biomaterials (plant proteins, chitosan beds), mineral adsorbents (LDHs, hydrotalcite), ion-exchange resins, and photocatalytic degradation have been emphasized.

Introduction

The unprecedented technological progress that has transpired during the last decades introduced an enormous number of “smart” appliances (e.g. personal computers, smartphones, electronic sensors, automatic controllers), advanced materials (e.g., nanomaterials, semiconductors, polymers, composites) and new synthetic chemicals (e.g., drugs, pesticides, surfactants, flame retardants) that have made human life more comfortable and simple. Unfortunately, in the cases of certain new chemicals, some unexpected and in some cases serious side effects to humans and natural environments have been reported (Lei et al. 2015).

Per- and polyfluoroalkyl substances (PFASs) are an excellent illustration of the technological progress of the last century. They were synthesized for the first time in 1949, and because of their exceptional surfactant properties, they have been widely used in many applications: varnishes, waxes, firefighting foams,

lubricants, metal spray plating, inks, oil, and water-repellent coating formulations for leather, paper, and textiles. Such ubiquity resulted in their worldwide dissemination, even in remote Arctic locations. The common distribution, combined with reported hormonal disruptions, bio-accumulation, and sometimes toxic effects on humans and animals, generated questions about their safety and the merits of their continued use. The potential hazards caused by PFASs to the environment and humans have recently been scrutinized as well as new technological attempts have focused on removing these chemicals from contaminated waters and decreasing human exposure to them. However, scientific investigations are time-consuming and often concentrate on a single, isolated aspect.

This paper provides an exhaustive, comprehensive, and up-to-date review of the most recent research related to the origin, properties, distribution, the environment's fate, health effects, human exposure, environmental regulations, and the latest findings on the separation and the degradation of PFASs.

Chemistry & origin

PFASs are a group of organic chemicals that consist of an aliphatic chain (or multiply chains) in which all the hydrogen atoms, attached to either all (i.e., per-) or at least one (i.e. poly-) C atom, have been replaced by fluorine substituents (to form a perfluoroalkyl moiety of C_nF_{2n+1}), and are terminated by a functional group (e.g., carboxylates $-COO^-$; sulfonates $-SO_3^-$; sulphonamides $-SO_2NH_2$, phosphonates $-PO(OH)_2$, alcohols $-OH$, etc.) (Buck et al. 2011). Depending on the number of C atoms in the alkyl chain, PFASs are frequently referred to as a “long-chain” (C7 or more perfluorinated carbons) or a “short-chain” (C6 or fewer perfluorinated carbons) (Buck et al. 2011; Boiteux et al. 2017). The distinction in the number of perfluorinated moieties is related to the bioaccumulation tendencies of the substances (Buck et al. 2011) and their possible toxicity to living organisms. Thousands of different PFASs have been synthesized and used by industry (Lindstrom et al. 2011). Researchers described 455 PFASs (including 9 fully and 446 partially fluorinated compounds) that were identified between 2009 and 2017 (Xiao 2017). The most common PFASs are listed in Table 1. The greatest scientific concern and regulatory attention have been focused on two C8 PFASs that are the most commonly detected in environmental samples: perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) (Table 1).

PFASs were previously sometimes improperly called perfluorocarbons (acronym PFCs). From a chemical point of view, however, the definition suggested that the substances only contain C and F atoms and no functional groups. It was, therefore, proposed (Buck et al. 2011), to narrow the acronym of “PFCs” for substances such as tetrafluoromethane CF_4 ; hexafluorobutane C_2H_6 or perfluorodecalin $C_{10}F_{18}$ (Buck et al. 2011).

The mass production of these new chemicals started in the 1950s. Two main PFASs synthesis methods were developed: electrochemical fluorination (ECF) and telomerization. In the ECF process, a hydrocarbon electrochemically reacted with HF to substitute all of the hydrogen atoms with fluorine. The main product of this process, with a yield of about 25%, was perfluorooctane sulfonyl fluoride (PFOSF), which was then used to make PFOS and PFOS-based compounds (Lindstrom et al. 2011).

The Minnesota Mining and Manufacturing Company of U.S. (3M) was the leading producer of PFOSF, and its total cumulative production was estimated to be approximately 96,000 tonnes in the peak years between 1970 and 2002 (Lindstrom et al. 2011). After 3M discontinued production in 2002, other companies began production to meet existing market demand (Lindstrom et al. 2011), and the growing mass production shifted to China, which produced an estimated 200 tonnes in 2006 (Wang et al. 2009). The total historical global production was estimated at around 120,000 tonnes in 2009 (Paul et al. 2009).

In 2002 DuPont invented the telomerization process, which involved the reaction of tetrafluoroethylene ($CF_2=CF_2$, called a taxogen) with pentafluoroethyl iodide (C_2F_5I , referred to as a telogen) to yield a mixture of perfluoroalkyl iodides with longer perfluorinated chains. In the second step, ethylene was added to produce fluorotelomer-based commercial PFASs, including PFOA (Buck et al. 2011; Lindstrom et al. 2011).

3M was also the primary producer of PFOA (until 2002). After 3M phased out its PFAS production, DuPont pioneered the telomerization synthesis of PFOA at its factory in Fayetteville (USA). PFOA was used by DuPont to manufacture the specific fluoropolymers, commercially branded as Teflon.

Properties & applications

The fluorinated “tail” of PFASs molecules is responsible for the strong hydro- and lipophobic properties of the chemicals, while the functional groups (heads) give the PFASs a high water-soluble aspect (hydrophilic) (Fig. 1). Such an amphipathic PFASs characteristic provides the ability to interact with both polar and non-polar phases and decreases the surface tensions of the water (Ghisi et al. 2019). Moreover, the presence of short (1.35 Å) and extremely strong (485 kJ/mol) C–F bonds in the PFAS molecules stabilizes them and they become persistent under most conditions (Liu et al. 2013; Fang et al. 2019, Lutze et al. 2018).

Such unique properties of PFASs as oil- and water-repellency combined with high resistance to heat as well as chemical and biochemical reactions (Post et al. 2012; Castiglioni et al. 2015) resulted in the wide use of these new chemicals in various commercial products and industrial processes as superior synthetic fluorosurfactants.

In commercial products, PFASs are often applied (Table 1) in coatings for food containers and nonstick cookware, as additives to detergents, floor waxes, cosmetics, shampoos, pesticides, and painting materials (Xiao 2017; Ghisi et al. 2019). Their water-repellent properties were exploited in manufacturing applications for waterproofing agents (ScotchGard, Teflon, Gore-tex) (Hepburn et al. 2019; Xiao et al. 2017) or stain-resistant coatings for fabrics, textiles leather, clothing, paper, packaging (Brett D et al. 2019), upholstery (Zhang et al. 2019), carpets, building and construction materials (Boiteux et al. 2017; Appleman et al. 2014), or corrosion inhibitors (Rodriguez-Freire et al. 2015).

Important PFASs applications include aqueous film-forming foam (AFFF), which usually contains as much as 1–5% (10–50 g/L) of PFASs (Vecitis et al. 2009). Due to the surface-tension-lowering properties of PFASs, AFFF spreads rapidly across the surface of burning hydrocarbon fuels and forms a film beneath the foam to prevent fuel vapors from transporting through the foam barrier to come into contact with oxygen in the air. Then the liquid fuel is cooled and the fire is retarded (Zhang et al. 2019; Hodkins et al. 2019; Hoisæter et al. 2019).

Industrial applications of PFASs include aviation hydraulic fluids, emulsifier, and wetting agents, (Buck et al. 2011). PFOA is commonly used in the production of semiconductors (Deng et al. 2015) as well as different fluoropolymers (Castiglioni et al. 2015; Deng et al. 2015); PFOS are predominantly used as superior mist suppressants (Boiteux et al. 2017; Liu et al. 2018; Gallen et al. 2018; Du et al. 2017) in metal electroplating (i.e., chrome plating in China) (Gao et al. 2017).

Release into environment

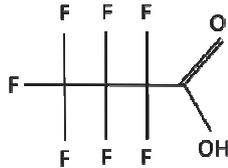
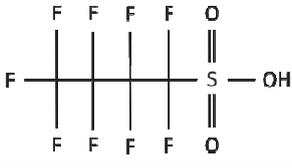
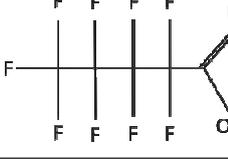
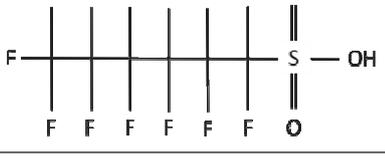
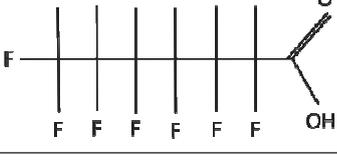
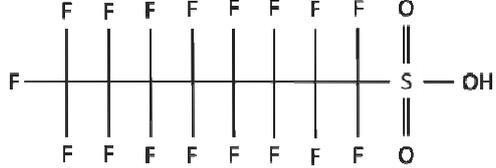
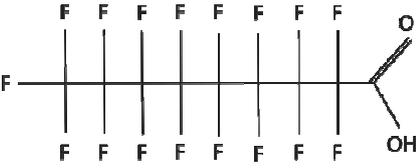
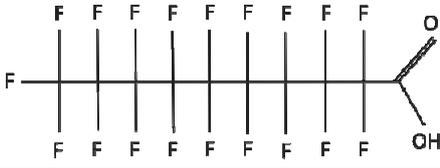
Due to the high water-solubility of PFASs (0.4 g/L for PFOS, 9.5 g/L for PFOA) they are predominantly released to the environment dissolved in the water phase (Fig. 2). They can enter the environment in many ways. Manufacturing plants, wastewater treatment plants, landfill leachates, AFFF spills,

biosolids, and fertilizers are the main point sources of PFASs emissions (Sorengard et al. 2019).

One important source of PFASs emissions into the environment is their production by the ECF process. PFOF, the raw material for producing PFOS and PFOS-related chemicals, is insoluble in water, and the technological washing

of crude PFOF with water is applied to remove soluble impurities (Du et al. 2015). The wastewater from this process contains a high concentration of mixed water-soluble PFASs (e.g., PFHxA, PFHpA, PFOA), which cause serious water pollution (Du et al. 2015). Estimates suggest that nearly 80% of the perfluorinated carboxylic acids (PFCAs) released into

Table 1. Most common PFASs and their applications (Ghisi et al. 2019)

Compound	Acronym	Applications/Origin	
Short-chain PFASs			
Perfluorobutanoic acid	PFBA	Synthetic, chemistry, was used in manufacturing of photographic films, breakdown product of other PFASs	
Perfluorobutane sulfonic acid	PFBS	Stain repellent	
Perfluoropentanoic acid	PFPeA	Breakdown product of stain- and grease-proof coatings on food packaging, couches, carpets	
Perfluorohexane sulfonic acid	PFHxS	Surfactant for textiles	
Perfluoroheptanoic acid	PFHpA	Identical as PFPeA	
Long-chain PFASs			
Perfluorooctane sulfonate	PFOS	Firefighting foam, textiles	
Perfluorononanoic acid	PFNA	Surfactant or synthesis of textiles and polymers	
Perfluorodecanoic acid	PFDA	Identical as PFPeA and PFHpA	

the environment are directly related to contamination during fluoropolymer manufacture and use (Zareitalabad et al. 2013).

Therefore, in locations near sites of PFASs production and common use (industrial zones, densely populated cities and regions) their concentration in wastewater is extremely high. Untreated industrial wastewaters may contain a few grams of PFASs per liter (Zareitalabad et al. 2013). Concentrations of up to 1650 mg/L PFOS have been detected in wastewater from semiconductor manufacturers (Chen et al. 2011) and about 1000 mg/L PFOA from photolitho-processes (Du et al. 2015; Lampert et al. 2007).

PFASs are often present in municipal wastewater treatment plants (WWTPs) at concentrations up to hundreds of ng/L (Arvaniti et al. 2014). Their origin is usually a result of the everyday use of PFASs-containing products by local residents (Ghisi et al. 2019). PFOS and PFOA were detected in a number of WWTPs in the USA with concentrations ranging of 1.1–130 and 2.5–97 ng/L (Yu et al. 2014), in all 14 tested WWTPs in Australia with maximum effluent concentrations of 240 ng/L and 48 ng/L, respectively (Gallen et al. 2018) and Thailand with mean influent concentrations of 465 ng/L and 142 ng/L, respectively (Kunacheva et al. 2011) as well as in New Zealand (Coakley et al. 2018), South Korea (Lam et al. 2014), Germany (Wilhelm et al. 2010), Netherlands (Eschauzier et al. 2013) and Italy (Castiglioni et al. 2010). These results indicate that the contamination of wastewaters by PFOA/PFOS is a serious worldwide problem.

Unfortunately, since the purification systems installed in most municipal WWTPs ineffectively remove PFASs, the WWTPs become a serious secondary source for the pollution of surface waters (Ghisi et al. 2019; Gallen et al. 2018; Hamid et al. 2018; Zhou et al. 2010) and drinking waters (Eschauzier et al. 2013). An Australian study estimated the country's annually load of PFOA and PFOS released from municipal WWTPs to be 67 kg and 32 kg, respectively (Gallen et al. 2018). Presence of both chemicals was revealed not only in the effluent but also in the sludge generated at Australian WWTPs, at mean concentrations of 64 ng/L and 11 ng/L, respectively (Gallen et al. 2018). The secondary pollution caused by industrial WWTPs is even higher. A work reported that WWTPs polluted by industrial waste may discharge up to 50 times more the load of WWTPs that receive municipal wastewater (Castiglioni et al. 2010).

Runoff and leaching from areas where firefighting foams are used can also considerably contribute to pollution by PFASs and their precursors (Ghisi et al. 2019; Kucharzyk et al. 2017). PFOS at concentrations of mg/L level were detected in groundwaters located near military bases and airports, where AFFFs were used for firefighting (Ghisi et al. 2019; Zheng et al. 2018; Tang et al. 2006). In Canada, over 7% of the tested airports were estimated to be contaminated by PFASs due to firefighting courses and/or accidents where fires happened (Milley et al. 2018).

PFASs can also be released from dumped PFASs-containing wastes through biological and abiotic leaching (Hamid et al. 2018; Eschauzier et al. 2013). A study revealed that PFOA remains one of the most abundant PFASs in landfill leachates in Canada, despite its restricted use in the country (Hamid et al. 2018). Similarly, although PFOS was phased out from all non-essential uses in consumer products in Australia

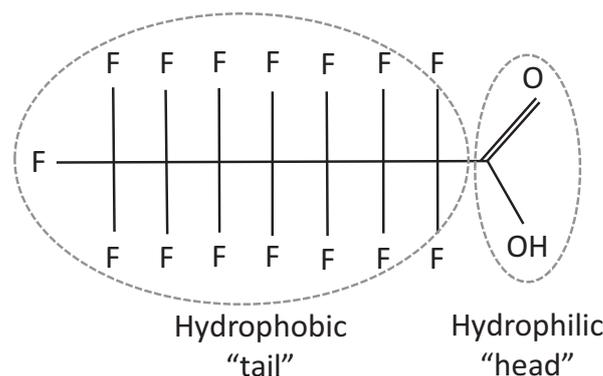


Fig. 1. Molecular structure of PFOA with indications of parts responsible for chemical's amphiphilic characteristics

over a decade ago, many Australian households still contain older items (carpets, furniture) that were treated with PFOS and other PFASs. These products constitute both a current and a future source of PFASs emissions (Gallen et al. 2014). As mentioned above, even if landfill leachates are directed to WWTPs, the facilities are usually not properly equipped to remove these classes of contaminants (Hamid et al. 2018; Zhou et al. 2010), and so the chemicals are distributed further within the environment (mainly, surface waters).

Therefore, PFASs have also been detected in the surface waters (and then in the drinking water produced from them), at most common concentrations range between 10^{-1} and 10^2 ng/L, of Germany (Wilhelm et al. 2010), France (Boiteux et al. 2017), the Netherlands (Eschauzier et al. 2013), Norway (Hoisæter et al. 2019), Australia (Hepburn et al. 2019; Gallen et al. 2018; Gallen et al. 2014), New Zealand (Coakley et al. 2018), and the USA (Yu et al. 2014). Elevated concentration of PFOA (8 397 ng/L) was recently detected in the Baiyangdian Lake in China (Ciu et al. 2018).

Data collected by Zareitalabd et al. (2013) revealed that the contamination of surface waters by PFASs is a worldwide problem that involves not only industrialized nations but even the countries considered relatively "clean" and industrially undeveloped, such as Kenya, Sri Lanka, Brazil (Zareitalabad et al. 2013), and Uganda (Dalahmeh et al. 2018).

Polluted surface waters might penetrate into and contaminate groundwaters at ng/L level (Eschauzier et al. 2013). The PFASs present in surface and groundwaters that serve as reservoirs for drinking waters are direct threats to humans.

PFASs can also be transported to lakes and global oceans (Weber et al. 2017; Hodkins et al. 2019) and contaminate lake sediments (for example, in northern Sweden: sum of PFASs ranged between 1 and 76 ng/g dry weight) (Mussabek et al. 2019) and ocean sediments (Tokyo Bay, Japan: sum of PFASs ranged between 0.29 and 0.36 ng/g dry weight) (Ahrens et al. 2010). The affinity to sediments may occur by either of two ways: 1) interaction of hydrophobic fluorinated carbon tails with an organic phase (Milinovic et al. 2015) or 2) the electrostatic interactions of the polar head group with charged clay fractions (Weber et al. 2017).

PFASs dissolved in ocean waters might be distributed to such remote locations as Arctic regions (MacInnis et al. 2019; Omorodion et al. 2018). During their transport, any single precursor may form multiple intermediate PFAS-

-transforming products occurring at different concentrations in time and/or distance from the release source (Higgins & Luthy 2006).

Beyond their predominant occurrence in the aqueous phase, PFASs have also been identified in soil, sludge, and dusts at levels between pg/g to ng/g (Arvanitiet al. 2014). Elevated levels of PFOA and PFOS (median: 8 ng/g and 12 ng/g dry weight) were detected in U.S. metropolitan areas in surface and subsurface soils, suggesting a downward movement of the contaminants toward groundwater (Xiao et al. 2015). Similarly, a Norwegian study showed soil contamination from released PFOS-based AFFF products down to the groundwater four meters below the surface (Hoisæter et al. 2019).

The soil surface can be contaminated by AFFF spills, field irrigation using contaminated water, runoff from disposal sites, applications of contaminated biosolids (sewage sludge) as soil conditioners or fertilizers, etc. (Ghisi et al. 2019; Zareitalabad et al.; 2013).

Soil contamination may also be caused by non-point sources such as particle-bound PFASs carried by the wind (Xiao et al. 2015). Atmospheric deposition might be another critical contributor. For example, high levels of PFASs were detected in the atmosphere of many places in China with a total concentration range of 80.1–206 pg/m³ (Yao et al. 2018) and in samples of outdoor (with a median concentration of 17 PFASs 18 pg/m³) indoor air (with a median concentration of 20 PFASs 76.6 pg/m³) collected in the Czech Republic (PFOS most commonly) (Karaskova et al. 2018).

PFASs in contaminated soils can potentially be taken by plants and soil organisms (Ghisi et al. 2019; Wei et al. 2017). Plant uptake, however, largely changes with chain length, functional group, plant species, and organs. Low accumulations of PFOA and PFOS have been found in peeled potatoes and cereal seeds, however high concentrations of the contaminants

up to 198 and 102 ng/g dry weight, respectively were detected in leafy vegetables (Ghisi et al. 2019).

Human exposure

PFASs released into the environment might be ingested by humans (Fig. 2). Contaminated drinking water and food are the most significant exposure sources to these chemicals (Ghisi et al. 2019; Appleman et al. 2014).

The PFASs present in surface and ground reservoirs of drinking water may pass undisturbed most conventional treatment processes installed in drinking water plants (DWP). This is possible because most DWPs are not properly equipped to produce PFASs-free water. Boone et al. (2019) studied the problem in American DWPs and concluded that 68% of studied installations provided minimal removal of PFASs (Boone et al. 2019).

PFASs may also be consumed by humans together with the contaminated food of plant and animal origins. PFASs were detected in vegetables, cereals, and fruit samples in European countries (Herzke et al. 2013; D'Hollander et al. 2015) as well as in yams, maize, and sugarcane cultivated in Uganda (Dalahmeh et al. 2018). Contaminated plants increase the daily intake of PFASs by humans not only directly as part of their diet (Klenow et al. 2013), but also indirectly as livestock fodder (Kowalczyk et al. 2013) and the consumption of contaminated food of animal origin. For example, a recent Polish study identified the presence of PFOA, PFOS, PFBA, and PFHxS in animal milk and milk products (cottage cheese, yoghurt, butter, kefir, sour cream, and Camembert-type cheese) with the highest concentration of PFOA measured for source cream and Camembert-type cheese, with median levels of 0.33 ng/g and 0.49 ng/g, respectively (Sznajder-Katarzynska et al. 2019).

PFASs can also enter the human body from the consumption of fish, animals, eggs, etc. For example, crucian carp (*Carassius*

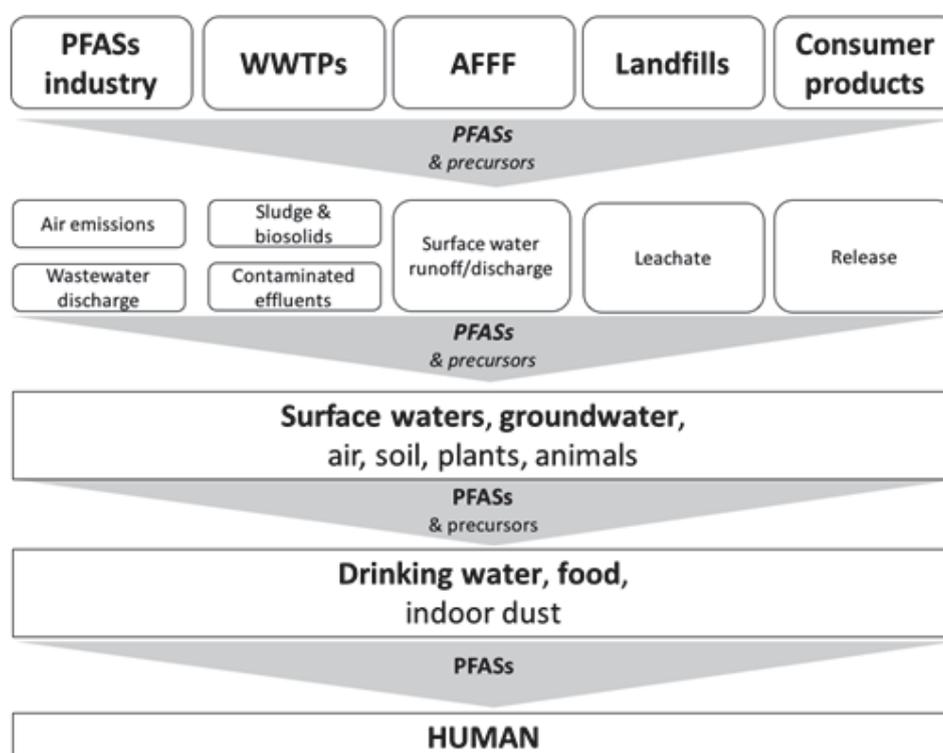


Fig. 2. Schematic pathways showing origin and distribution of PFASs within human environment

auratus) and mandarin fish (*Siniperca scherzeri*), collected from six major rivers and lakes in South Korea, were found to be contaminated by PFASs that had concentrated in blood (1.72–236.29 ng/g for carp and 31.08–296.72 ng/g for mandarin fish ng/g) and liver tissue (0.15–54.64 and 6.13–131.58 ng/g, respectively) (Lam et al. 2014). PFASs were detected in the marine mammals of the West Indian manatee (*Trichechus manatus*) in and around Florida and Puerto Rico (PFOS concentrations ranging from 0.13 to 166 ng/g wet weight) (Palmer et al. 2019). Avian eggs can also be contaminated by PFASs, even those collected in South Greenland (with PFOS as dominant contaminant detected within the range of 107–3890 ng/g dry weight) (Vorkamp et al. 2019). Unfortunately, cooking does not mitigate dietary exposure to PFASs (Taylor et al. 2019).

Beyond water and food, human exposure to PFASs may also result from the ingestion of chemicals from food packaging as well as house dust that may contain PFASs from chemically-treated carpets, upholstery, clothing, protective sprays, etc. (Appleman et al. 2014; Post et al. 2012).

PFASs consumed by people bio-accumulate in their bodies for years, predominantly in blood serum (at ng/ml levels) (Jian et al. 2018). A study revealed that PFASs are commonly detected in human populations from all over the world, including Korea, China, Japan, Norway, Poland, Denmark, Ukraine, Russia, Sweden, Germany, Belgium, France, Spain, Czech Republic, UK, Netherlands, Finland, USA, Canada, Australia, and even Uzbekistan and Afghanistan, Jordan (Jian et al. 2018). Geographical variations in PFAS concentrations may result from dietary intake, drinking water, dust, and the industrial levels of the studied areas (Jian et al. 2018).

PFOS and PFOA have been found in the blood of tested Americans (Brett et al. 2019; Wang et al. 2012) as well as New Zealanders (Coakley et al. 2018). In the latter study, higher PFAS concentrations were detected in older age groups and more in males than in females (Coakley et al. 2018). Concentrations of various PFASs in human serum were detected in Australia (Toms et al. 2019), although fortunately the trend has been declining. Another declining trend was recently reported in the U.S.: 10–20% per year in the PFAS levels in the blood serum of Californian women (Hurley et al. 2018). On the contrary, studies of young women in Uppsala (Sweden) showed permanent exposure to PFASs due to the consumption of drinking water contaminated by AFFF runoff from a military airport area north of the city (Eschauzier et al. 2013).

Health effects

PFASs, especially the long-chained, easily bio-accumulate in human organisms based on the following order: blood serum > plasma > whole body (Table 2). In the body, PFASs mainly concentrate in the liver. The chemicals show a low elimination rate in the human body: mean half-life values of 3.8 years for PFOA and 5.4 years for PFOS (Ghisi et al. 2019). Long-term exposure to PFASs may cause various health problems (Jian et al. 2018). Ongoing exposure to even relatively low intakes of long-chain PFASs substantially increases human body burdens, which remain elevated for many years even after the exposure ends (Post et al. 2017). PFASs increase cholesterol levels, enzyme activity and uric acid levels, alter thyroid parameters, and may cause pregnancy-induced hypertension (Ghisi et al. 2019). Potential health risks from exposure to

PFOA and PFOS include low birth weight, early menopause in women, low semen quality in young men, thyroid disease, children's attention deficit/hyperactivity disorder, lowered immune response to vaccinations as well as links to kidney and testicular cancers (Xiao et al. 2015).

A study in Norway showed a positive association between several PFASs and asthma as well as between PFOS and nickel allergy (Averina et al. 2019). Another study identified a strong association between the presence of PFASs in the blood serum of an US population at risk for cardiovascular disease (Huang et al. 2018). Other studies reveal that exposure to PFASs is associated with increased serum lipids and liver enzymes, decreased vaccine response, and decreased birth weight (Post et al. 2017). Harris et al. (2018) suggested a link between prenatal and childhood exposure to PFASs lower visual and motor abilities. Infants are a more sensitive subpopulation for PFASs developmental effects and usually receive higher exposures than adults (Post et al. 2017).

According to data obtained from experiments on animals (Post et al. 2017), PFASs may cause toxicity to the liver, the immune, endocrine, and male reproductive systems, and adversely affect developing fetuses and neonates (Post et al. 2017). Low-dose effects include persistent delays in mammary gland development and the suppression of immune responses (Post et al. 2017). The adverse effects associated with PFASs exposure in animal models also include tumor induction and neurotoxicity (Ghisi et al. 2019). Exposure to PFOA during pregnancy has induced both early and later life adverse health outcomes in mice (White et al. 2011).

Actions & regulations

Manufacturing regulations

Since the USA was the world's main producer of PFASs until 2002, it took pioneering actions to minimize the environmental and human health burdens caused by these chemicals. In 2006, the American EPA invited the leading manufacturers to the PFOA Stewardship Program whose goal was to reduce PFOA emissions and completely eliminate them by 2015 (Jian et al. 2018). European Union, restricted the market use of PFOS and related substances in Directive of 2006/122/EC. Similar actions were introduced in other countries for reducing the production of PFASs (Japan) to control the import and the use of PFOSE, PFOS, and its salts (New Zealand, Australia) (Coakley et al. 2018).

At the global level, in 2009 PFOS was listed under Annex B of the Stockholm Convention on persistent organic pollutants (POPs) (Hamid et al. 2018). The convention obtained agreements from nations to restrict production and use of PFOS. PFOA remains under review by the Stockholm Convention Committee (Hamid et al. 2018).

The above actions significantly decreased production and the release of PFASs in most developed countries. World statistics reveal, however, that from 2006–2015, their production drastically increased in China, India, Poland, and Russia (Wang et al. 2014).

At the same time, growing concern about long-chain PFASs surfactants (including PFOS and PFOA) as global environmental pollutants (Ochoa-Herrere et al. 2008) resulted in a situation where manufacturers adopted short-chain PFASs and other fluorinated options (e.g., perfluoropolyethers) as

alternatives (Ochoa-Herrere et al. 2008). The shift to short-chain PFASs introduced new uncertainties that must be scrutinized. For example, several studies have concluded that short-chain PFASs may have adverse effects, especially during long-term exposure, and can be transformed to more persistent products (Toms et al. 2019). Moreover, since the technical performance of the short-chain PFASs alternates is lower than the long-chain PFASs, much larger quantities of short-chain PFASs must be utilized to obtain similar performance (Lindstrom et al. 2011; Toms et al. 2019).

Drinking Water Regulations

After scientific reports indicated the presence of potentially toxic PFASs in drinking water supplies, some countries enacted regulations that established drinking water quality advisories/guidance (Table 3).

The first drinking water Health Based Guidance, which was established in 2006 by Germany's Drinking Water Commission (TWK), tracked PFOA detection in the drinking water in the city of Arnsberg (Wilhelm et al. 2010). The safe lifelong exposure proposed in the guidance was established at 0.3 µg/L (300 ng/L, 300 ppt) for PFOS and PFOA totals (Wilhelm et al. 2010). Since then other authoritative bodies, e.g., the Drinking Water Inspectorate of England and Wales (2006), the USEPA (2009), the Minnesota Department of Health (2007), and the New Jersey Department of Environmental Protection (2007) have issued values for PFOA and other PFASs (Wilhelm et al. 2010). In 2009, the U.S. EPA proposed a provisional health advisory for drinking water at levels of 200 ng/L for PFOS and 400 ng/L for PFOA (Liu & Avendano 2013).

The initial limits of PFASs in drinking water have gradually decreased worldwide. For example, the U.S. EPA's drinking water lifetime health advisory in 2016 decreased the levels to 70 ng/L for a combined amounts of PFOS and PFOA (Post et al. 2017). Even stricter drinking water guidelines for PFASs were adopted by California (6.5 ng/L and 5.1 ng/L, respectively), New Jersey (13 ng/L and 14 ng/L, respectively), Vermont and

Massachusetts (20 ng/L for sum of PFASs), and Minnesota (15 ng/L and 35 ng/L, respectively) (ASDWA 2018).

Although Europe-wide regulations are absent for PFOA (Jian et al. 2018), the proposed EU Drinking Water Directive set safe concentrations at 100 ng/L for any individual PFAS and 500 ng/L for the total PFASs (EU 2017). Other EU countries have enacted national regulatory actions, such as the abovementioned German Health Based Guidance or the Drinking Water Quality Criteria in Denmark (100 ng/L for both PFOS and PFOA) (EPA 2015).

Pioneering action was proposed by the Australian Government (Australia Government 2019), which in addition to the Health Based Guidance for Drinking Water (70 ng/L for PFOS, and 560 ng/L for PFOA) introduced Recreational Waters Quality Values at 700 ng/L for total of PFOA/PFHxS and 5600 ng/L for PFOA.

Removal methods

Growing awareness of the health threats caused by PFASs resulted in phasing-out their production by the primary manufacturers and decelerated the release of pollutants into the environment, at least in developed countries. However, since some specific PFASs properties cannot always be easily replaced by using other chemicals, PFASs are still used in semiconductor or metal plating industries. PFASs continue to be used in AFFFs and are present in many daily-life products. Therefore, releasing these chemicals into the environment is an ongoing process that causes pollution, mainly in aquatic environments. Therefore, removing chemicals from water is a critical and challenging task. Technological difficulties are associated with the high stability of C–F bonds and the exceptional persistence of PFASs to removal by most conventional and economically feasible remediation methods. A large number of novel processes as well as different modifications of conventional wastewater treatment methods have been recently tested worldwide with varied amounts of success and efficiency. A brief review of the most recent

Table 2. Reported adverse health effects of PFASs on humans (Xiao et al. 2015; Post et al. 2017; Harris et al. 2018; Huang et al. 2018; Jian et al. 2018; Averina et al. 2019; Ghisi et al. 2019)

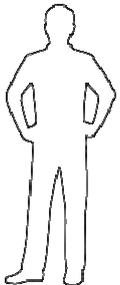
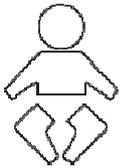
		
Bioaccumulation: blood serum > plasma > body (liver) Half-life (years): PFOS (5.4) / PFOA (3.8)		
<ul style="list-style-type: none"> – Pregnancy-induced hypertension – Early menopause 	<ul style="list-style-type: none"> – Low semen quality 	<ul style="list-style-type: none"> – Lower visual and motor abilities – Low birth weight – Attention deficit – Hyperactivity disorder – Low immune response to vaccinations
Others: increased cholesterol level, increased liver enzyme activity, increased uric acid level, thyroid disease, kidney cancers, testicular cancers, asthma, nickel allergy, increased risk of cardiovascular disease.		

Table 3. Comparison by drinking water quality values/advisories enacted in different countries

Country/State/Organization	PFOA	PFOS	PFOA+PFOS	Ref.
	ppt (ng/L)			
Germany	–	–	300	(Wilhelm et al. 2010)
Denmark	100	100	–	(EPA 2015)
EU (proposal)	100	100	500	(EU 2017)
U.S.A (EPA)	–	–	70	(Post et al. 2017)
(Vermont)	20	20	–	(ASDWA 2018)
(Massachusetts)	20	20	–	(ASDWA 2018)
(California)	14	13	–	(ASDWA 2018)
(New Jersey)	14	13	–	(ASDWA 2018)
Australia	560	70		(Australia Gov. 2019)
(recreational waters)	10,000	–	2,000 (PFOS+PFHxS)	(Australia Gov. 2019)

findings is summarized below, and the main comparison of the pros and cons of the selected methods is shown in Table 4.

– REMOVAL BY SEPARATION –

Adsorption

Different types of adsorbents have been tested for the removal of PFASs from water environments: carbon-based adsorbents, such as activated carbon (AC) (Du et al. 2015; Ochoa-Herrere & Sierra-Alvarez 2008; Zhi & Liu 2015), granulated AC (GAC) (Deng et al. 2015; Inyang & Dickenson 2017; Senavirathna et al. 2010a, 2010b; Szabo et al. 2017; Zhi & Liu 2016), powdered AC (PAC) (Zareitalabad et al. 2013; Meng et al. 2014; Murray et al. 2019), super fine powdered AC (SFPAC) (Murray et al. 2019), and carbon nanotubes (CNTs) (Zhang et al. 2019; Chen et al. 2011; Meng et al. 2014; Deng et al. 2012), graphite and graphene (Meng et al. 2012)); such biosorbents as biochars (Chen et al. 2011; Inyang & Dickenson 2017; Kupryianchuk et al. 2016), bioashes (Chen et al. 2011), sludge (Zhou et al. 2010; Arvaniti et al. 2014; Ochoa-Herrere & Sierra-Alvarez 2008), organic soil (Weber et al. 2017; Wei et al. 2017; Qian et al. 2017; Wei et al. 2017; Pereira et al. 2018)), plant and animal proteins (Brett et al. 2019); such mineral adsorbents as boehmite (Wang et al. 2012, 2015), vermiculate (Du et al. 2017), kaolinite (Zhang et al. 2014), montmorillonite (Zhang et al. 2014), layered double hydroxites (LDHs) (Hu et al. 2017), goethite (Tang et al. 2010), silica (Tang et al. 2010), alumina (Wang & Shih 2011), and mineral coagulants ($Al_2(SO_4)_3 \times 18 H_2O$, $FeCl_3 \times 6H_2O$, PACl) (Bao et al. 2014); such fabricated materials as cross-linked β -cyclodextrin (Xiao et al. 2017; Badroddoza et al. 2017), cross-linked chitosan beds (Zhang et al. 2011), nano-scale zerovalent iron particles (Zheng et al. 2018), and ammoniated magnetic particles (Liu et al. 2018); non-ion-exchange and anion-exchange resins (Gao et al. 2017; Du et al. 2015; Senavirathna et al. 2010a, 2010b; Woodard et al. 2017; Xiao et al. 2012)).

Carbon-based adsorbents

Activated carbon

AC is manufactured by the pyrolysis of biomass under an inert atmosphere in the presence of activation agents (KOH, $ZnCl_2$, H_3PO_4 , $FeCl_3$) (chemical activation) or the underflows of N_2 , CO_2 , or CO_2+H_2O (physical activation) (Sophia & Lima 2018).

AC shows a high affinity to PFOA (>90% removal efficiency) (Deng et al. 2015; Ochoa-Herrere & Sierra-Alvarez 2008; Meng et al. 2014; Rattanaoudomet al. 2012; Du et al. 2014; Espana et al. 2015)) and to other long-chained PFASs. AC is less effective toward short-chain compounds (Appleman et al. 2014; Inyang & Dickenson 2017; Eschauzier et al. 2012). The results obtained by Eschauzier et al. 2012 show that the adsorption coefficient of studied shorter PFASs decreases by 0.50–0.60 log units with each $-CF_2-$ group less in the molecule. Adsorption on AC is driven by hydrophobic and electrostatic interactions between PFASs and the adsorbent surface (Meng et al. 2014). Therefore, a decrease in AC's powder size increases its active surface area and improves the sorbent's performance in the following order: GAC < PAC < SFPAC.

Among ACs, GAC was historically used by 3M to remove PFOS from wastewater (Du et al. 2014). GAC exhibits slow kinetics for PFAS adsorption (up to 72 h may be needed to achieve adsorption equilibrium (Espana et al. 2015)) and medium sorption capacity (112–229 mg/g) (Ochoa-Herrere & Sierra-Alvarez 2008; Du et al. 2014). Among different GACs, the bamboo-derived type has exhibited exceptional characteristic for PFASs removal, i.e., fast kinetics (24 h) and high adsorption capacity (1160 mg/g for PFOS and 476 mg/g for PFOA) (Deng et al. 2015).

In contrast to GAC, PAC is characterized by twice bigger adsorption capacity and requires 4 h to obtain equilibrium for PFOA (Rattanaoudomet al. 2012), while SFPAC reportedly has even faster sorption kinetics and 480 times greater adsorption capacity than GAC (Murray et al. 2019).

ACs are the most widely used adsorbents for PFASs because of their good sorption capacities and reasonable prices. Their downside is problem related to treatment of their spent sorbents, whose utilization and regeneration require high cost. Spent ACs containing PFASs become a hazardous waste and require safe disposal or expensive thermal treatment to destroy the adsorbed contaminants.

The latter requires high temperature pyrolysis (>1000°C) for the complete degradation of PFASs (Kucharzyk et al. 2017) and the regeneration of AC sorption capacities. Prolonged AC use significantly decreases its effectiveness in removing PFOA/PFASs from water: by 65% after 223 days from the filter renewal (Takagi et al. 2011).

Carbon nanotubes (CNTs)

CNTs have more effective sorption performance (capacity 700 mg/g, equilibrium time 2 h) than GAC (Chen et al. 2011). However, the cost of their production and technological difficulties in safe application and the separation of nano-sized materials from treated water (nanomaterials are an emerging environmental pollutant) may limit their practical applications.

Biosorbents

Biosorbents are biological materials that naturally accumulate PFASs on their surfaces by physicochemical interactions. In recent years, they are attracting the attention of scientists as an economical alternative for removing contaminants from industrial wastewater and aiding environmental remediation.

Biochars and bioashes

Biochars and bioashes, which are less effective than GAC (Inyang & Dickenson 2017) for the removal of PFOA and PFOS (capacity < 170 mg/g) (Chen et al. 2011), require long equilibrium times of 384 h and 48 h, respectively (Chen et al. 2011).

Sludge and Soils

Sewage sludge, a semi-solid by-product from wastewater treatment, consists of dead bacteria (activated sludge), inorganic particles, and large amount of water. The adsorption of PFASs in sludge has been investigated (Zhou et al. 2010; Arvaniti et al. 2014; Ochoa-Herrere & Sierra-Alvarez 2008). Unfortunately, the results show scant removal effect, i.e. 8.5 µg/g for PFOS and 4.6 µg/g for PFOA (Ochoa-Herrere & Sierra-Alvarez 2008), and impractically slow kinetics (11 h) (Zhou et al. 2010). In a real WWTP process, lower pH and higher Ca²⁺ increased the sorption of PFASs into sludge, especially PFOS (increase of about 3.5 fold at pH change from 7 to 6, and multiplied in the presence of Ca²⁺), whereas PFOA basically remained in the treated water (Arvaniti et al. 2014).

Since the low adsorption of PFASs into sludge reveals the inability of municipal WWTPs to effectively remove the contaminants from incoming water, the WWTPs usually play a secondary role as a source of PFASs pollution.

Soils are also ineffective adsorbents for PFASs: 1.17–32.06 µg/g for PFOS (Wei et al. 2017). Investigations of different soils revealed that PFASs sorption was positively related to the content of organic matter (Milinovic et al. 2015; Wei et al. 2017; Qian et al. 2017; Wei et al. 2017; Pereira et al. 2018) and the hydrophobicity of the contaminant (Milinovic et al. 2015; Pereira et al. 2018) and inversely related to the soil's pH (Pereira et al. 2018). The low adsorptive properties of PFASs to soils indicate their high mobility in natural conditions and easy transport toward groundwaters. A very recent study concluded, however, that mobility can be drastically limited by the application of PAC or mineral adsorbents to polluted soil that effectively stabilizes these contaminants (Sorengard et al. 2019).

Protein-based sorbents

Plant proteins are novel and effective biosorbents for PFASs as recently reported by Brett et al. (2019). They used the plant proteins of hemp, soy, peas, and lupin and the powdered animal proteins of eggs and whey to remove PFASs from actual groundwaters. The plant proteins were much more

effective than animal ones, and hemp proteins exhibited superior removal performance, i.e. immobilized 98% of PFOS on the protein surface by hydrogen bonding and hydrophobic interactions in approximately 1 h (Brett et al. 2019).

Protein-based sorbents are natural products that are easily available from commercial suppliers. They do not require thermal or chemical activations and are about three times cheaper than commercial AC products (Brett et al. 2019). They may not require regeneration but can be thermally degraded with the adsorbed pollutants. They are attractive economic alternatives for the remediation of contaminated waters.

Mineral Sorbents

Minerals originate from natural rocks and are released during gradual erosion and weathering. Clays are loose minerals that contain particles with a grain size below 0.002 mm.

Many mineral sorbents have been investigated for the adsorption of PFASs. Among them, LDHs, especially hydrotalcite, have great potential for practical applications of PFASs removal. The materials are characterized by extremely fast adsorption kinetics (5–60 min) (Hu et al. 2017; Rattanaoudom et al. 2012) combined with high PFASs uptake (865 mg/g of LDHs) (Rattanaoudom et al. 2012). The use of LDHs for PFASs removal (at concentrations of 50–100 mg/L) from synthetic industrial wastewaters showed extremely high efficiencies of about 97–99.7% (Hu et al. 2017; Rattanaoudom et al. 2012).

Generally, the minerals and natural clays are low cost adsorbents (for example, montmorillonite is 20 times cheaper than AC (Sophia & Lima 2018)). Therefore, they provide lower capital and operational costs than other treatment options as well as a smaller volume of spent materials that require utilization (España et al. 2015).

Fabricated adsorbent

Cross-lined β-cyclodextrin

β-cyclodextrin, which is a cyclic oligosaccharide produced from starch by enzymatic conversion, consists of seven glucose sub-units located in a ring with two openings of different sizes (cone shaped). The molecule has a hydrophilic exterior surface, but the cone's interior has hydrophobic properties that host hydrophobic molecules.

A water insoluble β-cyclodextrin-based cross-linked polymer powder, namely decafluorobiphenyl-β-cyclodextrin (DFB-CDP), was successfully applied for the removal of PFOA (Xia et al. 2017). DFB-CDP reduced the PFOA from initial concentrations of 1 µg/L to just 10 ng/L within 24 h (i.e., the concentration was seven times lower than the level set by the U.S. EPA (2016), and 95% removal occurred within the first 13.5 h. The adsorbent was easily regenerated by washing with MeOH and ready for multiply reuse (US EPA 2016).

A β-cyclodextrin-ionic liquid polymer that covers the magnetic nanoparticles of Fe₃O₄ (Fe₃O₄-CDI-IL MNPs) was applied to remove PFOS and PFOA (Badroddoza et al. 2017) with adsorption capacities of 13.2 and 2.5 mg/g. The time required to reach an adsorption equilibrium was 4.6 h and 3 h for PFOS and PFOA. The Fe₃O₄-CDI-IL MNPs sorbent is easily regenerated by an application of NaOH/NaCl/magnetic field and repeatedly re-used without any significant loss of efficiency (Badroddoza et al. 2017).

Cross-linked chitosan beds

Chitosan is a polymer composed of β -(1-4)-2-amino-2-deoxy-D-glucopyranose units with active amino and hydroxyl groups sites on its surface that can form a number of bondings (amide and ester bonding) and formations (Schiff base formation) (Abraham et al. 2018). As a result, cross-linked chitosan beds have higher sorption capacity towards PFASs than many conventional adsorbents and can reach 2745 mg/g (Zhang et al. 2011; Du et al. 2014). A complex adsorption mechanism, including electrostatic and hydrophobic interactions, multilayer sorption, micelles, and hemi-micelles formations, occurred during the adsorption of PFASs on chitosan bed surfaces (Zhang et al. 2011). Unfortunately, one disadvantage is the long equilibrium time (32 h) required for complex adsorption (even longer at low pH and high concentrations of PFOS) (Zhang et al. 2011). Another downside is the very high adsorbent cost that surpasses the AC materials although it is cheaper than resins (Du et al. 2014).

Other fabricated adsorbents

Novel fluorinated ligands based on calix 4 arene functionalized with amide groups and fluorinated ponytails was used in the removal of PFASs (Omorodion et al. 2018). The functionalized host immobilized the PFOA by forming an inclusion complex; further studies are required to assess the efficiency of this novel adsorbent.

Other inorganic fabricated materials have also been successfully applied for PFASs removal, including nanoscale zerovalent iron (nZVI) (Zheng et al. 2018) and ammoniated magnetic adsorbent (γ -Fe₂O₃) (Liu et al. 2018). Among them, the ammoniated magnetic particles presented superior adsorption performance for both PFOA and PFOS with an equilibrium time of 120 min and a high adsorption capacity over a wide pH range (pH 3–9) (Liu et al. 2018). The possible separation and recyclability of these materials by a magnetic field and a NaCl solution were reported (Liu et al. 2018).

Resins

Non-ion-exchange polymeric resins consist of a hydrophobic backbone made of different copolymers (polystyrene, polydivinylbenzene, aromatic halogenated polystyrene or divinylbenzene, aliphatic methacrylate, etc.) that attract the perfluorinated “tail” of PFASs by hydrophobic interactions (Woodard et al. 2017). Anion-exchange resins have extra positively charged exchange sites that additionally attract the negatively charged “heads” of PFASs molecules using dominant electrostatic interactions (Gao et al. 2017; Woodard et al. 2017; Xiao et al. 2012).

Polymeric resins exhibited mixed feasibility in the removal of PFASs from aqueous solutions. The complex adsorption mechanism of anion-exchange resins results in higher sorption capacity (Zareitalabad et al. 2013; Senavirathna et al. 2010a, 2010b; Xiao et al. 2012) and faster equilibrium kinetics (Zareitalabad et al. 2013; Senavirathna et al. 2010a, 2010b; Xiao et al. 2012) than non-ion-exchange resins.

Senavirathna et al. (2010a, 2010b) tested the feasibility of both types of resins (including GAC for comparison) in the removal of PFOS at concentrations of 0.1–1.0 mg/L. Their work revealed a higher sorption of anion-exchange resins at a higher concentration range (ion exchange resins > non-ion-exchange

resins > GAC), and non-ion-exchange resin showed higher adsorption capacity at the lowest concentration range. For equilibrium time, the anion-exchange resin required 10 h, compared to the 80 h needed for the non-ion-exchange polymers (Senavirathna et al. 2010a, 2010b).

Gao et al. (2017) used an anion-exchange resin (Amberlite IRA67) to remove PFOS from aqueous solutions containing 25–400 mg/L of contaminant and from real wastewater that originated from the chromium-plating industry containing 189 mg/L of the PFOS. The adsorption capacity of the resins (2751 mg/g) was superior to most conventional solvents and comparable to cross-linked chitosan beds (Gao et al. 2017; Zhang et al. 2011; Du et al. 2014). The sorption capacity was pH dependent (higher at low pH and decreasing significantly at pH >10) and dropped in the presence of coexisting sulfate and chromate ions in wastewater (Gao et al. 2017). The time required to reach equilibrium was 20 h (Gao et al. 2017). The spent resins are easily regenerated by washing in NaCl/NaOH and methanol mixed solutions (Gao et al. 2017). The anion-exchange resin of IRA67 as well as the two non-ion-exchange resins of XAD4, XAD7HP, and AC removed PFOA and other PFASs (PFCAs, PFHxA, PFHpA) from actual wastewater (with high PFAS concentrations) generated during the manufacturing of PFOSF (Du et al. 2015). The study identified the superiority of the anion-exchange resin over the other tested adsorbents (Du et al. 2015). Since as much as 88% of the removal efficiency of PFOA was achieved with 0.2 g/L of IRA67, 1.8 g/L of the anion-exchange resin was needed to obtain removal efficiency that exceeded 90% for the three PFCAs (Du et al. 2015). The adsorption equilibria of the three PFCAs on the IRA67 was achieved within 33.5 h. Moreover, spent resins were easily regenerated by washing in NaCl/methanol solutions for stable removal of all the PFCAs in repeated adsorption cycles (Du et al. 2015).

Pilot tests with anion-exchange resin (Sorbix A3F) for the remediation of PFASs-contaminated groundwater were done at an abandoned air force base in New England that confirmed its feasibility and readiness for regeneration (Woodard et al. 2017).

Anion-exchange and ACs-based technologies are often compared and seen as competing solutions. However, what greatly distinguishes both materials is their post-treatment processing. Spent ACs become reusable after thermal reactivation; spent resins must be washed by mixed organic/inorganic solutions to regenerate their sorption properties. The first process is highly energy demanding, and the latter requires organic solvents that may be toxic (e.g., methanol). Both regeneration processes cause additional operational costs.

However, the effluent volumes produced by the regeneration of ion exchange resins and the necessity for further complex chemical processing of desorbed PFASs is a clear disadvantage of the technology.

Precipitation/Coagulation/Flocculation

This approach involves the conversion of soluble PFASs to insoluble precipitate which is then separated from the water by physical method such as sedimentation and/or filtration processes. The process requires addition of chemical coagulants and flocculation to increase particle size through aggregation.

The main types of coagulants are inorganic electrolytes (such as alum, lime, ferric chloride, ferrous sulfate) (ITRC 2020), organic polymers (for example, polyDADMAC,

Perfluorad) (ITRC 2020) or special particles generated by anode-cathode reactions of metal plates inserted into the water (electrocoagulation, EC).

Bao et al. (Bao et al. 2014) tested alum ($\text{Al}_2(\text{SO}_4)_3 \times 18 \text{H}_2\text{O}$), ferric chloride ($\text{FeCl}_3 \times 6\text{H}_2\text{O}$) and polyaluminum chloride (PACl) to remove PFOS and PFOA from water. Most effective removal was achieved with $\text{FeCl}_3 \times 6\text{H}_2\text{O}$ (i.e. 32% and 12%, respectively) which increased with pH modification (pH=4) to 94.7% and 47.6%, respectively (Bao et al. 2014). Electrocoagulation seems to have greater potential for practical application due to more effective removal of PFASs. Baudequin et al. (Baudequin et al. 2011) employed EC using aluminium anode followed by filtration, for pre-treatment of firefighting water containing PFASs (100 mg/L) and achieved removal efficiency of 71%. EC process with Fe anode is reported to remove 93% of PFOA from 100 mg/L of initial concentration after 90 min, which could be improved by H_2O_2 intermittent addition to 99% of PFOA removal within 40 min-EC (Yang et al. 2016). Studies performed by Lin et al. (Lin et al. 2015) revealed that EC-generated zinc hydroxide particulates can efficiently remove PFOA and PFOS within <10 min.

It must be noted, that the precipitation/coagulation/flocculation process can be costly, depending on reagents used and system controls, as well as generates hazardous precipitate containing PFASs requiring further disposal.

Membrane technologies

In the membrane processes, contaminants can be separated/rejected from water with semi-permeable (reverse osmosis, RO) or porous membranes (filtration by sieving) and high pressure. The membrane technologies for water and wastewater treatment are growing rapidly due to their simplicity and high effectiveness (Madhura et al. 2018). The processes divide the feed water into two effluent streams: a desired permeate (treated water) and a higher salinity concentrate (rejected) waste. Approximately 80% of the feed water passes through the membrane, and the remaining 20% is retained as high-strength concentrated waste (US EPA 2018).

The RO uses an extremely strong pressure gradient (10–100 bar) to overcome osmotic pressure and drive water through a non-porous membrane and separate the water molecules from other constituents. The process showed extreme efficiency in the removal of PFOS (> 99%) from solutions of a wide ranges of contaminant concentrations (0.5–150 mg/L) (Tang et al. 2006, 2007). However, at high PFOS concentrations (> 100 mg/L), severe flux permeate reduction was observed (Tang et al. 2007). A high degree of RO membrane fouling during the removal of PFASs from AFFF-containing water was also reported (Baudequin et al. 2011). Therefore, the RO process is more convenient for treating water that consists of low concentrations of PFASs and thus is often used in drinking water facilities to meet government criteria. For wastewater treatment, RO requires pretreatment (for example, by adsorption or nano-filtration) to avoid membrane fouling and to enhance the removal efficiency (España et al. 2015).

Nano-filtration (NF) is based on sieving the contaminated feed water through a tight porous membrane (pore size ca. 1 nm) at a high pressure of 5–20 bar (Madhura et al. 2018). The NF efficiency in the removal of PFASs is slightly lower than RO (Zhao et al. 2016, 2018; Hang et al. 2015). Zhao et al. (2016,

2018) investigated the removal of PFOS (100 $\mu\text{g}/\text{l}$ solution) using a commercial membrane (ESNA1-K1) and a novel membrane (NF270) and identified the PFOS rejection of 92.65 and 94.35% that rose above 97 and 99% in the presence of common ions (Ca^{2+} , Fe^{3+} , Na^+ , SO_4^{2-} , PO_3^{4-}) (Zhao et al. 2018) and Mg^{2+} (Zhao et al. 2016). The ions were found to bind and bridge the PFOS molecules and thus increased the sieving effect.

NF can support RO in drinking water treatment, but it can also be used for the treatment and the recovery of PFASs from highly contaminated wastewater (Hang et al. 2015). NF membranes were applied for the removal of PFOA from simulated wastewater containing a wide range of concentrations (100–10,000 mg/L). Almost 100% rejection of the contaminant was obtained at a PFOA concentration below 800 mg/L and 99.3% at higher concentrations (Hang et al. 2015). A concentrated rejected stream can be achieved by a one-step NF treatment that provides an opportunity for the beneficial recovery of the surfactant, and the NF membrane can be completely regenerated by a simple water rinse (Hang et al. 2015).

– REMOVAL BY DEGRADATION –

Chemical oxidation/reduction

Chemical oxidation and chemical reduction are examples of convenient methods used in water treatment. Although they effectively remove many contaminants, they are inappropriate for PFOA and PFOS due to the substitution of all the hydrogen atoms of the PFASs molecules by fluorine: the most electronegative element and the most powerful inorganic oxidant itself. To overcome the high inertness of PFASs, an addition is required to such supportive reagents as activated persulfate ($\text{S}_2\text{O}_8^{2-}$), hydrogen peroxide (HO_2^-), superoxide (O_2^-), high-valent metals, Fenton's agents, and/or additional pretreatment. For example, Burton and Sedlak (2018) applied a heat-activated persulfate and strong acidic conditions and transformed some PFOA into short-chain PFCAs (pH had the strongest effect on removal efficiency) and the PFOS remained resistant to the treatment.

Although some effective use of sulfate radicals (SO_4^-) was reported in the removal of other perfluorinated acids (carboxylic acetic, propionic, and butanoic) (Lutze et al. 2018), the energy requirement for the generation of sulfate radicals was discounted as excessively high compared to the costs of other treatment options (AC, RO, NF) (Lutze et al. 2018).

Other ions, such as hydroperoxide and superoxide, were successfully used in the degradation of PFOA (Mitchell et al. 2013; Ahmad 2012; Kerfoot 2014; Lin et al. 2012), PFOS (Kerfoot 2014; Lin et al. 2012) and other PFASs (Kerfoot 2014). For example, the ions oxidized as much as 68% of the PFOA within 150 min (Mitchell et al. 2013). Additional catalysts, such as Fe(III) (Ahmad 2012) and co-treatment with ozonation (Lin et al. 2012) (especially by nanobubble ozonation (Kerfoot 2014)), increased the effectiveness of the PFASs removal. The ozonation pretreatment increased the degradation of PFOA and PFOS by 56% and 42% under alkaline conditions (pH 11) and achieved almost complete degradation of both contaminants (85–100%) (Lin et al. 2012). Successful combination of chemical oxidation with nanobubble ozonation was patented by Kerfoot (2014), which reported that 97% of PFOA, 99% of PFOS, and 86–96% of the other PFASs can be destroyed in just 60 min of such co-treatment.

The chemical reduction of PFASs using zero valent iron (ZVI) (Hori et al. 2008) or magnesium amino clay coated nano zero valent iron (Mg-AC/nZVI) (Arvaniti et al. 2015)) showed low effectiveness (30–34%) on PFOA/PFOS degradation (Hori et al. 2008; Arvaniti et al. 2015).

Photolytic/Photocatalytic

The photolytic degradation of PFASs refers to the degradation of the chemicals under sunlight and/or UV (10–400 nm wavelength) radiation. In the case of photocatalysis, additional catalysts accelerate the degradation process.

The UV radiation range is essential to initiate the photodegradation of PFASs (Liu et al. 2013). A detailed study revealed that UV energy emitted at the 185-nm wavelength can cleave strong C–F bonds (Giri et al. 2012; Trojanowicz et al. 2018), and the presence of Fe³⁺ strongly supports the photodegradation of PFASs under UV irradiation (Jin et al. 2014). The efficient degradation of PFOA (98% of 50 µMol) in the presence of Fe³⁺ was obtained under natural sunlight within 28 days (Liu et al. 2013). A fiftyfold increase was found in its degradation in the presence of Fe³⁺ ions under UV radiation (Jin et al. 2014). The 100 µmolar concentration of Fe³⁺ (i.e. 5.584 mg) may decrease the PFOS concentration from an initial 20 µmol/L (i.e. 100.026 mg/L) to well below the detection limit within just 48 h of UV/Fe³⁺ treatment (Jin et al. 2014). More recently, almost complete degradation of PFOS (98% from its initial concentration of 32 µmol/L, i.e. 1.6 g/L) was achieved in a high photon flux UV/sulfite system, under slight alkaline conditions (pH 9.2), and within just 30 min (Gu et al. 2016). To achieve similar degradation levels with a vacuum ultraviolet (VUV)/sulfite system, a much longer time (4 h) is required (Gu et al. 2017).

Sonochemical

Sonochemical destruction is based on the application of acoustic energy to enhance the chemical activity of the chemicals present in solution (Rodriguez-Freire et al. 2015; Kucharzyk et al. 2017; Espana et al. 2015). Sonochemical treatment with an acoustic frequency of 200 kHz shortened the perfluorocarbon chains of PFOA and degraded PFOS with 28% efficiency (Moriwaki et al. 2005).

Another study (Vecitis et al. 2009) concluded that the sonochemical degradation of PFOS increases with the processing time. The ultrasonic irradiation of a mixture-PFASs solution (65–13,100 µg/L) for 120 min resulted in degradation of as much as 73% of PFOS and 36% of other surfactants (Vecitis et al. 2009). A more recent study (Rodriguez-Freire et al. 2015) revealed that the application of the megasonic frequency of 1 MHz may even be suitable for the treatment of high-content PFOS solutions (5.4–250 mg/L). The sonochemical approach can be applied to utilize the unused inventory of AFFF-stored products (Arvaniti et al. 2014; Vecitis et al. 2009).

Mechanochemical

Mechanochemical destruction refers to the forced reactions that take place at the chemical surfaces under the impact of mechanical forces (Zhang et al. 2013). Mechanical agitation acts by the transient temperature generated on the reagent surfaces during co-milling. Zhang et al. (2013) applied the method to investigate the fate of PFOS, PFOA, and other PFASs during ball milling in the presence of different co-milling

reagents (e.g., KOH, NaOH, CaO, SiO₂, Fe-SiO₂). KOH was identified as the best co-reagent, and under its presence nearly complete destructions of PFOS (99.88%), PFOA (100%), and other PFASs (90–100%) were achieved after 6 h, 3 h, and 4 h of treatment, respectively. The main final products were KF and K₂SO₄ (Zhang et al. 2013).

The method seems to be a good solution for the final destruction of unused solid PFASs or PFASs-loaded solid adsorbent (mineral, AC). To the best of our knowledge, however, no corroborative studies have been conducted.

Electrochemical

The electrochemical decomposition of PFASs has been reported (Fang et al. 2019; Zhou et al. 2012; Carter & Farrell 2008; Ochiai et al. 2011; Schaefer et al. 2015).

In this method, electricity decomposes the organic compounds followed by their mineralization into inorganic ions (F⁻), water, and/or gases (e.g., CO₂, HF) (Fang et al. 2019).

Interesting electrochemical degradation results were obtained for PFOA, PFOS, and other PFASs during the lab-scale treatment of actual AFFF-impacted groundwater (Schaefer et al. 2015). Their authors observed the gradual decomposition of PFASs when applying the current densities between 0 and 200 mA/cm² between a stainless steel cathode and a Ti/RuO₂ anode at 16 mm (Schaefer et al. 2015). The decomposition of PFOA and PFOS increased with growing current densities (for PFOS only until 2.5 mA/cm²) and resulted in 58% and 98% defluorination of PFOA and PFOS, while short-chain PFAAs were more recalcitrant (Schaefer et al. 2015). As many as 2–6 h were needed to reach satisfying levels of PFASs defluorination. The biggest limitation of the practical application of this method for real-scale remediation tasks is its cost as well as the generation of harmful perchlorate ions at the highest current densities (Schaefer et al. 2015). A very recent study suggested that the cost of the electrodes can be reduced by using spent PbO₂ material from lead-acid batteries (Fang et al. 2019). The activated and doped electrodes prepared from spent materials revealed high efficiency (> 99%) for the removal of PFASs and about 59% PFOA mineralization (Fang et al. 2019). However, leakage of the lead ions, the formation and the leakage of toxic HF, and the fouling of the electrode were observed during the treatment (Fang et al. 2019). The shelf-life of the PbO₂ panel was estimated to be only about 40 h (Fang et al. 2019).

Biodegradation

PFASs are resistant to degradation under natural environments (Llorca et al. 2018). Some evidence exists, however, on the partial biodegradation of PFASs under laboratory conditions (Beskoski et al. 2018). For example, the capability of microorganisms isolated from river sediments polluted by PFOA and PFOS, to biotransform these acids have been reported (Beskoski et al. 2018).

Surprising evidence for PFOS biodegradation by aerobic microorganism (*Pseudomonas aeruginosa*) was reported (Kwon et al. 2014). In this research, approximately 67% of the PFOS was biologically decomposed after 48 h of incubation over an initial concentration range of 1.4–1.8 mg/L (Kwon et al. 2014). The obtained results are very promising. Unfortunately, no further reports have confirmed the high efficiency of microorganisms in the biodegradation of PFASs under natural conditions.

Table 4. Comparison of selected PFAS contamination removal methods from water environment

Removal methods	Advantages/Disadvantages
Separation methods	
Adsorption on:	
<i>Activated carbon (AC)</i>	Most commonly used organic adsorbent Medium sorption capacity and medium adsorption kinetics that improve with decrease in powder size (GAC < PAC < SFPAC) <u>Pros:</u> – relatively cheap material <u>Cons:</u> – requires costly thermal treatment to destruct contaminants and regenerate AC adsorption properties
<i>Carbon nanotubes</i>	<u>Pros:</u> – better sorption capacity and faster kinetics than GAC and PAC <u>Cons:</u> – very expensive material – safety concerns related to nanomaterials
<i>Biosorbents</i>	Organic soils and sewage sludge: ineffective. Plant proteins are newly reported biosorbents for PFASs <u>Pros:</u> – cheap and commercially available material – good capacity and fast sorption kinetics – no chemical or thermal activation is required – thermally utilizing PFAS-loaded spent biosorbents is economically feasible
<i>Minerals</i>	<u>Pros:</u> – very cheap and abundant materials – medium to high adsorption capacity – medium to very fast sorption kinetics – suitable to treat high-PFAS-concentrated waters <u>Cons:</u> – spent PFAS-containing materials are hazardous waste that require further safe disposal
<i>Resins</i>	Anion-exchange resins have superior performance than non-ion-exchange resins <u>Pros:</u> – extremely high sorption capacity – medium sorption kinetics – easy regenerated and recycled by washing – applicable for wide range of PFAS concentrations <u>Cons:</u> – very expensive materials – generates concentrated elution solutions that require further treatment
<i>Fabricated adsorbents</i>	Cross-linked chitosan beds: extremely high sorption capacity and medium to long sorption kinetics. Cross-linked β -cyclodextrins: low sorption capacity and medium to fast sorption kinetics <u>Pros:</u> – easily regenerated and recycled by washing <u>Cons:</u> – expensive materials – generates concentrated elution solution requiring further treatment
Precipitation/ Coagulation/Flocculation	<u>Pros:</u> – medium (coagulation) to fast and highly efficient (electrocoagulation) removal of PFASs within wide concentration range <u>Cons:</u> – process can be costly depending on used reagents – treated water may require pH adjustment – the solid material containing the PFAS requires disposal
Membrane technologies	Reverse osmosis/Nanofiltration <u>Pros:</u> – extremely efficient removal of all PFASs within wide concentration range <u>Cons:</u> – expensive – membrane fouling (RO) when treating highly polluted wastewater – generates high strength concentrated waste solutions that require further utilization

Removal methods	Advantages/Disadvantages
Degradation methods	
Chemical oxidation/ reduction	Oxidation by sulfate and persulfate radicals: low effectiveness Oxidation by superoxide and hydroperoxide radicals is more effective, especially in combination with nanobubble ozonation <u>Pros:</u> – fast degradation of PFOA/PFOS to short-chain PFASs <u>Cons:</u> – high energy demand (expensive) Reductive destruction: little effectiveness
Photolytic/ photocatalytic degradation	UV radiation: low effectiveness Modifications to UV/Fe ³⁺ and vacuum UV/SO ₃ ²⁻ or high photon UV/SO ₃ ²⁻ systems increase degradation effectiveness <u>Pros:</u> – fast degradation <u>Cons:</u> – low to medium effectiveness (medium effective systems become extremely expensive) – applicable to low-concentrated solutions
Sonochemical degradation	<u>Pros:</u> – low (ultrasonic) to medium-high (megasonic) effective destruction of PFOA/PFOS to short-chain PFASs <u>Cons:</u> – expensive – dedicated to destruction of unused AFFF inventory
Mechanochemical degradation	Suitable for solid PFASs <u>Pros:</u> – low to medium effectiveness <u>Cons:</u> – expensive
Electrochemical degradation	<u>Pros:</u> – medium effective <u>Cons:</u> – extremely expensive – formation of harmful perchlorate ions
Biodegradation	Laboratory tests only <u>Pros:</u> – could be potentially applied for remediation of contaminated sites <u>Cons:</u> – low effectiveness

Conclusions

Per- and polyfluoroalkyl substances (PFASs), which are synthetic fluorosurfactants used in many commercial and industrial applications, were created in the middle of the 20th century. Unfortunately, their widespread applications over the last 70 years have resulted in ubiquitous distribution worldwide. They have been detected in various environmental compartments, animals, and humans. PFASs are persistent, bio-accumulative, and pose serious health risks to human and animals.

International organizations have identified selected PFASs as dangerous environmental pollutants that require control and minimization. Some national governments enacted regulations to protect humans from uncontrolled exposure to these chemicals. Some major producers phased-out PFAS production, and PFOA/PFOS applications have been severely limited. Efforts have been made to replace the most toxic and

bio-accumulative PFASs by less hazardous alternatives, and safe drinking water criteria were established in a few countries. Some reports, including those on the gradual decrease of PFOA/PFAS concentrations in the blood of Australians and Californian women, suggest the success of such actions, and others indicate that contaminated sites will pose a constant threat of PFAS exposure for future generations (Sweden).

Note, however, that the successes are generally limited to developed countries. PFASs manufacture has relocated to less developed countries where the environmental regulations are more lenient and enforcement is softer. Undeveloped countries continue to use toxic PFASs for economic reasons.

The replacement of PFOS and PFOA by short-chained alternatives seems risky because the health and environmental effects of these new compounds remain insufficiently investigated. Controlling PFASs concentrations in drinking water is critical. However, that remedy is just an “end-pipe” solution. Synchronized worldwide actions must be intensively

promoted worldwide to stop on-going pollution and fuel further research and collaboration on environment decontamination.

PFASs are persistent and difficult to be degraded by conventional removal methods. However, properly equipped drinking water facilities are already able to reduce PFASs concentrations (usually with a combination of RO and AC adsorbents) below the established water criteria. Unfortunately, the cost of effective treatment is prohibitive.

For industrial wastewaters and AFFF splits, new technological solutions have been proposed recently, and among them adsorption on biomaterials (plant proteins, chitosan beds), mineral adsorbents (LDHs, hydrotalcite), ion-exchange resins, and photocatalytic degradation seem the most promising methods, although they require further tests and improvements. The enforced biodegradation of the chemicals by aerobic microorganisms may also be a great step in the gradual decrease of toxic PFASs in the natural environment.

Novel interdisciplinary studies have special importance because they could lead to the development of effective and cheap remediation techniques for the removal/degradation of PFASs.

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