Adsorption as a Remediation Technology for Short-Chain Per- and Polyfluoroalkyl Substances (PFAS) from Water - A Critical Review

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Adsorption as a Remediation Technology for Short-Chain Per- and Polyfluoroalkyl Substances (PFAS) from Water - A Critical Review

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Abstract

Because of their ubiquitous presence in the environment and their potential toxicity to human health, per- and polyfluoroalkyl substances (PFAS) have drawn great attention over the past few years. Current conventional drinking and wastewater treatment approaches fail to effectively remove these substances from aqueous media, motivating researchers to focus on using sorption, a simple and cost-effective method, to remove PFAS from contaminated water. This work aims to summarize and critically evaluate the sorption capacities of PFAS by a variety of natural and engineered sorbents, including carbonaceous materials, ion exchange resins, polymers, different natural materials and other engineered sorbent materials. The specific focus of this review is on the performance of these different materials in removing short-chain PFAS due to their high solubility and mobility in aqueous media. A treatment train optimizing the removal these short-chain substances from water is proposed, and challenges and future recommendations discussed.

Water Impact Statement

The contamination of water environments by PFAS is a major concern. One challenge

of these emerging substances is their removal from aqueous solutions because of their high mobility in water and low adsorption potential. This review critically evaluates adsorption efficiencies of different sorbents for short-chain PFAS, highlighting current knowledge gaps and potential paths forward.

Introduction

PFAS are a family of anthropogenic chemicals that includes more than 4700 fluorinated chemicals, which have been produced since the 1940s, and some of which are being widely used in different applications.[1] In addition to being highly resistant to heat, biotic degradation, and being chemically stable thanks to the strong carbon-fluorine bond,[2] many of these compounds are characterized by a unique chain structure where the hydrogen atoms are either fully (per) or partially (poly) replaced by fluorine atoms, allowing these substances to be both hydrophobic and oleophobic.[3] These properties make PFAS excellent surfactants to be used in many consumer products, including in water and stain repellent textiles, cookware, food containers, pharmaceuticals, medical devices, laboratory supplies, personal care products, cosmetics, etc., and are also used in aqueous film-forming foams (AFFFs) for fighting Class B fires.[4] As a result of the large-scale use of PFAS, these substances have been detected in the environment, aquatic organisms, and humans. In the United States, PFAS are also detected in treated drinking water. According to a study by Boone et al., 2019, where 50 samples of source and treated drinking water were analyzed, PFAS were detected at concentrations ranging from 1 ng/l to 1102 ng/l, with no significant difference in PFAS concentrations between source and treated water, indicating that standard drinking water treatment plants (DWTPs) fail to remove these substances before distributing the water for public consumption.[5] Groundwater is easily contaminated by various chemicals including PFAS through point-source contamination from AFFF release, direct releases and spillages from manufacturing sites, and transfer from contaminated soil and surface water.[6]

While comprehensive data on toxicity for most PFAS is still lacking, human exposure to certain PFAS has been linked to the occurrence of different types of cancers such as bladder cancer, leukemia, and pancreatic cancer.[7] Studies also demonstrated potential correlation between PFAS exposure and developmental and reproductive complications, kidney and liver diseases, and diabetes.[8] Moreover, PFAS exposure has also been linked to altering immune system responses, more specifically PFAS exposure was related to immunosuppression where antibody production decreased and also hypersensitivity.[9] Because of the health and environmental threats that these compounds pose, the United States Environmental Protection Agency (USEPA) originally set health advisory levels of 70 ppt (ng/L) for perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) in drinking water in 2019. However, nine states deemed these advisory levels insufficient, and developed stricter guidelines ranging between 8 and 35 ng/l for PFOA and between 10 to 40 ng/l for PFOS.[10] Most recently, in June 2022, the USEPA set new interim health advisories of 0.004 ppt for PFOA, and 0.02 ppt for PFOS. In addition, final health advisories of 10 ppt and 2000 ppt were set for GenX chemicals and perfluorobutanesulfonate (PFBS), respectively [11]. The updated health advisories of PFOA and PFOS are based on human epidemiology studies, showing that health effects could be observed at lower levels than previously established. The new health advisories of GenX chemicals and PFBS are based on animal toxicity data for oral exposure, showing that GenX chemicals exposure is associated with effects on kidney, liver, and immune system development, while exposure to PFBS was linked to effects on the thyroid, kidney, reproductive system, and fetal development. [11]

These increasingly lower health advisory levels are of particular concern because environmental levels already approach or exceed many of them. For example, levels of PFOS, PFOA, PFBS, and perfluorobutanoic acid (PFBA) were reported to be present in groundwater in China at concentrations up to 21,200 ng/l, while GenX was present at a concentration reaching up to 30,000 ng/l.[12] Unsurprisingly, PFAS are also detected in wastewater treatment plants, where their concentration in the influent is up to 1,000 ng/l while it ranges from 15 to more than 15,000 ng/l in the effluent.[13] The contaminated effluent can be discharged in surface water and can potentially contaminate water supplies further downstream. The increased PFAS concentrations observed in the effluent compared to the influent are likely due to degradation of precursors into shorter-chain PFAS.[13]

As a result of legislative actions and voluntary programs to regulate the use of certain PFAS, many manufacturers have switched to the use of short-chain PFAS as alternatives. Short-chain PFAS are perfluoroalkane sulfonic acids (PFSAs) with carbon backbones of < 6 carbons and perfluoroalkyl carboxylic acids (PFCAs) with carbon backbone of < 7 carbons.[14] However, since the performance of these short-chain substances is lower than that of long-chain ones, larger quantities are required to achieve similar efficacy.[15] Additionally, short-chain PFAS are very mobile and very persistent in the environment, and therefore have high potential for long-range transport.[14] Fewer studies have focused on these short-chain substances, which leaves a knowledge gap when it comes to their fate in the environment and their long term effects, resulting in high uncertainty about the risks posed by these compounds.[16]

The persistence of PFAS in the environment stems from their resistance to all forms of degradation including thermal and biodegradation, which calls for more research on effective removal technologies.[17] Unfortunately, conventional treatment methods such a coagulation, flocculation, sedimentation, and filtration have proven ineffective in the removal of PFAS, especially when these contaminants are present at low concentrations in the environment.[18] Aerobic and anaerobic biological treatments of long-chain PFAS that are so-called precursor compounds result in the formation of short-chain PFAS, since these treatment methods are largely only able to break down carbon-carbon bonds in polyfluorinated substances.[19] Other removal technologies such as nanofiltration, reverse osmosis (RO), advanced oxidation, etc., are energy consuming and require expensive equipment.[20] Unsurprisingly, there are currently no removal technologies that guarantee the absolute destruction of PFAS, especially short-chain PFAS[21], given the persistent nature of these substances. Compared to other treatment methods, adsorption has been confirmed to be a promising remediation technology for long-chain PFAS in aqueous solutions thanks to its high efficiency, cost effectiveness and simplicity.[22] However, short-chain PFAS are not easily removed by adsorption because they do not readily bind to particles and remain soluble in the water phase, due to their high water solubility and their low adsorption potential.[14] Over the past few years, various laboratory-based studies investigated the potential for different adsorbents to remove PFAS from aqueous environments, including granular activated carbon (GAC), powdered activated carbon (PAC), ion exchange resins, sediments, metals, and multiwalled carbon nanotubes (MWCNTs), among others.[23,24,25] Despite the increasing use of short-chain PFAS over the past few years and their increasing detection in the environment,[26] studies focusing on the removal of short-chain PFAS by adsorption remain limited because of the challenges that these substances pose, leaving a research gap when it comes to their removal by adsorption from contaminated waters. Other reviews have been published wherein the removal mechanisms of different adsorbents are summarized and the different removal mechanisms involved in the remediation process are discussed. However, most of these studies focused on the removal of long-chain PFAS, especially PFOS and PFOA, and provide little information on the removal of short-chain PFAS and the challenges involved in their remediation from aqueous media, leaving therefore an important knowledge gap that needs to be addressed.[19,20,27,28] This review aims to provide a comprehensive summary of the studies assessing the removal of PFAS through adsorption in aqueous solutions, and to critically evaluate the efficiency of adsorption as a remediation technology with a focus on short-chain PFAS, given that knowledge is lacking on these short-chain substances. A treatment train that targets the removal of short-chain PFAS is proposed, and the feasibility and limitations of such treatment are discussed.

Methods

Literature Review

Articles investigating adsorption as a removal technology for PFAS were identified and screened for inclusion. Studies were considered up until the present and only abstracts written in English were considered. Scopus, JSTOR and Science Direct were searched using the following search terms: (PFAS AND (removal OR remediation OR adsorption OR treatment)) AND (water OR (aqueous AND solutions) OR (drinking AND water) OR wastewater OR groundwater) (search date: May 25th 2020- May 1st 2022). In addition, the University Library System (ULS) of the University of Pittsburgh was searched for 'adsorption of PFAS' and 'poly- and perfluoroalkyl substances adsorption technologies'. Articles were excluded if the removal technology did not involve adsorption, or if the removal matrix was other than water. Additionally, references in the selected articles were screened for additional relevant studies. Primary studies were extracted from review articles. Data were collected for the following variables: publication year, publication journal, first author, publication title, substances investigated, PFAS class as: PFCAs, PFSAs, PASF-based substances, and fluorotelomer-based substances, perfluoroether carboxylic and sulfonic acids (PFECAs and PFESAs), and perfluoroalkyl sulfonamides (FASAs). Data were also collected for substance chain length, number of carbons, number of fluorinated carbons, type of adsorbent used, type of adsorption interactions, the matrix of the experiment, and adsorption metrics. To concisely summarize and unify the data, if not represented as percent removal or removal efficiency, adsorption metrics reported in the results of each study were converted into percent removal of the PFAS.

Calculation of Percent Removal

When the adsorption metric is presented as adsorption capacity, q in *mmol/g*, the percent removal is calculated as:

$$\% \text{ removal} = \frac{q \times m}{V \times C_i} \times 100$$

Where m is the adsorbent mass used in *g*, V is the solution volume in *l* and C_i is the initial PFAS concentration prior to the start of the adsorption experiment in *mmol/l.* If C_i was presented in *g/l*, the molar concentration was calculated by dividing the given concentration by the molecular weight of the PFAS in *g/mmol:*

$$Ci \text{ (in mmol/l)} = \frac{C_i \text{ (in } g/l)}{\text{PFAS molecular weight (in } g/mmol)}$$

Similarly, when the adsorption capacity is given in *mg/g,* the percent removal is calculated as:

$$\% \text{ removal} = \frac{q \times m}{V \times Ci} \times 100$$

Where C_i is the initial PFAS concentration in *mg/l*.

In studies where the sorption behavior was presented as sorption isotherms of C_s (PFAS concentration in the sorbent) in mg/g vs C_{eq} (PFAS concentration in the aqueous phase) in mg/g and linearity was assumed, values of C_s and C_{eq} were determined by linear regression and the percent removal was calculated similarly to (1) and (2):

$$\%\ \text{removal} = \frac{C_s \times m}{V \times C_i} \times 100$$

Studies of which the adsorption metrics were not convertible to percent removal are reported in Table S2.

Results and Discussion

Search results

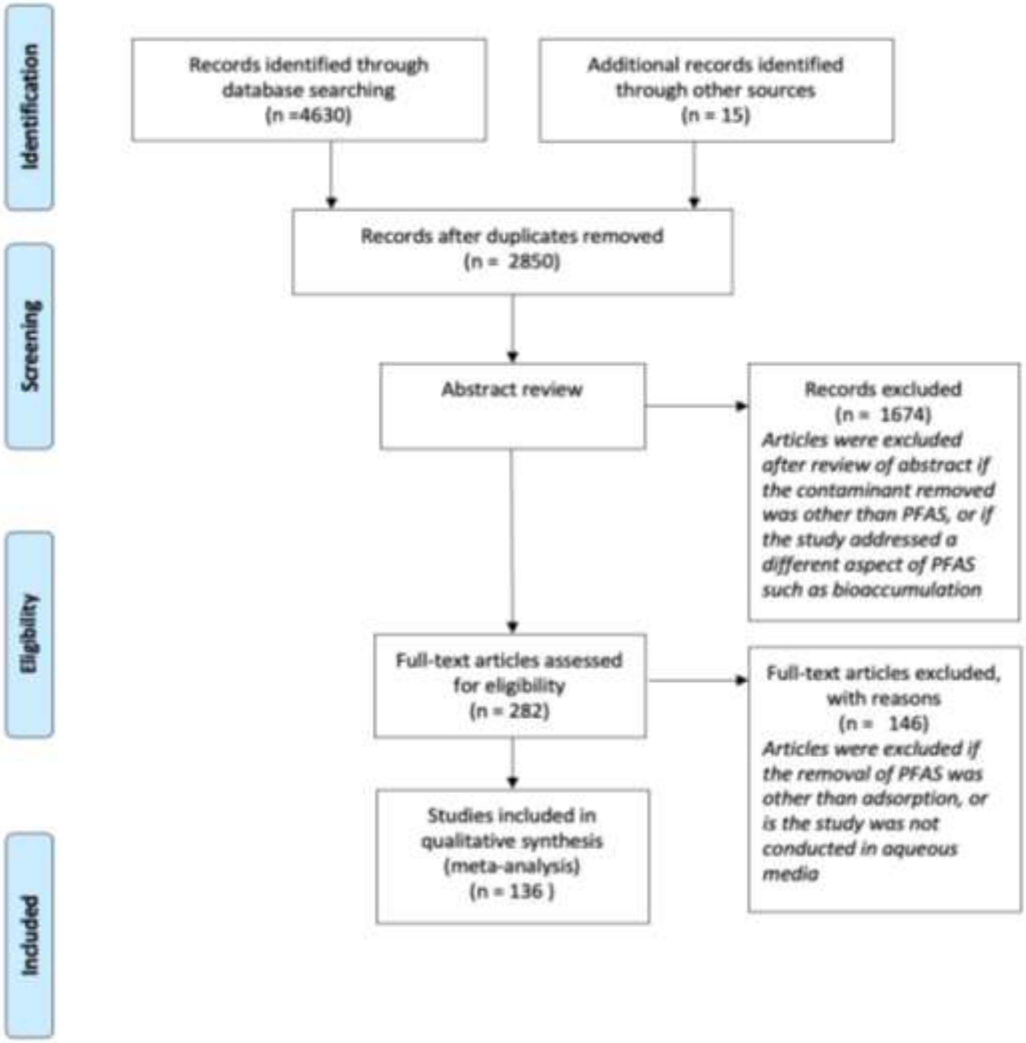

Fig. 1: Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) flow chart of the study selection process. This PRISMA diagram summarizes the screening process and transparently allows the inclusion the number of articles generated from screening, from elimination and from inclusion steps, while reporting reasons for exclusions.[29]

The initial database search yielded 4630 studies; additional searches through review paper references and library search identified 15 studies (Fig. 1). A total of 2850 studies remained after removing duplicate articles. Studies were excluded after abstract review if the study was not relevant to the scope of our review (e.g. the contaminant removed is something other than PFAS, or if the study addresses a different aspect of PFAS such as bioaccumulation, etc.). After scanning the remaining articles for inclusion criteria (Fig. 1) a total of 136 studies were evaluated for this study. [1,12,16,20,22–25,30–161]

Characteristics of included studies

The number of studies investigating the removal of short-chain PFAS is significantly smaller than those investigating long-chain substances, which were included in all studies (Fig. 2). More specifically, PFOS and PFOA are the most studied substances; 81% and 74% of studies investigated PFOS and PFOA, respectively (Supporting Information, SI, Fig. S1), since they are the two most widely occurring PFAS, with concentrations detected at concerning levels in the environment, wildlife, and humans. For instance, PFOS concentrations in surface waters can reach up to 8.97 mg/l near source zones such as training areas using extensive amounts of AFFFs. [162] Moreover, PFOS and PFOA are known to be bioaccumulative and toxic.[22] These concentrations are therefore alarming, particularly in comparison to the new low health advisory levels set by EPA.[11] Generally, and not surprisingly, PFAS concentrations in humans and wildlife are highest at contaminated sites.[164]

As a result of voluntary measures aiming to phase out long-chain PFAS, there has been an increase in the industrial shift towards the use of short-chain PFAS as alternatives.[16] The most widely studied short-chain PFAS in terms of their remediation through adsorption are PFBS, perfluorohexanoic acid (PFHxA) and perfluoroheptanoic acid (PFHpA) (SI, Fig. S1). This focus is a result of their high occurrence in the environment; Li et al., 2020 reported that PFBA, PFBS, PFHpA, and perfluoropentanoic acid (PFPeA) are the most frequently detected short-chain PFAS in the environment.[90] The perfluoroalkyl acids, including PFCAs and PFSAs, are far more well studied compared to other PFAS classes (Fig. 2) due to their presence in the environment, humans, and biota. [165] According to Kwiatkowski et al., 2020, PFAAs are globally detected and are present in almost all United States residents.[166]

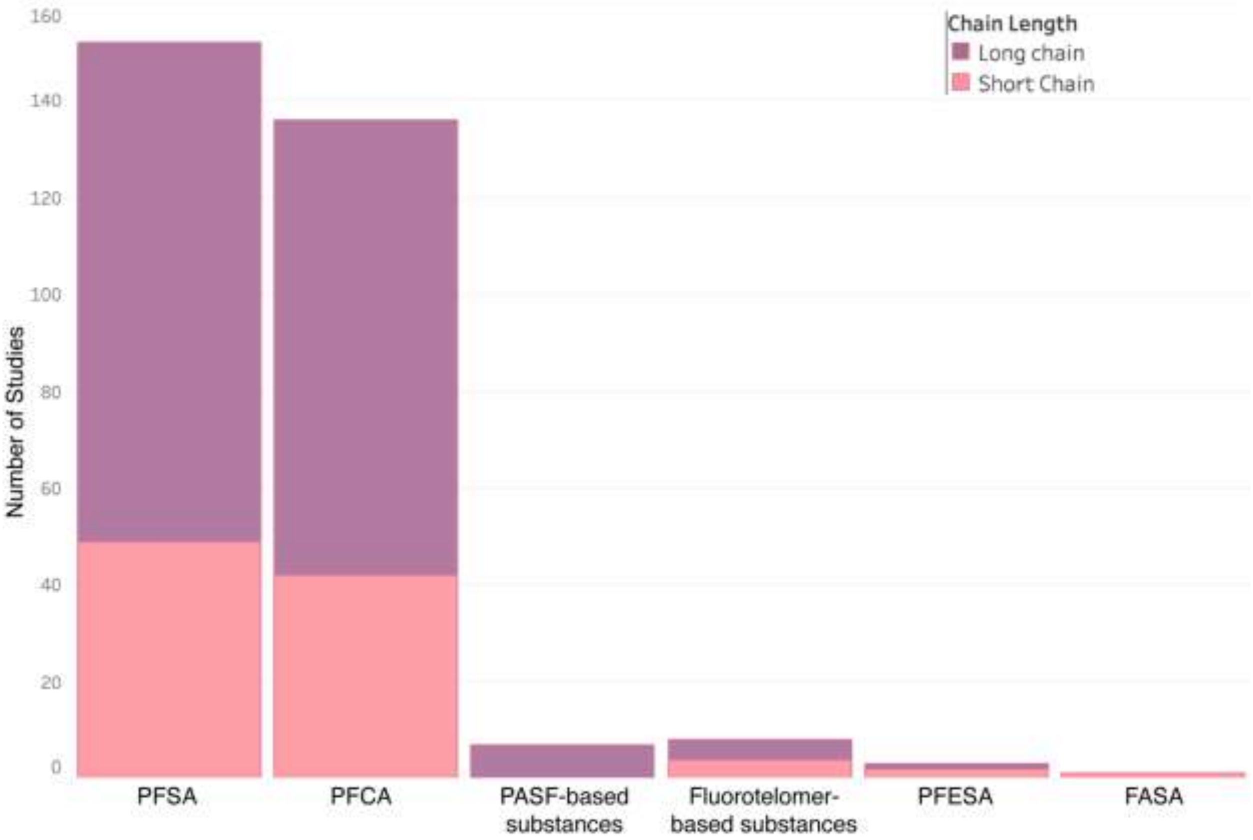

Fig. 2 Distribution of PFAS classes included in this review. Short-chain PFAS are defined as perfluoroalkane sulfonic acids (PFSAs) with carbon backbones of < 6 carbons and perfluoroalkyl carboxylic acids (PFCAs) with carbon backbone of < 7 carbons

Types of adsorbents

Carbonaceous materials and resins are the most widely used sorbents for PFAS removal (Fig. 3). Many studies have tested carbon-based sorbents for the removal of both long- and short-chain PFAS.[32] In addition to the most commonly used carbon-based adsorbents such as GAC and PAC, other engineered carbonaceous adsorbents have been developed to remediate PFAS from aqueous solutions. For example, a study by Chen et al., 2017 prepared polyacrylonitrile fiber derived activated carbon fibers to compare the adsorption capacity of PFOS to PAC and GAC.[51] Carbon nanotubes (CNTs) have also been used as sorbents in many studies to evaluate their adsorption performance for PFAS. Deng et al., 2015 used pristine MWCNT along with MWCNT with hydroxyl and carboxyl groups to evaluate their adsorption capacities for both long- and short-chain PFAS.[57] Ion exchange resins have also been widely implemented by many studies to access their sorption capacity to PFAS, including to short-chain PFAS. Woodard et al., 2017 investigated the removal of PFBS, PFBA, PFHxA, PFHpA, and perfluoroheptanesulfonic acid (PFHpS) using ion exchange resins and compared their sorption capacity to GAC.[23] Another study by Park et al., 2020 used magnetic ion-exchange (MIEX) resins to treat PFAS contaminated groundwater at environmentally relevant concentrations. Thanks to their magnetic properties, MEIX can rapidly agglomerate into larger particles and are easily settleable which facilitates the separation of PFAS from the treated water. [113]

Several other studies have explored the removal of PFAS from aqueous solutions by polymers. Ji et al., 2018 evaluated the removal of long-chain and short-chain PFAS by two amine-functionalized covalent organic frameworks which are porous polymer materials characterized by their fast uptake and high adsorption capacity.[82] Other polymer materials such as polyaniline nanotubes (PANTs)[140], and molecularly imprinted polymers (MIP) have also been tested for their PFAS adsorption capacities.[145,44] Meng et al., 2017 experimentally evaluated the removal of PFAS by engineered aminated polyacrylonitrile fibers (APANFs) containing amine functional groups.[105]

In addition to commercially available and engineered sorbents, many natural sorbents such as soil, sediment, sand, sludge, minerals etc., have been tested for their PFAS adsorption capacities. For example, a study by Sörengård et al., 2020 tested the capacity of a wide range of natural sorbents such as minerals, biochar, sediment, metals, sludge, etc., to adsorb both short-and long-chain PFAS from aqueous solutions.[122] Additionally, Rostval et al., 2018 tested PFAS removal from wastewater by other natural sorbents such as sand, lignite (a type of brown coal typically used as a sorbent thanks to its different functional groups), and xylite, a carbonized wood fiber derived from lignite.[119] All the specific sorbents included in the meta-analysis under "other" category are listed in Table S3.

Despite the increasing number of different engineered sorbents evaluated over the past few years (this review includes studies from 2006 to 2018), in efforts to find effective remediation technologies to treat PFAS-contaminated water, carbon-based sorbents and ion exchange resins remain the most widely used sorbents for the removal of PFAS and have been reported in large-scale application of groundwater treatment.[23]

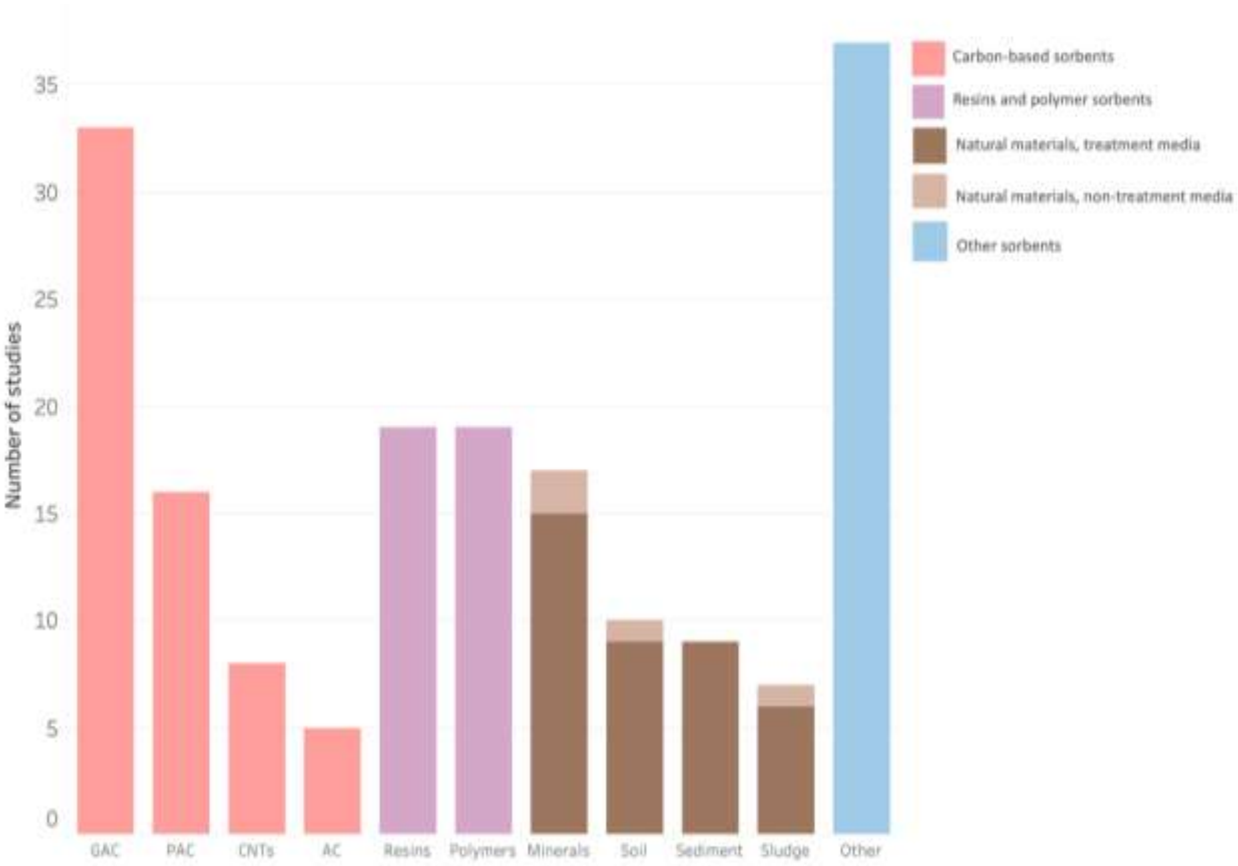

Fig. 3 Distribution of the number of studies of different sorbents, sorted by category (carbon-based sorbents in peach, resins and polymers in purple, natural materials in brown, with those studies that used natural treatment materials as a treatment method in dark brown, and those simply reporting sorption to natural media rather than treatment shown in light brown, and others in blue).

Removal efficiency of different adsorbents

Carbon based sorbents The removal efficiency of long-chain PFAS is higher than that of short-chain PFAS across all sorbents (Fig. 4). This observation is consistent with the clear relationship between fluorinated carbon chain length and adsorption performance that has been widely reported by various studies.[19] GAC displays a high removal efficiency for long-chain PFAS via hydrophobic interactions,[146] while it is less effective in removing the shorter chain substances due to their faster diffusion through the pores and therefore shorter sorption equilibrium time.[65] It is observed that PAC displays a slightly higher adsorption efficiency for short-chain PFAS, which can be explained by its smaller pore size, shorter internal diffusion compared to GAC and its better site accessibility.[24] Other activated carbon (AC) materials such as the ultrafine magnetic activated carbon (MAC) used by Meng et al., 2019, showed a high adsorption capacity for studied PFAS compared to GAC, which the authors suggest is due to the loading of magnetite and is explained by the decrease in particle size after milling. In addition, the authors reported the ball mining used to create ultrafine particles contributed to the increase of the adsorption capacity due to the decreased internal diffusion. The study also reported that ultrafine MAC had an increased adsorption capacity for short-chain PFAS such as PFBS since the latter has a molecular length smaller than that of the ultrafine MAC and therefore it easily enters the pores of the adsorbent. Moreover, the addition of magnetite facilitates the regeneration process since the MAC can be easily retrieved from the solution by a manget.[105] Wu et al., 2020 reported that smaller size ACs exhibited an almost complete removal of long-chain PFAS whereas ACs of a large particle size exhibited limited adsorption capacity and that there is a clear association between decreased particle size and enhanced adsorption capacities attributed to increased specific surface area. [167] In a study comparing ACs to resins, and consistent with the results of this meta-analysis (Fig. 4), Wang et al., 2019 reported that ACs outperformed resins in the removal of GenX (perfluoro- 2-propoxypropanoic acid).[131]

The removal capacity of PFAS by CNTs is lower than that of other carbon-based materials, especially for short-chain PFAS (Fig. 4). CNTs have been used in different studies to investigate the removal of PFAS from aqueous solutions thanks to their high specific area, hydrophobicity, hollow nanostructure and thermal and chemical stability.[96] Deng et al., 2012 studied the sorption capacity of different PFAS by MWCNTs and reported that the sorption was governed by hydrophobic interactions and therefore the sorption decreased with the decreasing C-F chain length, indicating that MWCNTs are not very effective for the removal of short-chain PFAS.[62] Efforts are made to increase the sorption capacity of CNTs by introducing functional groups such as hydroxyl and carboxyl groups to increase the electrostatic interactions with ionized head groups on PFAS. Moreover, improving their textural properties by incorporating metal nanoparticles can increase the affinity of CNTs towards PFAS by creating more adsorption sites, and generating different interactions with the PFAS, such as electrostatic interactions and ligand exchange.[96] However, the lower performance of CNTs and their high cost compared to carbonaceous materials calls into question whether more research is needed to improve the affinity of these sorbents, especially for less hydrophobic and mobile short-chain contaminants, or if the potential gains in performance will not be able to outweigh the added costs.

Resins Resin materials, more specifically ion exchange resins, exhibit higher adsorption capacity for PFAS compared to GAC and PAC (Fig. 4). Many studies have reported the efficiency of ion exchange resins in the removal of PFAS. Kothawala et al., 2017, Park et al., 2020 and other studies reported that ion exchange outperformed GAC in the removal of short-chain PFAS.[85,114,102,19] Hydrophobic and electrostatic interactions (described in the next sections) are the two governing mechanisms of PFAS removal by ion exchange resins. The hydrophobic backbone of the ion exchange resins contributes to the hydrophobic interactions with PFAS while the positively charged sites exchange ions for the PFAS functional head group.[20] These electrostatic interactions were confirmed by the increased concentration of chloride ions in the effluent as PFAS are adsorbed,[64] and by the effect of the solution pH during the sorption process, where the adsorption efficiency decreases with increasing solution pH, as a result of the sorbent surface becoming neutral, therefore weaking the attraction for anionic PFAS in the solution.[168]

While short-chain PFAS are primarily removed by ion exchange resins via electrostatic interactions, the adsorption of long-chain PFAS is enhanced by the formation of micelles and hemimicelles on the positively charged surface of the sorbent.[27] In general, the adsorption capacity of resins to long-chain PFAS is strongly dependent on the functional group of the sorbent; the more hydrophobic the functional group, the higher the removal efficiency of the resins. Therefore, it is important to select highly hydrophobic resins in the removal of these long-chain substances.[147] Today there are many commercially available PFAS-specific resins produced by industries such as Calgon Carbon Corporation, DuPont Water Solutions, Purolite etc., which are used in the remediation of PFAS contaminated water. These resins are typically used in a single-use-and-dispose mode. The used resins are disposed of via thermal destruction. This option is often preferred over the multi-used resins because the regeneration of the latter requires high energy and organic solvents, such as methanol, and due to the existing challenge of managing PFAS contaminated methanol and its risk of leaching in treated waters.[168] It is however, critically important to conduct thermal destruction at high enough temperatures in order to mineralize the PFAS to minimize the transfer of contamination from water to air.[169]

Polymers Polymeric materials have been employed as sorbents for PFAS removal in various studies. For example, Wu et al., 2020 compared cyclodextrin polymers (CDPs) to AC and reported that CDPs achieved a near complete removal of both long and short-chain PFAS in environmental groundwater. This high PFAS removal efficiency was facilitated by adding a protonated crosslinker that is able to encapsulate anionic PFAS, therefore offering more adsorption sites via electrostatic interactions. Moreover, it was reported that the cavity of the CDPs monomer most likely contains the active adsorption sites.[167] Nanomaterial-based PANTs exhibited a very high adsorption efficiency for PFOS (100%) and PFOA (88%) mainly via electrostatic interactions, which was verified by varying solution pH and observing a decreased adsorption capacity by increased solution pH, in addition to contribution from hydrophobic interactions.[140] MIP have been reported to have a low adsorption efficiency towards short-chain PFAS (between 14% and 52%) while they exhibited a higher removal efficiency of longer chain PFAS (up to 83%), indicating that the uptake of PFAS by MIP is strongly related to the hydrophobicity of the carbon chain length.[44] On the other hand, organic frameworks (OFs), another type of crystalline and porous polymeric adsorbent, exhibited a high affinity for both short-chain and long-chain PFAS (up to 90% and 98% removal efficiency, respectively). OFs displayed high uptake capacity of PFAS of different chain length and fast kinetics at environmentally relevant concentrations thanks to the different amine functionalities incorporated into their pores such as the covalently-linked amine OFs (NH_2-COFs), therefore proving the potential of this sorbent in short-chain PFAS remediation.[82]

Natural materials Natural materials, such as soil and sludge, have been used in different studies as sorbent materials. In addition, minerals are also frequently used as sorbents thanks to their tunable mesopores and modifiable structure such as the ability to add cationic surfactants for the selective removal of PFAS.[27,170] However, their sorption capacities, especially for short-chain PFAS, is limited compared to other sorbent materials (Fig. 4). Mineral materials such as boehmite, alumina, silica, kaolinite, montmorillonite, and other minerals have been tested for their PFAS uptake capacity.[128,126,123,151] Sorption in clay minerals is reported to be driven by hydrophobic interactions, responsible for PFAS adsorbing to the surface of the mineral to avoid water molecules, in addition to weak electrostatic interactions and hydrogen bonding.[155] The authors reported a clear relationship between the sorption capacity of the minerals and the hydrophobicity of the PFAS, further confirming the dominance of hydrophobic interactions in the adsorption process. Li et al., 2019 studied the adsorption of PFAS of different chain lengths onto soils and reported increased adsorption capacity with increased chain length as a result of the impact of hydrophobic interactions. Interestingly, the authors also reported a significant contribution of hydrogen interactions because of hydrogen bonds formed between fluorine atoms of PFAS and hydrogen atoms in the aluminum oxide or iron oxide in the soil. These hydrogen interactions thus become stronger as the C-F chain length increases.[91] In efforts to increase their affinity towards PFAS, mineral materials were functionalized with other materials. Bhattarai et al., 2014 coated silica by β-cyclodextrin (β-CD) and reported an increase of PFOA adsorption with the increase of β-CD loading, achieving a removal efficiency of 90% thanks to enhanced hydrophobic interactions in addition to hydrogen bonding.[40] However, enhancing the adsorption capacity of silica using doping with β-CD yields lower adsorption efficiency compared to the use of cyclodextrin alone,[37] therefore calling into question the advantage of the novel adsorbent comprising β-CD coated silica.

As part of understanding the removal mechanisms of PFAS in wastewater treatment plants (WWTP), some studies investigated the performance of sludge as a sorbent of PFAS, such as a study by Arvaniti et al., 2014 which looked into the behavior of PFAS sorption at environmentally relevant concentrations. They reported an increase in the sorption capacity with the increase of C-

F chain length.[33] The sludge adsorption capacity reached 90% for the removal of perfluoroundecanoic acid (PFUnDA), a long-chain PFCA with ten fluorinated carbons, while it only achieved 33% for the removal of PFOA, indicating that the sorption process is likely driven by hydrophobic interactions, which can explain the unsatisfactory adsorption efficiency of short-chain PFAS, as observed in Fig. 4.

Other sorbents Efforts have been made by many studies to test other sorbents outside the conventional and most common ones. IFGEM-7 and AGEM-2, so-called "green" sorption media comprising recycled materials, are made mainly of sand, with small amounts of clay and recycled iron and aluminum. They have been tested for their removal capacity of PFOS and PFOA, with reported removal efficiencies up to 46% for PFOS because of the hydrophobic interactions of PFAS with sand, in addition to their electrostatic interactions with clay and iron.[111] Many other engineered materials have been used as sorbents. For example, mesoporous cetyltrimethylammonium bromide (CTAB)-functionalized magnetic microspheres (mesoporous Fe_3O_4@SiO_2@CTAB-SiO_2) were fabricated and tested for their adsorption capacity to trace amounts of PFOS in acidic conditions. The study reported the efficiency of this novel sorbent to adsorb PFAS at ng/L levels thanks to its large specific area and the duality of hydrophobic and electrostatic interactions between PFOS and CTAB.[93] Also at environmentally relevant conditions, Ateia et al., 2018 evaluated the removal of long- and short-chain PFAS from water by poly(ethylenimine)-functionalized cellulose microcrystals (PEI-*f*-CMC) that showed high adsorption capacity for long-chain PFAS. The authors reported a positive correlation between the chain length and the removal capacity of the sorbent, indicating the importance of the hydrophobic interactions in the sorption process, in addition to electrostatic interactions.[36] The performance of

PEI-*f*-CMC in removing short-chain PFAS, however, was less than satisfactory. The sorbent showed the worst performance for PFBA and PFPeA with a removal efficiency of 2.1% and 1.1%, respectively. The removal performance of PFHxA, PFBS, and perfluoropentane sulfonic acid (PFPeS) was slightly higher, with a removal efficiency of 12.9%, 7% and 26.2% respectively, while the removal of PFHpA achieved a removal percentage of 38.9%. Compared to the removal of long-chain PFAS, e.g., 98.8% for PFOS and 87.6% for PFOA, the overall removal efficiency of short-chain PFAS is much lower than that of long-chain PFAS, highlighting once again the challenges of the removal of these short-chain substances from aqueous solutions because of their low hydrophobicity.

Despite the large number of sorbents studied, either engineered or manufactured, to effectively remediate PFAS from the environment, there is a clear knowledge gap on the removal of short-chain PFAS. A large number of the studies reported in this review focus solely on long-chain PFAS, especially PFOS and PFOA. More studies are needed to closely explore the adsorption processes for short-chain PFAS in order to develop sorbents specifically targeted for these substances. Clearly, adsorption mechanisms targeted for short-chain PFAS cannot heavily rely on hydrophobic interactions, given the hydrophilic nature of these compounds.

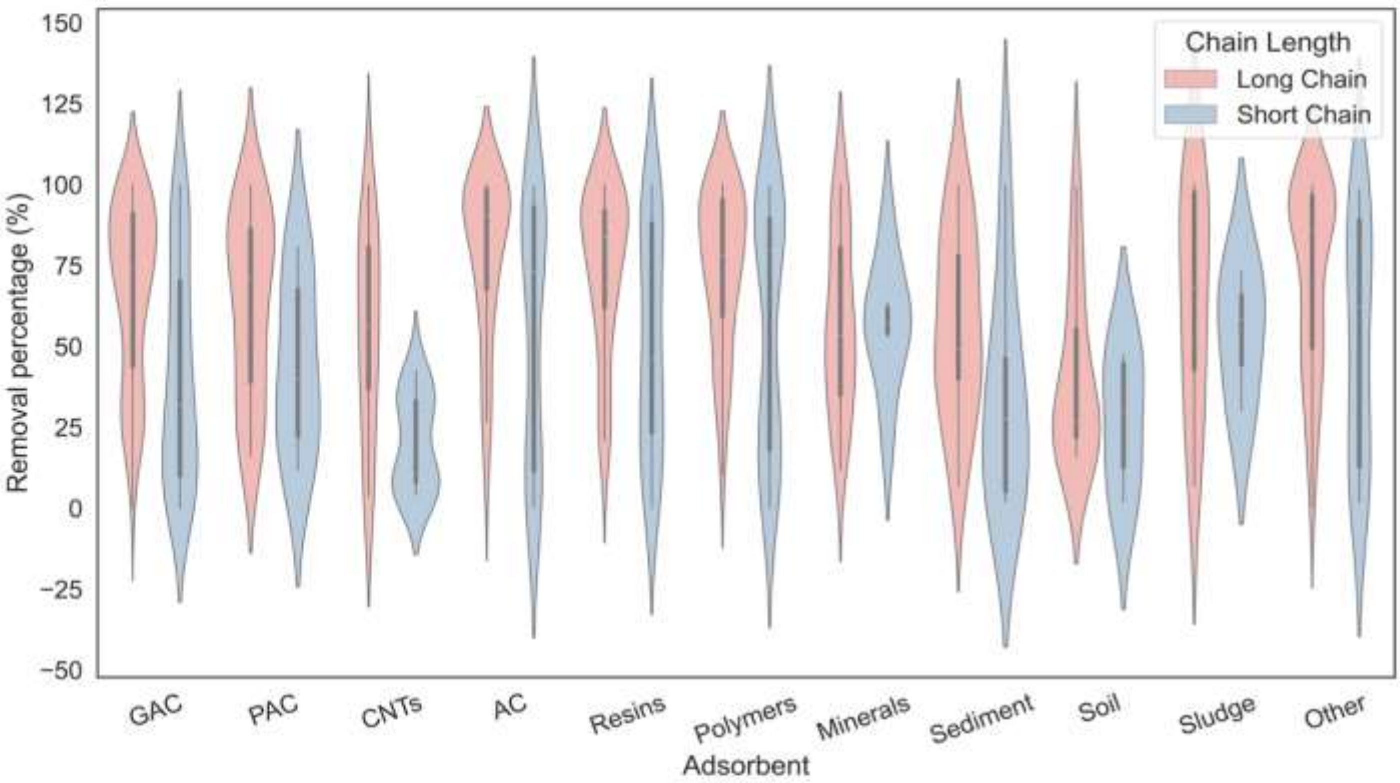

Fig. 4 Removal percentage of long-chain and short-chain PFAS across different sorbents. This violin plot shows the distribution of the removal efficiencies of the different sorbents reported in addition to the kernel density estimation representing the probability distribution for the removal efficiency of each sorbent. Long-chain PFAS distributions are in red, short-chain PFAS in blue. The removal efficiency of long-chain PFAS is higher than that of short-chain PFAS across all sorbents.

Adsorption kinetics and mechanisms

Out of the 136 studies reviewed, only 109 of them noted the type of interaction that could be responsible for the observed adsorption behavior. Of these, 34 studies reported hydrophobic interactions as the dominant mechanism in the sorption of PFAS, 19 studies reported electrostatic interactions, while 48 studied attributed the observed sorption to a combination of both hydrophobic and electrostatic interactions. Eight additional studied reported that other interactions, such as hydrogen bonding, fluorine-fluorine interactions, or ligand exchange, even if weak, contributed to the adsorption of PFAS. Table 1 summarizes the different adsorption mechanisms governing the interactions between PFAS and various sorbents included in this study.

Hydrophobic interactions Hydrophobic interactions are described as the interactions between moieties with hydrophobic properties, e.g. non-polar moieties, causing them to aggregate and therefore minimize their contact with water molecules. The adsorption of PFAS, specifically long-chain PFAS, can be dominated by hydrophobic interactions between the long hydrophobic tail and the hydrophobic surface of the adsorbent even when negatively charged, therefore overcoming the electrostatic repulsion of anionic PFAS. Although PFAS are amphiphilic, they tend to sorb to surfaces rather than stay in aqueous solutions, even if these surfaces are hydrophobic.[27] An example of the hydrophobic interactions in PFAS adsorption is the formation of micelles and hemimicelles around the adsorbent surface which have been reported by many studies[51]. This is especially relevant for long-chain PFAS. PFAS form hemimicelles and micelles when present at concentrations near or higher than the critical micelle concentrations (CMCs) (e.g. 9 mM for PFOS and 38 mM for PFOA).[146] While their formation can enhance the adsorption capacity by attracting more PFAS molecules, micelles and hemimicelles can also block the access of PFAS to the active adsorption sites and therefore reduce the sorption capacity, especially in microporous surfaces. [171] The formation of micelles and hemimicelles is less common for short-chain PFAS since their CMCs are much higher (e.g. 450 mM for PFBS, 199 mM for PFPeA, and 89 mM for PFHxA).[172] Therefore, short-chain PFAS are less likely to self-aggregate on the hydrophobic surfaces of the sorbent, which implies that these short-chain substances are less favorable to be adsorbed via hydrophobic interactions.

Hydrophobic interactions play a crucial role in the removal of PFAS by GAC. In a GAC column study, Park et al., 2020 reported that the breakthrough curves of the PFAS adsorbed by GAC get shallower as the hydrophobicity of the PFAS increases, confirming the importance of the hydrophobic interactions in the adsorption mechanism of PFAS by GAC. The authors also attributed the high concentrations of short-chain PFAS in the effluent to competition for sorption sites by more hydrophobic PFAS and with their displacement by dissolved organic matter (DOM), in addition to pore blockage by other existing micropollutants or organic matter[39], indicating that short-chain PFAS are weakly adsorbed by GAC via hydrophobic interactions.[114] CNTs are characterized by their extreme hydrophobicity, so unsurprisingly the primary interaction with PFAS is also through hydrophobic interactions, as reported by Deng et al., 2012 [62].

Electrostatic interactions Electrostatic interactions are defined as the attraction or repulsion forces between charged molecules.[173] The adsorption of PFAS by positively charged groups present in sorbents such as anion exchange resins, chitosan beads, or alumina, is dominated by electrostatic attractions since some PFAS such as PFCAs and PFSAs are present as anions in the environment. On the other hand, when the adsorbent surface is negatively charged, electrostatic repulsions are established between the sorbent and the PFAS, therefore hindering the adsorption process. However, these electrostatic repulsions can be overcome by hydrophobic interactions, especially for long-chain PFAS.[20]

It has been reported that the electronegativity of acidic PFAS is not only from the functional group (e.g. carboxylate or sulfonate) but is also due to a negatively charged shell stemming from the highly electronegative fluorine atoms, which can provide very weak interactions with positively charged sorbents.[27] The presence of electrostatic interactions in the process of PFAS adsorption has been verified by the effect of varying pH solution in many studies. It has been reported that the adsorption capacity of the positively charged sorbents decreases with increasing pH, since the basic groups of these sorbents are deprotonated and become neutral. Wang and Shih, 2011 reported that alumina's adsorption capacity for PFOS and PFOA decreased with increasing solution pH as a result of the decrease in available positively charged active sites.[128] Electrostatic interactions in PFAS adsorption are also affected by the solution's ionic strength, for example decreasing with the increase of cation concentration (ionic strength).[174] This is explained by the compression of the electric double layer causing the electrostatic interactions between PFAS and the positively charged adsorbent to weaken and reduce the number of effective adsorption sites.[38] The removal of short-chain PFAS is heavily dominated by electrostatic interactions, since the hydrophilicity of these substances limits their sorption by hydrophobic interactions in comparison to long-chain PFAS. Moreover, the electrostatic interactions of the short-chain PFAS in ion exchange resins are facilitated by their ability to orient their functional head groups towards the ion exchange active sites and therefore allow more effective pairing with the positively charged resins. Long-chain PFAS, in addition to having electrostatic interactions with the charged head of the ion exchange resins, also interact with the hydrophobic resins thanks to hydrophobic interaction between their hydrophobic tail and the hydrophobic non-functionalized surface of the resin.[90] Therefore the resin itself plays more of an active role in the adsorption of long-chain PFAS.

Hydrogen bonding The hydrophobicity of the C-F chain makes it hard for PFAS to form hydrogen bonds with the functional group of the sorbent containing nitrogen or oxygen.[20] However, it is possible for hydrogen bonds to form between the fluorine atoms in PFAS and sorbents containing hydroxyl groups (-OH) which play the role of hydrogen donors.[129] Li et al., 2017 reported that hydrogen bonds formed between melamine-formaldehyde resin microspheres (MMFRS) and deprotonated PFOS and dominated the adsorption process at a pH of 2.[92] In general, hydrogen bonding that may form between PFAS and sorbent is easily outcompeted by hydrogen bonds formed between water molecules in the bulk solution and the oxygen atoms in the sorbent's functional groups, therefore making hydrogen bonding an insignificant mechanism in PFAS sorption processes.[27]

Ligand and ion exchange and fluorine-fluorine interactions Ligand and ion exchange have also been reported as possible mechanisms of adsorption for PFAS, especially to sorbents containing hydroxyl groups and ions, such as metal oxides, that form inner sphere complexes.[171] Shih and Wang, 2012 reported that PFAS replaced the hydroxyl functional group in the adsorption process on boehmite via ligand exchange interactions that can be enhanced by decreasing solution pH, resulting in an increase of positive sites on the sorbent surface.[126]

Another mechanism that can contribute to the PFAS adsorption process is fluorine-fluorine interactions. These types of interactions occur between the fluorine atoms of the C-F chain and fluorine atoms of the sorbent. Efforts have been dedicated to synthesize fluorine containing sorbents to increase the uptake of PFAS from aqueous solutions. Du et al., 2017 synthesized a novel fluorinated adsorbent, magnetic fluorinated vermiculite, to enhance the sorption of PFOS in wastewater.[67] Cao et al., 2017 added a functional monomer, trifluoromethyl acrylic acid (TFMAA) to MIP and reported an enhancement of PFOA adsorption and fast kinetics thanks to fluorine-fluorine interactions.[45] Similar efforts were made in a study by Guo et al., 2018 in which TFMAA was similarly employed as a functional structure to MIP to enhance the sorption of PFOS by increasing fluorine-fluorine interactions.[74]

Table 1: Sorption mechanisms governing the interactions between PFAS and sorbents studied.

Adsorbent	**Hydrophobic interactions**	**Electrostatic interactions**	**Hydrogen bonding**	**Ligand and ion exchange**	**Fluorine-fluorine interactions**
GAC	+	−	+		
PAC	+	−			
CNTs	+	+ / −			
AC	+	−	+		
Resins	+	+			
Polymers	+	+			+
Minerals	+	+	+	+	+
Soil	+	+			
Sediment	+	+ / −			
Sludge	+	−			
Other	+	+ / −	+	+	+

(+): indicates that the interaction contributes to the adsorption of PFAS, (−) indicates the interaction hinders the adsorption, such electrostatic repulsions**, (+ /−)** indicates that both electrostatic repulsions and attractions are present between PFAS and the sorbent, while blank cells indicate the absence of the interaction with that specific sorbent.

Overcoming the challenges of short-chain PFAS removal through adsorption

Our meta-analysis showed that fewer studies have focused on the treatment of short-chain PFAS compared their long-chain homologues (Fig. 2). While these short-chain substances have been treated as “emerging” replacements for long-chain PFAS over the past few years, they are now in ubiquitous use. Because of this, there is increasing need to remediate environments contaminated by these substances. [14,16] The challenge of the removal of short-chain PFAS from aqueous solutions is largely due to their problematic physicochemical properties. Short-chain PFAS are more hydrophilic, more mobile in water, and are characterized by their long-range transport potential, which is indicated by their higher water solubility and lower pK_a values (e.g. 0.394, 0.569 and 0.840 for PFBA, PFPeA and PFHxA, respectively)[175] compared to their long-chain homologues. Because of their lower absorbability, the removal efficiency of short-chain PFAS through adsorption is unsatisfactory (less than 50% removal efficiency across all sorbents, Fig. 4). In general, conventional adsorbents are not very effective in lowering short-chain PFAS concentrations to recommended levels under environmentally relevant conditions, [176] (e.g. 10 ppt for GenX chemicals and 2000 ppt for PFBS).[11]

In addition to the adsorption challenges caused by their physicochemical properties, short-chain PFAS removal can also be hindered by the presence of long-chain PFAS, and in the case of anion exchange, by other inorganic anions such as Cl-, NO^{3-} and SO_4^{2-}.[177] However, in the case of activated carbons or other negatively charged adsorbents such as polymers, short-chain PFAS removal can be enhanced by the addition of divalent cations thanks to the surface charge neutralization of the adsorbent surface and to the cation bridging effects between the PFAS headgroup and the negatively charged sorbent surface containing functional groups such OH or COOH.[174] Several studies have reported the use of treatment train approaches for the remediation of PFAS. [28,178,179] The most common PFAS treatment trains are tandem treatment trains and parallel treatment trains. The tandem treatment train combines different types of remediation techniques, such as removal technologies involving adsorption, filtration, or reverse osmosis, with degradative technologies involving electrochemical, sonochemical or photochemical degradation. Parallel treatment trains combine similar removal technologies, e.g. conducting two or more degradative or adsorptive technologies in succession.[180]

Since both hydrophobic and electrostatic interactions are important mechanisms in the removal of PFAS, and since short-chain PFAS lack the hydrophobicity needed to establish sufficient hydrophobic interactions to ensure effective removal from contaminated samples, it is important to focus on increasing the electrostatic interactions when designing experiments aiming to remove short-chain substances. This could be achieved by a combination of technologies when treating environmental samples, such as GAC, ion exchange resins and polymeric adsorbents. Based on the preceding review of available technologies, we propose a treatment train involving different adsorption materials to specifically target the removal of short-chain PFAS. First, the removal of long-chain PFAS and any other competing hydrophobic ligands such as fatty acids present in the environmental sample could be performed by flowing the sample through a GAC column (Fig. 5A). This first step can help minimize competition of other molecules with short-chain PFAS. Then, the pre-treated sample can undergo a second treatment through ion exchange, targeted for the removal of short-chain PFAS (Fig. 5B). In this second step, it is important to select a sorbent surface with high point of charge pH (pH_{pzc}) to achieve a positive surface potential to attract anionic short-chain PFAS present in solution.[21] Moreover, ensuring an acidic pH increases the number of positive active sites in the sorbent surface.[168] Finally, the sample can go a final treatment step using a polymeric adsorbent such as β-CDPs in which increasing divalent and trivalent cation concentrations in the solution along with decreasing solution pH helps suppress the negative potential and prevent the deprotonation of the sorbent surface functional groups, respectively to further adsorb any short-chain PFAS substances left (Fig. 5C).

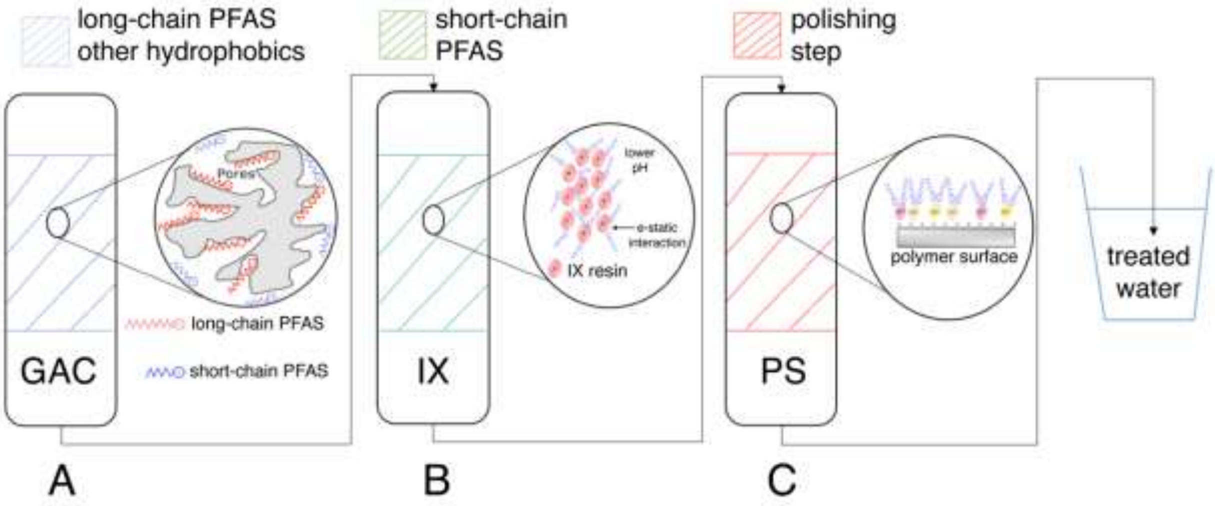

Fig. 5 Proposed treatment chain: pre-treatment using **(A)** granular activated carbon (GAC) for the initial removal of long-chain PFAS and any other hydrophobic ligands present in the environmental sample through hydrophobic interactions, leading to **(B)** subsequent treatment of short-chain PFAS by ion exchange (IX) resins and then to **(C)** a final treatment step to remove remaining short- chain PFAS by a polymeric sorbent (PS).

Economic considerations of the proposed treatment train and future recommendations

The treatment train proposed maximizes the adsorption of short-chain PFAS by minimizing competition with any other long-chain PFAS and hydrophobic substances that might exist in the water sample, and by favoring the electrostatic interactions by optimizing the solution chemistry (e.g., increasing cation concentrations, lowering the solution pH, etc.). However, implementing such a treatment train comes with increased costs. The cost of PFAS treatment by GAC is a function of both the concentration of PFAS in solution and the targeted concentration goal in the effluent. As an illustrative example, Belkouteb et al., 2021, estimated an annual cost of 0.058 euros per m^3 for a treatment goal of 25 ng/l using GAC. [39] Logically, the annual operation cost would increase as the treatment goal dictated by the regulatory limits decreases, which means that the cost of implementing this treatment train would be higher to meet the most recent regulations set by the USEPA. In addition, the regeneration cost, which is also included in the annual operating costs, would increase as lower treatment goals are adopted. The cost of the removal of PFAS by ion exchange resins and polymer adsorbents is also tied to the quality of the influent, to the unit media cost and to the media changeout frequency.[181] Although its performance is superior to that of GAC when it comes to the removal of short-chain PFAS (Fig.4), adsorption using ion exchange resins is less cost effective than carbonaceous materials, namely GAC and PAC. In fact, Murray et al., 2021 estimated the unit media cost for ion exchange to be 6.5 times higher than that of GAC.[181]

Estimating the cost of a PFAS treatment train is difficult given the different governing factors such as system conditions (influent quality, concentration of PFAS, media selection), in addition to maintenance and regeneration costs. Promoting such a treatment train for remediation of PFAS-contaminated waters requires the optimization of the treatment processes and reducing the total cost of materials and energy consumption. Treatment costs for GAC could be optimized by decreasing the operational flow rate in order to increase the operational life of the column[39]. Moreover, the use of efficient sorbents with higher service volume will help reduce the operational costs, for example, using regenerable ion exchange resins and polymer materials will increase the economic viability of the treatment train, though optimization of ion exchange regeneration methods is required, since it is argued that single-use-and-dispose might be preferred because of simplicity of use.[168] However, the ultimate solution to treat contaminated waters is to phase out or, at least, reduce the production and use of short-chain PFAS, especially the non-essential ones by assessing whether these substances are essential for the health and safety of society and whether there are any other "technically and economically feasible alternatives".[4]

Conclusion

This review summarizes and critically evaluates the sorption capacities of different sorbents on the removal of both long- and short-chain PFAS from aqueous solutions. Carbonaceous materials, namely GAC and PAC, in addition to resins are the most widely used sorbents for PFAS remediation. The adsorption capacities of short-chain PFAS across different sorbents remain limited compared to their long-chain homologues because of their low hydrophobicity. In general, carbon-based sorbents are more effective in the removal of long-chain PFAS, since the adsorption process is highly dominated by hydrophobic interactions. Ion exchange resins display higher removal efficiency for short-chain PFAS compared to carbon-based sorbents such as GAC and PAC, since the adsorption process is a governed by both hydrophobic and electrostatic interactions. Polymers, natural materials such as minerals, soil, and sediments, have also been used in various studies as sorbents. However, their removal efficiency, especially for short-chain PFAS, remains limited. The meta-analysis conducted in this study showed that there is a lack of research on the removal of the emerging PFAS, and most studies focus mainly on the treatment of long-chain PFAS, especially PFOS and PFOA. In addition, there is a research need to move beyond only focusing on PFCAs and PFSAs. As the production of emerging PFAS is increasing as a result of the phase out of legacy PFAS, research on the removal of these more hydrophilic substances from aqueous solutions at environmentally relevant concentrations is urgently needed. Based on the technologies reviewed, a treatment train focusing on the removal of short-chain PFAS, by enhancing electrostatic interactions, was proposed. However, the treatment and maintenance costs for implementing such an approach remain a challenge. Therefore, the improvement of cost efficiency of adsorption as a technology including regeneration costs is critical.

Author contributions

H. Smaili was responsible for data curation, formal analysis, investigation, and writing the original draft. C. Ng was responsible for conceptualization, methodology, project administration, resources, supervision, and review and editing.

Conflict of interest

The authors have no conflicts to declare.

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