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Review

Perfluorooctanoic Acid (PFOA) and Perfluorooctanesulfonic Acid (PFOS) Adsorption onto Different Adsorbents: A Critical Review of the Impact of Their Chemical Structure and Retention Mechanisms in Soil and Groundwater

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Abstract: Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) are emerging contaminants of concern as they persist in natural environments due to their unique chemical structures. This paper critically reviewed the adsorption of PFOA and PFOS, depending on their chemical structure, by different adsorbents as well as soil. Adsorption of PFOS generally surpasses that of PFOA across various adsorbents. Despite having the same number of carbons, PFOS exhibits greater hydrophobicity due to two major structural differences: firstly, it has one extra CF_2 unit and secondly, the sulfonate group in PFOS, being a relatively hard base, readily adsorbs on oxide surfaces, enhancing its adsorption compared to the carboxylate group in PFOA. While comparing activated carbon (AC) adsorption performance, powdered activated carbon (PAC) demonstrates higher adsorption capacity than granular activated carbon (GAC) for PFOS and PFOA. Anion exchange resin (AER) outperforms other adsorbents, with a maximum adsorption capacity for PFOS twice that of PFOA. Carbon nanotubes (CNTs) exhibit two-fold higher adsorption for PFOS compared to PFOA, with single-walled CNTs showing a distinct advantage. Overall, the removal of PFOS and PFOA under similar conditions on different adsorbents is observed to be in the following order: AER > single-walled CNTs > AC. Moreover, AER, single-walled CNTs, and AC exhibited higher adsorption capacities for PFOS than PFOA. In situ remediation studies of PFOA/S-contaminated soil using colloidal activated carbon show a reduction in concentration to below acceptable limits within 12–24 months. The theoretical and experimental studies cited in this review highlight the role of air–water interfacial adsorption in retaining PFOA and PFOS as a function of their charged head groups during their transport in unsaturated porous media.

Keywords: PFOA; PFOS; adsorption; ion exchange; PFAS functional head groups

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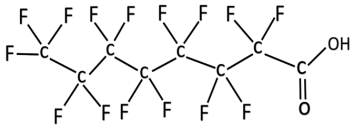
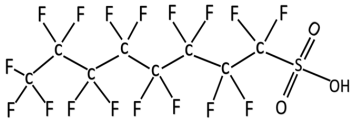
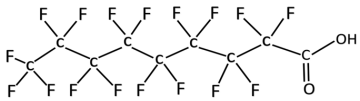
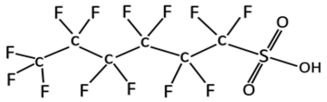
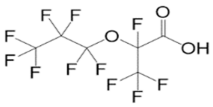
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1. Introduction

Per- and Polyfluoroalkyl Substances (PFAS) are a group of organic compounds of industrial origin, classified as anti-friction agents, surfactants, and repellents. These are persistent in the environment due to their chemical structure. Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) are the most commonly found PFAS, having a carbon backbone with a unique functional head (Table 1). PFOA and PFOS consist of the

hydrophobic carbon fluorine (C–F) chain and hydrophilic carboxyl and sulfonate functional head, respectively [1,2]. This strong C-F covalent bond makes these compounds thermally and chemically stable [3,4]. These compounds have been extensively used in both industrial processes and consumer goods over recent decades. PFAS have been reported to pose harmful impacts on terrestrial and marine animals as well as humans [5]. Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) collectively referred to as PFOA/S are among the widely used PFAS. The release of PFOA/S during manufacturing, usage, and disposal has led to their widespread presence in the environment. The US EPA has established legally enforceable levels for several PFAS compounds found in drinking water. A new guideline established in April 2024 has set limits on five individual PFAS, including perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS), perfluorononanoic acid (PFNA), perfluorohexanesulfonic acid (PFHxS), and hexafluoropropylene oxide dimer acid (HFPO-DA) (also known as "GenX Chemicals"), as well as mixtures of four PFAS compounds: PFNA, PFHxS, PFBS, and "GenX chemicals". For PFOA/S, the maximum contaminant level (MCL) goal is set to be zero. This stricter limit is based on the latest scientific information that there is no safe level of exposure to these contaminants [6,7]. Enforceable MCLs are set at 4.0 parts per trillion for PFOA and PFOS individually, aiming to minimize exposure to these PFAS compounds in drinking water [6–8].

Table 1. Physicochemical characteristics of five legacy PFAS (N/A indicates data not available).

Compound	Abbreviation	Chemical Formula	Chemical Structure	Molecular Weight ($g \cdot mol^{-1}$)	Boiling Point (°C)	Log Kow	pKa
Perfluorooctanoic acid	PFOA	$C_7F_{15}CO_2H$		414.07	192	4.59	−0.20 [9] −0.5 to −3.8 [10,11]
Perfluorooctanesulfonic acid	PFOS	$C_8F_{17}SO_3H$		500.13	249	4.49	−3.27 [9,10,12]
Perfluorononanoic acid	PFNA	$C_8F_{17}CO_2H$		464.08	N/A	5.48	−0.21 [13]
Perfluorohexanesulfonic acid	PFHxS	$C_6HF_{13}O_3S$		400.12	238.5 °C	3.16	0.14 [9]
Hexafluoropropylene oxide dimer acid (GenX)	HFPO-DA	$C_6F_{11}O_3H$		330.06	N/A	N/A	2.8 [14,15]

PFAS have polar head groups with either cationic or anionic properties and hydrocarbon tails [16–19]. Depending on their specific chemical structure and the surrounding environmental conditions, these surfactants exhibit two notable characteristics. Firstly, they can adsorb at the interfaces of aqueous solutions, effectively reducing the surface tension of water. Secondly, they display distinctive behavior when dissolved in aqueous solutions. These molecules tend to self-assemble into aggregates, typically as the concentration increases to a certain level known as the critical micelle concentration (CMC). This results in the segregation of their hydrophobic parts from water. Hence, the compounds produced in this way have high surface activity with both lipophobic and hydrophobic

properties. As a result, it is well-established that fluorinated surfactants when compared to their counterparts (hydrocarbons) have greater surface activity and display greater hydrophobic characteristics [20–22]. Due to the larger atomic size of fluorine compared to hydrogen, perfluorinated tails have limited conformational flexibility, resulting in a heavier and more stable structure [23].

Generally, organic matter particularly organic carbon (OC) has proven to be a significant adsorbent for PFAS [24,25]. The role of several soil components such as OC [26–28], aluminum and iron oxides [29–32], and clay minerals [33–35] still needs to be explored, especially in regards to the changes in their relative contributions with pH variations. PFAS adsorption onto metal hydroxides and organic matter is strongly dependent on pH, but the surface such as clay or silica with small or no charge does not involve pH-dependent binding [31,36]. This happens because the overall contribution of hydrophobic interactions to adsorption is significant. Therefore, in soils where silicates dominantly form hydrophobic interactions, the binding of PFAS would be independent of pH compared to soil consisting of metal hydroxides and organic matter as primary adsorbents.

There is a plethora of literature on the removal of PFAS through adsorption depending on the structural aspects such as chain length [37–39]. The available literature has primarily focused on PFAS removal through adsorption under certain environmental [40] and experimental conditions including PFAS concentration [41,42], adsorbent dosage [43], temperature, and pH [40,43]. However, important structural aspects such as the functional head group and how their adsorption behavior relates to changes in the above-mentioned variables, have not been critically reviewed. In order to develop advanced adsorbents with efficient adsorption of PFOA/S, it is important to focus on strategies to control these variables, for example, by using responsive materials and tailored surface chemistries. The existing literature is also limited in its focus on the removal efficacy through adsorption from surface water [44] and drinking water [40,45].

Therefore, to fill the existing knowledge gaps, this review paper aims at providing a comprehensive overview of the effect of PFOA and PFOS head groups (–COOH and $–SO_3H$ groups for PFOA and PFOS, respectively) on the process of adsorption onto different adsorbents, and critically analyzing the effect of operational parameters such as pH on these respective functional head groups. Additionally, it explains the significance of adsorption taking place at the air–water interface and its occurrence in groundwater as a relevant adsorption mechanism. Finally, it establishes the surface tension and adsorption of PFOA/S at the air-water interface as a function of the head group by explaining the surfactant nature of PFOA/S through their surface activity. Since PFOA/S adsorption at the air–water interface is contingent on the compound's surface activity, it is directly influenced by the ionic strength of the solution and the size and concentration of PFOA/S.

2. Per- and Polyfluoroalkyl Substances (PFAS) Physicochemical Characteristics and Occurrence in the Environment

Understanding the physicochemical properties of PFAS is essential to comprehend their behavior and transport in the environment. PFAS take advantage of the ideal overlap between 2s and 2p orbitals of fluorine and the carbon orbitals in the C–F bonds, resulting in several dipolar resonance structures along the perfluoroalkyl chain [46]. The C–F bond strength becomes even greater as more fluorine atoms are attached to the central carbon atom. The three lone pairs on fluorine atoms, along with their partial negative charge, contribute to both steric and electrostatic shielding. Kinetic stability arises from the fluorine atoms shielding the central carbon, protecting PFAS from nucleophilic attacks on that carbon [46,47]. Hence, the C–F bond is highly stable thermodynamically, making PFAS molecules inert and persistent [48].

The strong electronegativity of fluorine makes the C–F bonds in the perfluorinated tail highly polarized. In the C–F bond, the shared electrons are drawn toward the fluorine atom (δ−) because the sp^3-hybridized carbon is strongly electropositive (δ+). Additionally, the small atomic radius of fluorine contributes to its strong polarization energy [49,50].

PFAS display both lipophobic and hydrophobic characteristics, mainly due to the low polarizability of fluorine atom. With the shortening of the carbon-chain length, the water solubility of PFAS is enhanced [51] and its lipophilicity is decreased, as evident through changes in their octanol/water partition coefficients (Kow) (Table 1). At environmentally relevant pH levels, these compounds exist as anion, as reflected by their low pKa values (Table 1). PFAS possess additional attributes, including resistance to biological [19], chemical [52,53], and thermal degradation [54], as well as being stable during redox processes [55]. These distinctive characteristics make PFAS favorable for numerous commercial, military, and industrial contexts and have resulted in a broad dissemination of these compounds within the natural environment [56–60]. Details including the compound name, chemical formula, chemical structure, molecular weight, boiling point, Log Kow, and pKa of eight of the most reported PFAS compounds associated with environmental pollution are shown in Table 1.

While the C–F chain of typical PFAS exhibits hydrophobic characteristics, the presence of the functional head (such as carboxylate or sulfonate) in PFOA/S can enhance their water-solubility and hence mobility within an aqueous environment [61,62]. Consequently, PFOA/S are often found in stormwater runoff [63], coastal water [64,65], wastewater [66], surface water [67–69], groundwater, sediments [69], sea water [70], and drinking water [71]. PFOA/S concentrations in samples from surface water and groundwater have been recorded in the range of up to several hundreds of micrograms per liter (μg/L) [67–69]. In the case of soils and sediments, concentrations are reported within the range of several hundreds of micrograms per kilogram (μg/kg) to a few thousands of milligrams per kilogram (mg/kg) [72]. The latest analysis on the occurrence of PFOA and PFOS in groundwater revealed measured concentration levels of up to 300 μg/L and 2000 μg/L, respectively [60]. The recent US Environmental Protection Agency (US EPA) and Food Standards Australia and New Zealand (FSANZ) guidelines regarding PFAS are shown in Table 2.

Table 2. "Health based guidance values" established by the Commonwealth Department of Health, Australia, US EPA, Health Canada, and European Union providing limits for PFOA and PFOS.

Toxicity Reference Value	PFOS	PFOA	Authority	References
Drinking water, MCL (μg/L)	0.004	0.004	US EPA	[6,7]
Latest restriction toxic PFAS in drinking water	0	0		
Tolerable daily intake (μg/kg/d)	0.02	0.16	Commonwealth Department of Health, Australia	[73]
Drinking water quality guideline (μg/L)	0.07	0.56		
Recreational water quality guideline (μg/L)	0.7	5.6		
Sum of all PFAS	<30 ng/L		Health Canada	[74]
Sum of all PFAS	<500 ng/L		European Union	[75]
Sum of 20 selected PFAS	<100 ng/L			

Research shows PFOA/S contamination in groundwater and soil at numerous firefighting training facilities and other locations [16,58,76–78]. Although a significant number of sites contaminated by PFOA/S are linked to defense installations, contamination of groundwater has been detected in settings other than defense and military, such as airports and manufacturing plants [56,57,60].

Human exposure to PFOA/S can primarily occur through various pathways, including consumption of food contaminated during farming activities or directly coming in contact with cookware and food packaging containing PFOA/S-based coating or material [79], drinking contaminated water [80], and inhaling air and dust containing PFOA/S [81]. However, the primary exposure pathway of PFOA/S is likely through the contaminated-food consumption [82]. Epidemiological investigations have shown strong associations between certain PFOA/S compounds and a range of negative health outcomes, including reproductive and developmental issues, liver and metabolic toxicity, immune system impairments, the development of tumors, disruption of endocrine functions, neurological damage, and the promotion of obesity [83].

3. Adsorbents for Perfluorooctanoic Acid and Perfluorooctanesulfonic Acid (PFOA/S) Removal

This section provides an overview of the three main adsorbents investigated in the available studies for the removal of PFOA/S from water.

3.1. Activated Carbon (AC)

AC is a carbonized organic material produced through the process of pyrolysis under anaerobic conditions [84,85]. The material becomes porous and increases in surface area through thermal or chemical activation resulting in improved adsorption [86]. AC is commercially available as granular activated carbon (GAC), powdered activated carbon (PAC), and carbon fibre, and is used for the removal of several contaminants in water treatment facilities. AC prepared through sewage sludge showed 91% of PFAS removal [87]. Similarly, the leaf waste of *Vitis vinifera* was also used to prepare AC with the removal efficiencies of 94% and 95% for PFOA and PFOS, respectively [88]. Chemically activated maize tassel (CAMT) was also investigated for PFOA/S removal and showed the adsorption capacities of 239.1 mg/g and 204.8 mg/g for PFOA and PFOS, respectively [89].

3.2. Anion Exchange Resins (AERs)

Anion exchange is an important adsorption mechanism. It is the process where negatively charged ions such as HCO_{3-}, Cl^{-}, and OH^{-} on the surface of polymeric resins are reversibly exchanged to the compounds in the aqueous media [90]. The use of anion exchange became common because of its effectiveness through great exchange capacities, small footprint, easy operations, and regeneration [91–95]. The intrinsic properties of AER are based on their functional groups (tertiary ammonium/quaternary ammonium), cross-linkages (gel-base or macroporous), and polymeric matrix (styrenic vs. acrylic). Moreover, the fundamental properties such as exchange capacity (equivalent (eq) per L of resin), water content, and particle size [96–100] also make them effective adsorbents for PFAS removal.

3.3. Carbon Nanotubes

Carbon nanotubes (CNTs) are another carbon-based adsorbent such as AC [101,102]. CNTs have some favourable properties that make them effective adsorbents for several environmental pollutants including PFAS. Their high adsorption capacities are based on strong hydrophobicity and large surface area [102,103]. Chen, Xia [103] conducted a study on the adsorption behavior of PFOS on three different CNTs and observed a rapid adsorption equilibrium (2 h). PFAS-contaminated water was successfully treated with multi-walled carbon nanotubes (MWCNTs) modified with nano-metals such as Zn, Cu, and Fe [104]. In addition to high adsorption capacity, the ability of CNT to resist acid and alkali makes them suitable for applications where materials need to withstand corrosive environments.

4. Perfluorooctanoic Acid and Perfluorooctanesulfonic Acid (PFOA/S) Adsorption Mechanism

The primary mechanisms of the adsorption of PFOA/S onto various adsorbents are electrostatic and hydrophobic interactions. Additional mechanisms include hydrogen bonding. The efficiency of PFOA/S adsorption is influenced by various parameters, including the molecular structure of PFOA/S, the chemical and physical properties of the adsorbent material (such as functional groups on adsorbent surface, polarity, and porosity), and the liquid phase composition [61] such as temperature, pH, ionic strength, surface tension, surface activity, and the air–water interface [105,106].

4.1. Electrostatic Interactions

Electrostatic interactions take place between anionic PFOA/S and positively charged adsorbent materials. Therefore, changes in ionic strength and solution pH resulting from the presence of co-occurring inorganic anions can impact adsorption capacity by introducing electrostatic repulsions between PFOA/S and the adsorbents [61]. A shift in the solution pH can influence the charge properties of PFOA/S molecules as well as the surface characteristics of adsorbents [107,108].

4.2. Hydrophobic Interactions

Long-chain PFAS, including PFOA and PFOS, are primarily retained through hydrophobic interactions [38]. Additionally, adsorbents featuring amine groups tend to exhibit greater adsorption capacities for these compounds [61]. Adsorption plays a crucial role in influencing PFOA/S distribution at solid–liquid interfaces and its behavior in the aquatic systems. A number of adsorbents, including CNTs and AC, have been studied for the adsorption of PFOS [19,61,109–112]. The hydrophobic perfluorinated (C–F) chain of PFOA/S adheres directly to the hydrophobic adsorbent sites through hydrophobic interactions [19,61,102]. Additionally, the adsorption of PFOA onto CNT reveals that PFOA adsorption through the tail (C–F chain) touches perpendicular to CNT with the hydrophilic head (–COOH) being in water [102].

4.3. Anion and Ligand Exchange

This mechanism is relevant to anionic PFAS such as PFOA and PFOS which contain–COOH and $–SO_3H$ functional groups, respectively. Hence, PFOA/S are adsorbed onto the adsorbent surface through anion exchange and ligand exchange [113]. Moreover, in soils, the adsorption of PFAS is enhanced through the formation of complexes between the hydroxy bonds of aluminum and iron (hydro) oxides present in soils [61,114].

4.4. Hydrogen Bonding

Hydrogen bonding is another significant adsorption mechanism for PFAS but its role in soil remains contentious [115]. This is because of the C–F bond that is hydrophobic and water repelling [116] making it hard to form hydrogen bonds with the hydrogen atoms attached to the oxygen and nitrogen atoms of functional groups in soil. However, the oxygen atoms in PFAS functional groups can form hydrogen bonds with functional groups found in soil [61,117]. Additionally, in soils, the surface hydroxyl groups of iron and aluminum (hydro) oxides can form hydrogen bonds with the PFAS terminal groups. Oxygen atoms from the functional group can become an acceptor of hydrogen bond, thereby enhancing the adsorption of PFAS through iron and aluminum (hydro) oxides present in the soil [118].

4.5. Charge-Assisted Hydrogen Bonding (CAHB)

In bulk solutions, PFAS face competition from water molecules, making hydrogen bonding insignificant for PFAS adsorption in such cases. However, charge-assisted hydrogen bonding (CAHB) can take place between the functional groups on the adsorbents and functional groups of PFAS [119]. Hence, the potential formation of CAHB between PFAS and the organic functional groups on the adsorbents having nitrogen and oxygen atoms should be given due significance since the strength of CHAB is greater than the ordinary hydrogen bond [61,119].

5. Adsorption as a Function of Perfluorooctanoic Acid and Perfluorooctanesulfonic Acid (PFOA/S) Head Group

There are a limited number of studies focusing on the removal of PFOA/S based on their functional head groups. Therefore, through this review, we have cast light on the structural aspects of PFOA/S that have been overlooked in previous review papers but are significant determinants of the adsorption behavior of PFOA/S compounds. This section discusses the adsorption capacities of PFOA and PFOS onto different adsorbents such as activated carbon, resins, and carbon nanotubes. Despite having a similar C–F chain length and number of carbons, a major difference of the adsorption of PFOA/S is attributed mainly to their different functional groups [120] and an additional C–F unit on PFOS resulting in its stronger hydrophobicity [19,121–123]. As evident from Figure 1, PFOS showed the adsorption capacity as compared to PFOA for all tested adsorbents under a pH range of 4–7 at 25 °C. Surface basicity of PFOS is believed to be a more dominant property than hydrophobicity or polarity [53,124]. PFOS having a sulfonate head group is more readily adsorbed onto oxide surfaces [112]. Adsorbents having charged groups (e.g., amine) also show lesser uptake of PFOA [125,126].

Figure 1a,b represent the adsorption of PFOA and PFOS onto AC and consistently demonstrate higher adsorption capacities of PAC than that of GAC under the same experimental conditions [10,112,127]. The difference is linked to the greater surface area of PAC to its volume ratio as compared to GAC. Figure 1c,d indicate that similar to AC, AER with a few exceptions, also has a higher affinity for PFOS [128]. The maximum measured adsorption of AER for PFOS was two times higher than PFOA.

Moreover, PFOA adsorption onto CNT was lower than PFOS by two-folds. Previous studies have indicated hydrophobic interactions as the dominant force for the adsorption of organic compounds onto CNTs [102,109,110,129]. While the C–F chain of PFOA adsorbs onto a single-walled carbon nanotube (SWCNT) by hydrophobic interactions, the carboxyl head being hydrophilic stretches out to the aqueous solution due to the electrostatic repulsive forces between the CNT surface and carboxyl group [109]. The adsorption of C–F chain happens normally in the same direction of the CNT axis, which allows the chain to rigorously adsorb along the curvature of the CNT surface. The surface of CNT is only partially covered by anionic PFOA: firstly, because of the steric hindrance developed by the adsorbed PFOA to the approaching molecules and secondly, due to the electrostatic repulsion between the polar head groups, which are also anionic in nature [109]. Additionally, adsorption of PFOS by a magnetic mesoporous CNT (MMCNT) is also higher than PFOA [130]. The persistently higher adsorption amount of PFOS in comparison to PFOA onto different types of CNT is attributed to the structural difference due to the functional heads of PFOA/S [130] and relatively higher hydrophobic attraction of PFOS than PFOA due to an extra C–F unit [120].

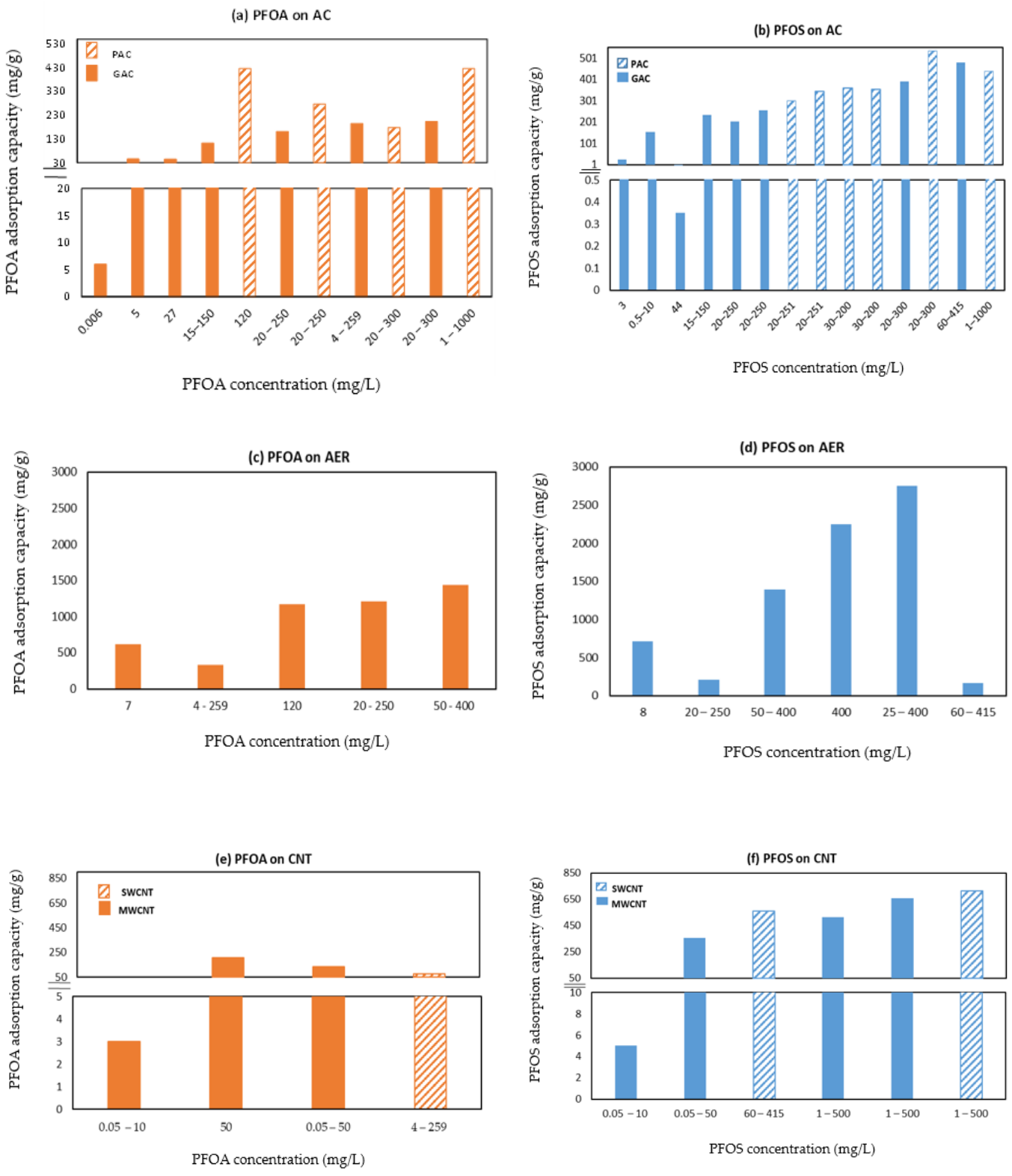


Figure 1. Reported adsorption capacities of PFOA and PFOS through the Langmuir isotherm model, on different adsorbents. (**a**) PFOA adsorption on AC (n = 8), (**b**) PFOS adsorption on AC (n = 9), (**c**) PFOA adsorption on AER (n = 4), (**d**) PFOS adsorption on AER (n = 6), (**e**) PFOA adsorption on CNT (n = 4), and (**f**) PFOS adsorption on CNT (n = 5) (matrix: deionized water (DI), pH: 5–7, temp: 25 °C, varying adsorbent doses) (data for all figures are available in Supplementary Materials, Table S1). Data with a wide range of adsorption capacities are plotted on break-in axis bars (**a**,**b**,**e**,**f**).

Furthermore, while comparing the adsorption of PFOA/S onto two different CNTs (SWCNT and MWCNT), SWCNT showed higher adsorption capacity for PFOS (Figure 1f) [102,103] because of its higher specific surface area [40,102]. Recently, SWCNT has gained great attention as an adsorbent for a range of water pollutants including PFAS due to several favorable physiochemical properties such as strong hydrophobicity, distinctive one-dimensional hollow tubular structure, and higher specific surface area [102,103]. On the contrary, the relatively lower adsorption capacity of MWCNTs is attributed to their lower Brunauer, Emmett and Teller (BET) surface area [103,120]. Practically, MWCNT twists or reunites together due to Van der Waals forces that results in fewer number of surface sites available for adsorption [131]. The flat C–F chains are adsorbed onto the surface, making hemi-micelles and micelles impossible on the surface of MWCNT, resulting in its lower adsorption capacity. However, MWCNT provides a positive surface to the hydrophilic carboxyl head of PFOA and allows for adsorption through electrostatic attraction [132]. In addition, MWCNT contains some amorphous carbon and metal catalysts, directly weakening their sorption properties [132]. Although MWCNT is not favored for PFOA/S adsorption when compared to SWCNT, their performance can however be improved by engineering them with hydroxyl and carboxyl groups [133]. In addition, the treatment of MWCNT with strong oxidant or acid can also enhance its adsorption capacity [107].

Finally, when the adsorption affinities of microporous AC, AER, and CNT, for the removal of PFOA/S were examined under similar experimental conditions, adsorption occurs in the following order: AER > single-walled CNTs > AC. However, the latter two did not vary significantly. PFOS adsorption was 1.9, 1.8, and 1.2 times higher onto AER, single-walled CNT, and AC, respectively, than that of PFOA, because of its more favorable structural properties [134,135] discussed earlier in this section. The higher adsorption onto resin can be explained by its swellable properties. The Freundlich isotherm model explains the swellable properties of resins and other polymeric adsorbents by a transitional mechanism between its original glassy state (hard) to a rather rubbery (soft) state [136,137]. The glassy phase has limited sorption sites; therefore, the hole-filling mechanism dominates, making the process of adsorption more competitive and non-linear (concentration-dependent). A rubbery phase, on the other hand, has ephemeral sorption sites and dissolution dominates the process, making adsorption linear and not competitive [53]. Another compelling reason for the higher adsorption capacity of resin is its unique pore structure and great hydrophobicity in addition to the better swelling characteristics [138]. For example, due to the swelling properties, resin was able to adsorb the floating oil as well as the heavy organic solvents underwater with high selectivity and great adsorption potential [138].

6. Combined Impact of Perfluorooctanoic Acid and Perfluorooctanesulfonic Acid (PFOA/S) Head Group and Solution pH on Adsorption

Solution pH significantly affects PFOA/S adsorption [115,139]. The effect of pH on adsorption has been studied extensively, but its effect with respect to the PFOA/S functional head group has received limited attention in the available critical review papers. That aspect is discussed in this section focusing on adsorbents such as AC, AER, and CNTs, which show different adsorption performances.

Surface properties of both the adsorbent and adsorbate are strongly dependent on the solution pH [11,140]. The reported pKa values of PFOA (in the range from −0.2, −0.5, to 3.8) [10,121,141] and PFOS (−3.27) are lower than the pH range (3–7) mostly investigated in the available studies. PFOA partly and PFOS fully exist in deprotonated forms above pH 3 [10]. Generally, as seen in Figure 2a,b, the adsorption of both the

compounds onto AC increased as the pH increased from 3 to 5, and then decreased with the further increase in pH for adsorbate concentrations within a comparable range. With significant dissociation in the investigated pH range, the increase in adsorption with pH indicates that the electrostatic interaction is the dominant adsorption mechanism between the anionic heads of PFOA/S and positively charged AC surfaces [140,142]. However, adsorption through the hydrophobic interaction can be more pronounced in PFOS than PFOA due to an additional CF_2 [112,143].

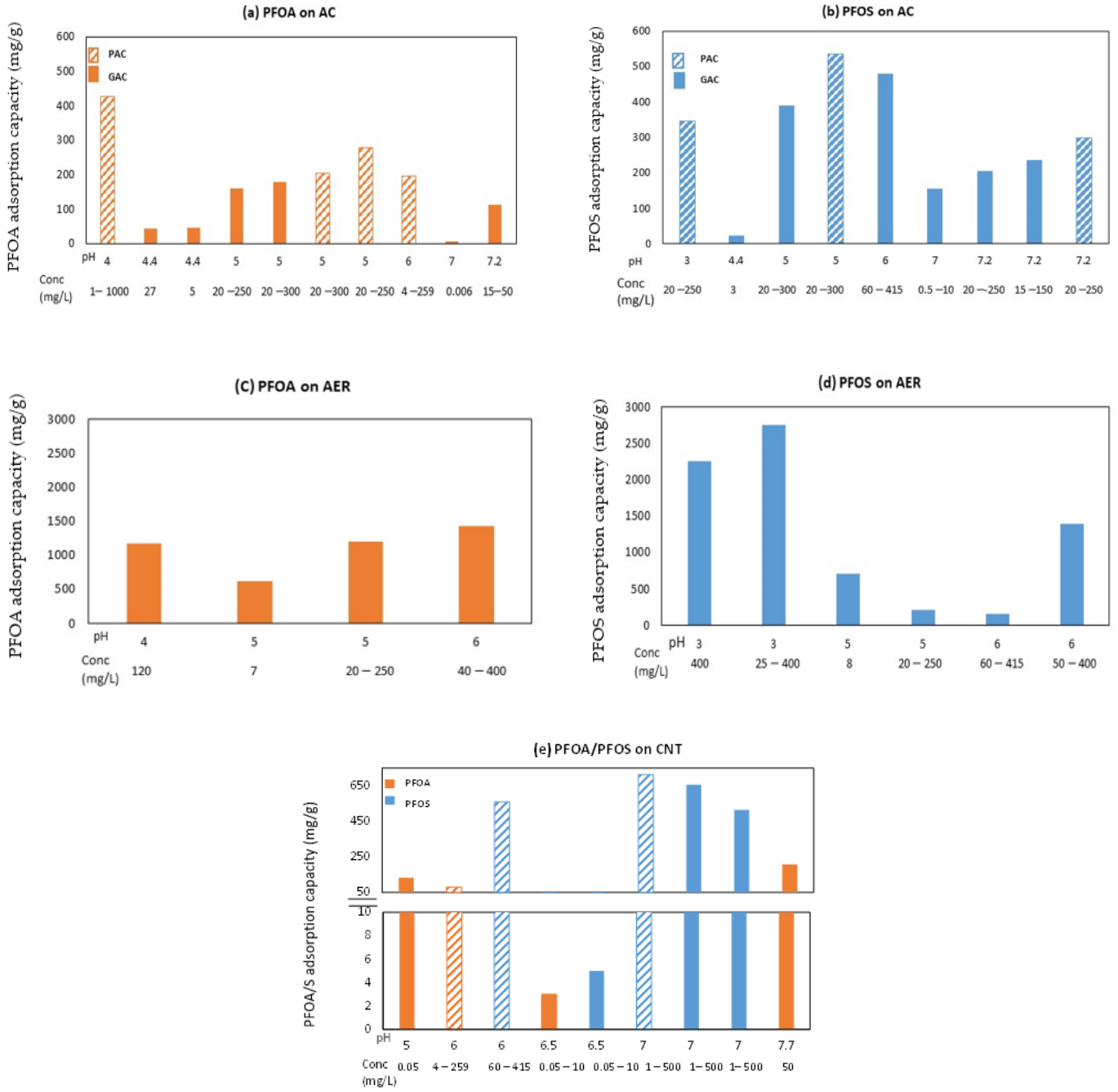


Figure 2. Reported adsorption capacities of PFOA and PFOS through the Langmuir isotherm model on different adsorbents. (**a**) PFOA adsorption on AC (n = 7), (**b**) PFOS adsorption on AC (n = 6), (**c**) PFOA adsorption on AER (n = 4), (**d**) PFOS adsorption on AER (n = 6), and (**e**) PFOA/S adsorption on CNT (n = 6). (Data for all figures are available in Supplementary Materials, Table S1). Data with a wide range of adsorption capacities are plotted on break-in axis bars (**e**).

In addition to the hydrophobic and electrostatic interactions, the anion exchange through surface basicity of AC is also a significant mechanism influencing PFOA/S adsorption onto AC [144]. Because of the presence of different acidic and basic groups on the AC surface, changes in pH result in variations in pKa values. Hence, a significant difference in PFOA/S adsorption by AC at pH 7 and 3 is ascribed to the changing anion exchange capacity as the pH changes [145].

The available literature discusses the removal of PFOA/S through adsorption mainly based on three types of adsorption mechanisms: hydrophobic interactions, anion exchange, and electrostatic interactions. However, another important interaction is based upon the formation of negative/positive charge-assisted hydrogen bonding ((−)/(+) CAHB) [119]. (−) CAHB is a relevant interaction for the sorption of PFOA/S but is inadequately covered in the available literature. (−) CAHB can form between the carboxylate head of PFOA and carboxyl/hydroxyl groups on the adsorbent surface. Since both adsorbate and adsorbent have similar pKa values in the case of PFOA, (−) CAHB is a significant interaction that needs to be considered [146]. The strength of H-bonding in (−)/(+) CAHB is described as the difference in proton affinity of H-donor and H-acceptor. To determine how strong the H-bonding in (−) CAHB is, one needs to evaluate the difference between the pKa of donor (pKa, DH) and acceptor group (pKa, AH+). The higher this difference, the weaker the cationic and anionic hydrogen bonding (CAHB) and vice versa. High CAHB means the bond strength of an ordinary H-bond is exceeded [146,147]. A ΔpKa ($pKa_{,DH} - pKa_{,AH+}$) value below 5 is considered essential to establish CAHB. With PFOS pKa value of −3.27, the condition of ΔpKa < 5 is not met. Hence, with its acidity very strong for such bond formation, PFOS is not able to form (−) CAHB [142]. However, in an experiment, the migration pattern of PFOS onto the nanobubble surface showed PFOS forming (−) CAHB onto the water surface [148]. The results showed that during adsorption, the sulfonic head of PFOS approached the interface region first and anchored to attach to the surface layer of water, helping it to stay in bulk water. The negatively charged sulfonic head of PFOS formed (−) CAHB with water molecules [148]. Similarly, in another study, the formation of (−) CAHB enabled the PFOS sulfonic head to be effectively adsorbed at the air–water interface (AWI) [149]. Meanwhile, the C–F chain kept swinging in the air away from the water surface [148]. Hence, PFAS accumulation at AWI during aeration was confirmed [150]. On the other hand, PFOA adsorption at pH 3 is supported by (−) CAHB due to the high H^+ concentration at lower pH. As the pH increases to 7, adsorption decreases significantly due to the decreased H^+ concentration. In contrast, PFOS, which rarely forms (−) CAHB, adsorbs more preferably and evenly at different sites of AC surface through hydrophobic interactions [142]. However, the electrostatic repulsion of the carboxylic head of PFOA with the carboxylic groups on the AC surface is more significant than its adsorption through (−) CAHB, resulting in an overall, higher adsorption of PFOS than PFOA. Hence, it is learnt that PFOA forms (−) CAHB onto the AC surface in contrast to PFOS, which forms such bonds onto the water surface in the presence of nanobubbles during aeration.

In addition to AC, adsorption of PFOA/S onto AER can generally be explained by its physicochemical aspects such as functional group, polymer matrix, and porosity [151–153]. AERs usually adsorb PFOA through the ion exchange mechanism. The sorption takes place between the negatively charged functional head of PFOA and the positively charged surface of resin. The hydrophobic tail of PFOA/S is also quite effectively taken up by AER through hydrophobic interactions [154,155]. In the case of PFOS, the solution pH was found to have no effect on the properties of both PFOS and resin; therefore, sorption of PFOS on AER was found independent of pH [156,157]. However, AER was reported to have relatively high adsorption capacity for PFOA at pH 6 (Figure 2c,d).

To date, the adsorption of PFOA/S on CNTs has been comparatively less explored [158]. Nonetheless, the sorption mechanisms involved in the adsorption of PFOA/S on CNTs include hydrophobic interactions, hydrogen bonding, and electrostatic interactions. The hydrophobic C–F chain of PFOA/S and hydrophobic sites on CNTs lead to the hydrophobic interaction. However, as much as the C–F chain contributes to the adsorption process, the functional heads are equally important. The reported adsorption of PFOS onto CNTs is higher than PFOA because of its higher hydrophobicity, i.e., higher log Kow (5.26, Table 1) due to the presence of sulphonic head [103,143,159]. On the contrary, the carboxylic head of PFOA leads to a relatively lower log Kow (4.59, Table 1) of PFOA, resulting in a lower adsorption capacity through hydrophobic interactions [143,159].

The adsorption of PFOA/S also depends on the types of soil, for example, tropical soils are different from temperate soils as well as the PFAS interactions. Soil formation is significantly influenced by the climate through moisture and temperature. In tropical regions, heavy rainfall and raised temperatures promote leaching and sedimentation of tropic soils. These soils are also rich in aluminium and iron oxides resulting in accelerated mineral weathering [61]. Tropical and temperate soils vary in charge characteristics and the net negative charge of the former is usually lower [160,161]. Hence, PFOS adsorption by tropical soils is enhanced through electrostatic and hydrophobic interactions [24]. In temperate soils, the adsorption sites are dominantly occupied by Ca^{2+}. While in tropical soils, weathering causes Fe^{3+} and Al^{3+} to be released and dominantly adsorbed onto soil surfaces [162]. However, electrostatic interactions between the charged surfaces of minerals and organic phases are the key player in the adsorption of PFAS, and the fraction of carbon partitioned to soil is another significant mechanism. In the case of acidic tropical soils, PFOA/S adsorbed onto the soil could desorb if the pH of soil increases in the case of management practices such as liming [30]. Moreover, at low pH, for tropical soils rich in Al and Fe oxides, there is an increase in the anion exchange capacity (AEC), negative surface charge, and electrostatic repulsion for negatively charged PFAS. Despite the electrostatic repulsion between the negatively charged head of PFAS and increased negative surface charge on the soil surface, the hydrophobic C–F tail also adsorbs to the soil surface with great affinity.

7. In Situ Treatment of Perfluorooctanoic Acid and Perfluorooctanesulfonic Acid (PFOA/S)-Impacted Groundwater

The persistence of PFOA/S and the growing environmental concerns related to this group of compounds have led to increased research on addressing PFOA/S contamination in various environmental compartments, including soil, surface water, wastewater, and groundwater. Owing to the distinctive physical and chemical properties of PFOA/S and their stringent regulatory standards, the remediation of PFOA/S-affected groundwater poses multifaceted challenges [163,164]. Numerous research initiatives are currently in progress to develop groundwater treatment technologies, encompassing both ex situ and in situ approaches, mostly through sorption-based technologies [165–167].

The preceding discussion concerning the structural characteristics of PFOA/S has clearly demonstrated that the sorption of PFOA/S is highly sensitive to factors such as physicochemical attributes of the compound, the physical and geochemical characteristics of the porous media, and water chemistry. Therefore, to achieve a precise assessment of PFOA/S transport and retention, it is imperative to conduct a comprehensive examination of the influence of these factors [168,169]. Research conducted in the last decade has notably enhanced our knowledge of how PFOA/S sorption behaves within subsurface systems. The forthcoming sections will primarily focus on the sportive mechanism at the air–water interface [19].

In this section, studies regarding the remediation of PFOA/S-contaminated groundwater have been reviewed. The in situ remediation technology involves the introduction of colloidal activated carbon (CAC) through the direct push method. Samples for PFOA/S-contaminated water were collected from the monitoring wells located within the PFOA/S plume. Over the course of the experiments (12–24-month period), the dispersal of CAC was evaluated by examining cores from the aquifer (Table 3). In addition to the in situ treatment, a study on numerical modeling to predict the efficiency of this treatment technique to remediate PFOA/S impacted groundwater through direct injection of CAC [170], is also included in this section.

Although there is a dearth of relevant information, of the available studies, nearly all adsorption studies, with only a few exceptions, consistently demonstrated a reduction in PFOA/S concentrations below the acceptable limits (70 ng/L for PFOS and 10 µg/L for PFOA) and their respective MDLs (0.2–30 ng/L) (Table 3). Figure 3 represents the findings from various applications of in situ PFAS treatment in groundwater (Table 3). The findings indicate that the direct injection of CAC is a promising in situ technology for the remediation of the high concentration of PFOA/S-contaminated groundwater.

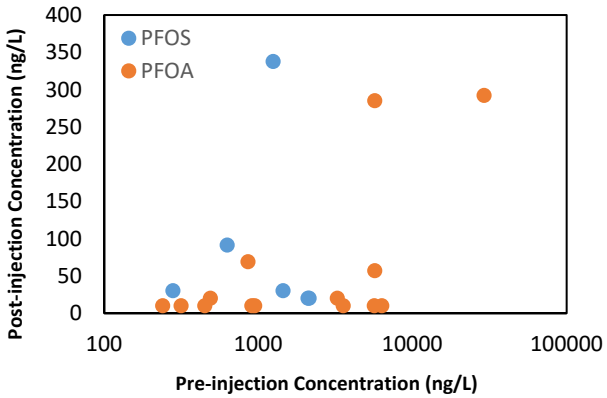


Figure 3. PFOA/S pre- and post-injection concentrations (data from the independent studies included in Table 3).

To evaluate the effective distribution of CAC into the contaminated zones, certain key parameters of the aquifer are identified and summarized in Table 3. Some significant factors such as the hydraulic gradient and hydraulic conductivity are included in the discussion. The distribution patterns (vertical and horizontal/lateral) of AC are critical factors influencing the effectiveness of the in situ remediation program [171–174]. The success of any in situ treatment is contingent upon the efficiency of delivering the injected reagents, which, in turn, is constrained by the hydraulic conductivity (K_H) of the aquifer into which these reagents are being introduced. Typically, the delivery and dispersion of reagents are more efficient in areas with higher K_H, resulting in a greater quantity of reagent being transported to these zones compared to areas with lower K_H [171,173,174]. K_H testing from these studies showed that a substantial portion of the affected aquifer were fine and coarse sand with the hydraulic conductivity values ranging from 1.1×10^{-6} to 10.3×10^{-3} m/s (Table 3). Moreover, the distribution of CAC increased with the increasing depth of the aquifer (Table 3). As a result, the activated carbon displayed an effective distribution, with the radii of influence extending several meters from their respective target zones [171,174–177]. Subsequent testing of the aquifer solids following the injection confirmed that CAC was efficiently dispersed within the designated injection zones, which in most of the studies were silty sand aquifers [171,173–175]. Moreover, a numerical modeling study forecasts that CAC can persistently extract PFOA/S from the groundwater for a few decades following its injection [170].

7.1. In Situ Treatment of Perfluorooctanoic Acid and Perfluorooctanesulfonic Acid (PFOA/S)-Impacted Groundwater Using Ion Exchange Resins

While exploring the applicability of other adsorbents for the in situ remediation of PFAS from groundwater, ion exchange resins (IERs) of different types were observed to be effective. Hence, this section aims at evaluating the efficacy of IER as a suitable adsorbent for groundwater treatment.

In the following three studies, injectable adsorbent suspensions (IASs) prepared from PAC, carbonaceous-clay-organic material (ROAC), activated charcoal, surface-modified organoclay-carbon composite (NMC+n), two anion exchange resins (A-IXR and L-IXR). [178], polymer-stabilized ion exchange resin (S-IXR) [179], non-hydrophobic A600E, mildly hydrophobic A520E, and highly hydrophobic A532E [180] were investigated.

In the first experiment, A-IXR outperformed other amendments (PAC, ROAC, activated charcoal, and NMC+n) by 2.5-folds [178]. In the second experiment, S-IXR suspension provided a uniform adsorption zone and resulted in an enhanced PFOA/S adsorption by more than five orders-of-magnitude in comparison to controls [179]. Similarly, in the third study conducted by Zaggia, Conte [180], resins outperformed GAC by orders-of-magnitude [180]. However, the comparison between three types of resins (A600E, A520E, and A532E) used in this study revealed that A600E and A520E being non-hydrophobic and mildly hydrophobic, respectively, had lower adsorption capacities compared to GAC and A532E. On the contrary, A600E and A520E are advantageous for in situ treatment due to their effective reactivation with dilute solutions of 0.5% NH_4OH and 0.5 NH_4Cl. While A532E being a highly hydrophobic resin requires a concentrated solution of 1% NH_4Cl and methanol/ethanol. Therefore, A532E is not considered regeneratable. Hence, A532E is not desirable for full-scale in situ treatment [180]. Moreover, PFAS removal from these resins was also based on three factors: the functional group of resin, the higher the hydrophobicity of the functional group, the higher the adsorption; the PFAS chain length, the longer the chain, the higher the adsorption; the PFAS function head, the sulphonic head was more effectively adsorbed than the carboxylic head [180].

Therefore, these findings suggest that in addition to GAC, IERs can also be used for effective in situ remediation of PFAS-impacted groundwater. The adsorption of short-chain PFAS makes the IERs even more considerable during the decision-making of in situ treatment removal from groundwater.

7.2. Adsorption of Perfluorooctanoic Acid and Perfluorooctanesulfonic Acid (PFOA/S) at the Air–Water Interface in the Vadose Zone

Many of the PFAS compounds of concern exhibit surfactant properties and PFOA/S tend to accumulate at the AWI due to their geochemical and physical properties [169,181–184]. Hence, it is important to recognize that air–water interfacial adsorption is a relevant retention mechanism. Recent in-depth characterizations of the occurrence and fate of PFOA/S at field sites revealed that vadose zone sources constitute a primary subsurface reservoir of these compounds, serving as long-term contributors to groundwater contamination [182,183,185,186]. This draws our attention to the critical importance of understanding PFOA/S transport and fate within the vadose zone. Reviewed field studies reveal that the measured concentrations of PFOA/S in soil and porewater were significantly higher than those observed in the underlying aquifer and groundwater [168,171,173–177,185,187,188]. Moreover, PFOA/S concentrations in the groundwater continued to decrease over time. The declining pattern indicates that the introduction of CAC effectively reduced PFOA/S mass loading into the shallow groundwater due to air–water interfacial adsorption [171,184].

The persistence and mobility of PFOA/S in the environment pose significant long-term challenges. Thus, relying solely on natural attenuation and long-term monitoring is not an

effective strategy for addressing PFOA/S contamination. Instead, active treatment methods must be employed to either remediate the contamination or contain it to prevent leaching into groundwater or drinking water reserves [166,173,189]. While sorption technologies exist for the removal of PFOA/S from both water and soil, focusing on the latter may be particularly interesting because PFOA/S strongly bind to soil [171,189]. PFOA/S-contaminated soil remediation technologies such as thermal treatment and soil washing have been applied on sites, but they are energy-intensive and expensive [190]. Other technologies such as electron beam, chemical oxidation, and ball milling are also being explored in the labs for their effectiveness [190]. Overall, these findings suggest that CAC effectively reduces PFOA/S concentrations by more than 85% to over 99% (Table 3).

Table 3. In situ treatment of PFOA/S-impacted groundwater. Final concentrations are measured and reported with reference to the method detection limits (MDLs).

PFOA/S	mbgs	Aquifer Properties	Time After Injection	C_0 (ng/L)	C (ng/L)/ Removal %	f_{cac} (%)	ŋe	Vep (%)	References
PFOA	0.9–1.7	i_H 0.06 m/m, mean K_H 2.6 m/day, Darcy Flux 0.8 m/day	3, 6, 9, 12, 18 (18 months)	490–3260	<MDL (20)	0.02	N/A	N/A	[175]
PFOS				280–1450	<MDL (30)				
PFOA	5.0–6.2	K_H 1.1 × 10^{-6} to 8.6 × 10^{-4} m/s	18 months	6340	<MDL (10) 96.5%	N/A	0.002	33	[171]
PFOA	5.3–6.2			3560					
PFOA	5.5, 7.0	Averaged i_H 0.008 m/m, K_H 4.7 × 10^{-5} m/s–4.7 × 10^{-4} m/s, v ~6 m/year	92, 184, 278, 366, 549 days (18 months)	450	<MDL	0.08	0.2	40	[173]
PFOA	9.5–12	Averaged i_v 0.018, i_H 0.003, K 3.5 × 10^{-3}–3.9 × 10^{-2} cm/s	182, 273, and 366 (12 months)	910	<MDL	0.76	0.2	50	[174]
PFOS				2105					
PFOA	3.2	K_H 4.8 × 10^{-6} to 6.3 × 10^{-4} m/s, v 9 m/year	122, 248, 362, 547, and 724 (24 months)	950	<MDL (10 ng/L)	0.07	N/A	30	[188]
PFOS				2140	<MDL (20 ng/L)				
PFOA	N/A	N/A	41, 88, 116, 152, 178, 230 days	316	<MDL (0.2)	0.26	0.15	70	[177]
PFOS				14.2	<MDL (0.3)				
PFOA	N/A	N/A	90, 124, 145, 176, 208, 232, 329 days	5660	<MDL (5)	0.25	0.23	70	
PFOS				670	<MDL (2.5)				
PFOA	N/A	N/A	47, 321, 386, 482, 542 days	240	<MDL (0.01 µg/L)	0.26	0.25	80	
PFOS				280					
PFOS	N/A	N/A	27, 58, 100, 132, 170, 358, 595 days	60	<MDL (0.01 µg/L)	0.06	0.25	46	
PFOS	N/A	N/A	104, 227, 619 days	500	82–99%	0.32	0.33	70	
PFOA	N/A	N/A	19, 47, 110, 146, 200, 291, 370 days	858	>92%	0.14	0.15	80	
PFOS				3540					
PFOA	N/A	N/A	Data collection every month for 3 months post application.	29,200	95–99%	0.21	0.23	70	
PFOS				153,000					
PFOA	N/A	N/A	30, 60, 120, 210, 365, 730 days	5700	95–99%	0.11	0.25	39	
PFOS				8					
PFOS	3	K 10^{-3} to 10^{-5} m/s	1, 7, 11, 24, 60, 95, 113 days	1250–319,000	73%	N/A	0.37	N/A	[191]
PFOA	0.4	Aquifer cell (64 cm length × 40.5 cm height × 1.4 cm internal thickness), flow cell packed under water-saturated conditions with 40–50 mesh Ottawa sand, pore-water velocity 1.52 m/day	Every 3 h, 70 h	50,000	630–1360 Overall, 85.5%	N/A	N/A	N/A	[189]
PFOS					230 Overall, 99.2%				
PFOA	3	Soil chamber (L = 15 cm, d = 3.6 cm), length to diameter ratio > 4 to simulate field conditions and minimize transverse dispersity. Soil column (L = 2 cm, d = 3.6 cm), flow rate 288 mL/day	150 days	510	99.7%	0.031	N/A	400 PV	[192]
PFOS				270					

In the table, mbgs denotes the meters (depth) below ground surface, C_0 and C are the initial and final concentration (nanogram/liter), respectively, f_{cac} is the fraction of colloidal activated carbon (CAC) in soil, ŋe is the effective porosity, Vep is the effective pore volume in (PV) or percentage (%). In the table, K is the hydraulic conductivity, K_H is the horizontal hydraulic conductivity, V is the groundwater velocity, i is the hydraulic gradient, i_H is the horizontal hydraulic gradient, i_v is the vertical hydraulic gradient, and N/A indicates that data are not available in the cited studies.

Since CAC had proven to be highly effective for the removal of PFOA/S through air–water interfacial adsorption (AWIA); therefore, it is necessary to enhance its performance for better removal. The mechanism behind the effective removal of PFOA/S through AWIA is facilitated by nanobubbles [193]. In an experiment, the introduction of nanobubbles into a liquid-phase environment caused the PFOA/S molecules in the liquid to be concentrated at the gas–liquid interface. This resulted in the formation of PFAS-nanobubble complexes which were readily taken up by the AC surfaces; therefore, enhanced adsorption. Generally, upon the introduction of AC, the adsorption process is aided with aeration, continuously. For example, in a similar study, aeration showed 21–29.2% increase in PFOS removal, while it decreased by 27.7% after degassing [194]. In another study, PFOS removal by graphite was observed to decrease by 74% after vacuum degassing [193]. Additionally, PFAS adsorption onto AC through AWIA can be improved by the addition of a co-foaming agent [195].

7.3. Air-Water Interfacial Adsorption of Perfluorooctanoic Acid and Perfluorooctanesulfonic Acid (PFOA/S) as a Function of Surface/Interfacial Tension

Previous research explored the influence of PFAS physical properties such as chain length on the adsorption at the AWI through surface tension studies. These studies confirmed that the degree of adsorption at AWI is directly influenced by the length of the C–F chain of PFAS [184,196,197]. However, there have been a limited number of studies involving unsaturated-flow transport based on the charged functional head of PFOA/S. Hence, this section aims to explore how the AWIA coefficients (Kaw) can help in evaluating the adsorption of PFOA/S with respect to their functional heads during their transport in unsaturated porous media. The Kaw is calculated from the surface tension data. The available studies employ the Szyszkowski equation/Gibbs adsorption equation across all measured data sets to calculate the surface excess and surface/interfacial tension followed by Kaw. It has been found that the Szyszkowski equation offers a precise representation of the surfactant surface tension and interfacial tension data [184,198–206] including PFOA/S [53,176,207] Similarly, many studies have referred to the Gibbs adsorption equation as a promising calculation method for surface access and surface/interfacial tension [176,187,206,208–211] to further calculate Kaw.

Table 4 shows the relationship between the surface tension and AWIA coefficient (Kaw). These coefficients can either be measured or estimated. Equations (1) and (2) show Szyszkowski and Gibbs adsorption equations, respectively [198,201].

Table 4. Air–water interfacial adsorption coefficients (Kaw) values (cm) determined from the surface-tension data at environmentally relevant PFOA/S concentrations and ionic strengths.

PFOA/S	PFOA/S Conc (mg/L)	Surface Tension/Interfacial Tension (mN/m) Background Solution [a/b]	Ionic Strength of Background Electrolyte	Surface Tension/Interfacial Tension (mN/m) in Electrolyte Solutions	Calculated Kaw (cm)	Reference
PFOA	0.4	N/A	N/A	N/A	0.064 ± 0.048	[212]
	10	0.06996 [a]	0.023 M, $NaHCO_3$, $CaSO_4{\cdot}2H_2O$, $MgSO_4$ and KCl	N/A	0.0086	[184]
	1	0.06982 [a]	0.01 M NaCl	0.07022 [b]	0.0027	[176]
	1	0.07076 [b]	0.01 M NaCl	0.07106 [b]	0.002 ± 0.0005	[187]
	1	71.96 [a]	N/A	N/A	0.00274	[205]
	1	N/A	N/A	71.77 [b]	0.00285	[187]
	2.41	74.69 [b]	N/A	N/A	0.0234	[53]
	0.01	N/A	0.01 M NaCl	71.48 [b]	0.0032	[209]
	10	N/A	0.01 M NaCl	69.45 [b]	0.0037	[210]
	0.0068	N/A	0.0015 M NaCl	72.96 [b]	0.00193	[211]
	0.0068	N/A	0.0015 M CaC_2	72.90 [b]	0.00529	
	0.0068	N/A	0.01 M NaCl	72.80 [b]	0.00536	
	0.0068	N/A	0.01 M $CaCl_2$	72.86 [b]	0.00662	
	0.0068	N/A	0.03 M NaCl	72.73 [b]	0.00771	
	0.0068	N/A	0.03 M $CaCl_2$	72.71 [b]	0.00830	
Na-PFOA	1	73.39 [b]	deionized water	N/A	0.00023	[206]
	0.1	72.56 [b]	deionized water	N/A	0.00023	
	0.1	N/A	0.01 M NaCl	71.75 [b]	0.0017	
	0.1	N/A	0.1 M NaCl	71.12 [b]	0.0087	
	0.1	N/A	0.01 M KCl	72.38 [b]	0.0015	
	0.1	N/A	0.01 M $CaCl_2$	72.38 [b]	0.017	
	0.1	72.29 [a]	N/A	N/A	0.006	
PFOS	0.01	72.68 [a]	0.01 M NaCl	72.15 [b]	N/A	
	1	0.07409 [b]	deionized water	N/A	0.0076	[168]
	10	0.07271 [b]	deionized water	N/A	0.0007	
	1	67.42 [a]	0.01 M NaCl	69.33 [b]	0.02	[176]
	10	60.81 [a]	0.023 M $NaHCO_3$, $CaSO_4{\cdot}2H_2O$, $MgSO_4$ and KCl	N/A	0.0129	[184]
	9.8	N/A	0.01 M NaCl	N/A	0.18 ± 0.029	[212]
	1.99	74.69 [b]	N/A	N/A	0.0755	[53]
	1	N/A	0.01 M NaCl	70.76 [b]	0.027	[210]
	0.01	N/A	0.001 M NaCl	71.82 [b]	0.033	[206]

Note(s): In the table, [a] is synthetic groundwater (SGW), [b] is deionized water (DIW), N/A indicates that data are not available in the cited studies.

The Szyszkowski equation is as follows:

$$\gamma = \gamma^0[1 - B\ln(1 + C/A)] \quad (1)$$

Gibbs adsorption equation is as follows:

$$Ki = \Gamma/C = -(1/RTC)(\partial\gamma/\partial lnC) \quad (2)$$

where γ refers to the interfacial tension at a given concentration and γ^0 represents the interfacial tension when the concentration of PFOA/S is zero, typically denoting the surface tension of pure water. The variables A and *B* in Equation (1) are parameters linked to the characteristics of a particular compound and the homologous series, respectively. In the second equation, *Ki* represents air–water interfacial coefficients (Kaw), Γ is the surface excess (mol/cm^2), *C* is the aqueous concentration (mol/cm^3), *T* is temperature (°K), *R* is the universal gas constant (dyne-cm/mol °K), and γ is the surface tension (dyne/cm or mN/m). Hence, in this section, we have explored the adsorption of PFOA/S through their Kaw values calculated from the surface tension/interfacial tension data at environmentally relevant PFOA/S concentrations (Table 4).

7.3.1. Effect of Solution Concentration on Air–Water Interfacial Adsorption Coefficients (Kaw)

It has been observed that perfluorooctane sulfonates (PFSAs) and perfluorocarboxylic acids (PFCAs) with identical perfluorinated chain lengths exhibit similar levels of interfacial sorption [213]. From Table 4, it is noted that Kaw values decreased as the concentrations increased. These results are in line with non-linear adsorption behavior [168,184,187]. Lower concentrations yield greater Kaw values, consequently augmenting the contributions of interfacial adsorption to retention, and conversely, higher concentrations result in smaller Kaw values, diminishing the impact of interfacial adsorption on retention [168,184,187].

7.3.2. Effect of Ionic Strength of the Solution on Air–Water Interfacial Adsorption Coefficients (Kaw)

The findings from the available studies highlight the significance of considering the solution chemistry: ionic strength and anion/cation type, while assessing the fate and transport of PFOA/S under unsaturated conditions. The findings discussed in this section reveal a noteworthy reduction in PFOA/S mass flux to the underlying groundwater. Table 4 confirms that the increased ionic strength of an electrolyte solution (from 0.01 M to 0.1 M NaCl) results in reduction in surface tension, which in turn increased surface activity. For instance, the surface activity of PFOA is greater for higher ionic strength; hence, having a notable effect on the retardation of PFOA in unsaturated porous media. Furthermore, it is seen that Ca^{2+} had a more pronounced effect on the retardation of PFOA compared to Na^+ at same ionic strengths [211]. The electrolyte in the solution decreases the electrostatic repulsion among the ionic headgroups at the interface, concurrently increasing the activity of the hydrophobic tail in the solution. The latter effect leads to an increase in the driving force for the adsorption process.

Finally, these results also indicate that Kaw values, derived from surface-tension data, are suitable for representing the AWIA of PFOA/S during their transport in unsaturated media [106,176,210].

8. Future Research Directions

At present, published conceptual and mathematical models of PFOA/S transport and fate in the subsurface exclusively account for solid-phase adsorption as the singular

retention process. However, the distinctive physicochemical properties of PFOA/S suggest a potential inclination for partitioning to other retention phases [168] such as air–water interfacial adsorption and gas-phase partitioning [214,215]. To supplement our understanding, further investigation is needed to examine the effects of different water saturation and water flux on PFOA/S mass flux through the vadose zone. Additionally, in-depth research is required to assess PFOA/S mass flux under diverse conditions including variations in soil properties, hydraulic characteristics, and PFOA/S loading conditions. Thus, continued research will contribute to a more multifaceted comprehension of the intricate dynamics governing PFOA/S transport in vadose zone environments. Finally, the current comprehension of PFOA/S transport in unsaturated porous media remains limited due to substantial variability in solution chemistry. In the current studies, surface-tension measurements are commonly carried out using research-grade compounds often subjected to additional purification. In contrast, commercial products may encompass various isomers of a specific compound, alongside multiple surfactants, and additional constituents [106]. Further research should explore this aspect concerning other commercial products and novel adsorbents.

9. Conclusions

The primary factors affecting the adsorption of PFOA/S onto different adsorbent materials include hydrophobic and electrostatic interactions, as well as additional mechanisms such as hydrogen bonding and (−) CAHB. The efficiency of PFOA/S adsorption is influenced by several parameters, such as the molecular structure of PFOA/S, the physical and chemical properties of the adsorbent material (including polarity, surface activity, functional groups, and porosity), and the solution matrix. While observing the adsorption of PFOA/S onto different adsorbents (e.g., AC, AER, and CNT) under similar experimental conditions, AER exhibited the highest performance, followed by SWCNT, while AC showed the lowest (although still significant). However, to date, only AC has been practically used in situ, but IERs should be given equal consideration.

Additionally, the surface properties of both the adsorbent and adsorbate are significantly influenced by the solution pH. In the adsorbate/adsorbent matrix, (−) CAHB was only significant at a certain ionic strength, slightly increasing the PFOA adsorption, whereas PFOS scarcely formed any (−) CAHB.

Furthermore, in situ remediation technology using CAC showed that CAC effectively reduced PFAS concentrations above 85% up to 99%.

Moreover, the reduction in PFOA/S is attributed to their accumulation at the air- water interphase. Additionally, the adsorption of PFOA is influenced by the cation type: Ca^{2+} has a more significant effect on the retardation of PFOA compared to Na^{+} at the same ionic strength.

Finally, it has been observed that consistent with non-linear adsorption behavior, the Kaw values decrease as the concentrations increase, which reduces the impact of interfacial adsorption on retention.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w17091401/s1, Table S1: PFAS adsorption capacities onto different adsorbents.

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